Synthesis and Properties of Polyethylene with Environmentally Benign Characteristics
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by

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Abstract

Various copolymers were synthesized by polymerizing different kinds of monomer in the presence of macroinitiators based on polyethylene.

Polyethylene (PE) and polypropylene (PP) were reacted with benzoyl peroxide (BPO) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to prepare PE-TEMPO and PP-TEMPO macroinitiators respectively. Molecular weight of PP decreased while that of PE increased during the reaction with BPO/TEMPO system. Polystyrene (PS) branches were grafted to PE and PP backbone chains as a results of bulk polymerization of styrene with the PE-TEMPO and PP-TEMPO macroinitiators. A significant amount of PS homopolymer was produced as byproduct. Weight of the resulting PE-g-PS and PP-g-PS increased with the polymerization time up to 20 hrs and then leveled off. Melting point of PE and PP domains in PE-g-PS and PP-g-PS respectively lowered as the content of PS in the copolymers increased. However glass transition of the copolymers was almost identical with that of PS homopolymer indicating that the constituents in the copolymers was all phase-separated from each other.

In scanning electron microscopy (SEM) of the incompatible PE/PS, PP/PS and PE/PP/PS compounded with PE-g-PS and PP-g-PS, any clear indication of enhanced adhesion between the phases was not observed. But phase domains in the blends were, nevertheless, reduced significantly to raise mechanical properties such as maximum stress and elongation at break by 2075%.

Low density polyethylene (LDPE) was reacted with BPO and TEMPO to prepare a latent macroinitiator, PE-TEMPO. Little polymer was synthesized when maleic anhydride (MAH) was bulk polymerized in the presence of the PE-TEMPO. However addition of styrene accelerated the polymerization rate and PE-g-(styrene-co-maleic
anhydride) (PE-g-(styrene-co-MAH)) was produced to a high yield. Chemical reaction between MAH units and hydroxyl groups of starch was nearly undetectable in PE/PE-g-(styrene-co-MAH)/starch blend system, and the tensile properties of the blend were not enhanced significantly. However addition of tetrabutyl titanate (TNBT) during the blending procedure improved the tensile properties significantly through an increased interfacial adhesion between the components in the blend system.

Styrene/MAH living radical copolymerization was carried out using BPO and TEMPO. Styrene/MAH copolymerization proceeded faster and yielded higher molecular weight products compared to styrene homo polymerization.

When styrene/MAH copolymerization was approximated to follow the 1st-order kinetics, the apparent activation energy appeared to be lower than that corresponding to styrene homopolymerization. Molecular weight of products from isothermal copolymerization of styrene/MAH increased linearly with the conversion. However products from the copolymerization at different temperatures had molecular weight deviating from the linear relationship indicating that the copolymerization did not follow the perfect living polymerization characteristics. During the copolymerization, MAH was preferentially consumed by styrene/MAH random copolymerization and then polymerization of practically pure styrene continued to produce copolymers with styrene-co-MAH block and styrene rich block.

Poly(vinyl acetate)-TEMPO (PVAc-TEMPO) macroinitiators were synthesized by bulk polymerization of vinyl acetate (VAc) in the presence of BPO followed by termination with TEMPO. Radicals were mainly transferred to the acetoxy methyl groups in PVAc during the polymerization.

Bulk polymerization of styrene was performed in the presence of the macroinitiator. Due to chain transfer to polymer reactions during the bulk polymerization of vinyl acetate, the copolymerization produced graft copolymers of PVAc and PS instead of the
corresponding block copolymers. The PVAc-TEMPO macroinitiator had several TEMPO-dormant sites. All the TEMPO-dormant sites of PVAc-TEMPO macrorinitiators participated in the styrene polymerization with almost equal reactivity. Methanolysis of PVAc-g-PS broke the PS branches apart from the PVAc backbone chain. Hydrophobic and hydrophilic porous membranes with controlled pore size could be prepared by removing the PVAc domains and the PS domains respectively from the graft copolymer.

The PVAc-g-PS copolymers had a phase-separated morphology, and the phase-separation was realized more completely in the copolymer with the highest VAc content (PS124TP115). PS124TP115 enhanced elongation at break of PVAc/PS blend significantly. The size of the PVAc domains in PS/PVAc/ PVAc-g-PS blends decreased and adhesion strength measured by the peel test for hot pressed PS and PVAc sheets with the copolymer inserted in between increased in the order of PS124TP115 >> PS145TP110, PS144TP096 >> PS162TP089, indicating that PVAc-g-PS copolymers having similar content of the components were more effective in compatibilizing the PS/PVAc blends.

Poly(ethylene-co-vinyl acetate) (EVA) powders containing 10wt% and 20wt% of VAc units was saponified in ethanol/KOH solution in a heterogeneous manner. Intermolecular interaction between vinyl alcohol (VOH) units in the produced poly(ethylene-co-vinyl alcohol) (EVOH) promoted the crystallization of intervening segments composed of ethylene units. Ring opening polymerization of ε-caprolactone in the presence of EVOH gave EVOH-g-PCL graft copolymers with relatively short chain branches. Even though the graft copolymerization was carried out in a homogeneous solution, all the VOH units are not equally reactive for the PCL grafting. And the unreacted VOH units decreased very slowly with the graft copolymerization time. EVOH-g-PCL decreased the domain size of the dispersed phase in LDPE/biodegradable master batch (MB)
blends, and thus increased their tensile properties significantly. 

Vinyl monomers with phenol and benzoic acid as pendant groups were synthesized, and their biocidal activities were examined using the halo zone test. For both bacteria and fungi, the biocidal activity decreased in the order of \( p \)-hydroxyphenyl acrylate (M2) > allyl \( p \)-hydroxyphenyl acetate (M1) > \( p \)-2-propenoxyphenol (M3). The outer cell membrane of gram negative bacteria did not protect the cells effectively against the biocides. Polymerization of the monomers decreased their biocidal activity significantly, but the order of the biocidal activity of the polymers was the same as that of the corresponding monomers. Glassy polymers are difficult to exhibit biocidal activity when compounded with low molecular weight biocides due to the extremely slow diffusion, and the biocidal polymers could find a successful application such as coating on glassy polymers in spite of the lower biocidal activity compared to the respective monomers. EVOH was prepared by the conventional saponification of EVA using a solution of potassium hydroxide in ethanol. An organic fungicide, 2-benzimidazole carbamoyl (CBZ) group supported on EVOH (EVOH-CBZ), was prepared by the transesterification reaction of methyl CBZ with EVOH. The antifungal activity of the synthesized polymers was examined by the halo zone test against *Aspergillus fumigatus* and *Penicillium pinophilum*. The synthesized EVOH-CBZ showed a strong antifungal activity.
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<th>Abbreviation</th>
<th>Full Name</th>
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<tr>
<td>AA</td>
<td>acrylic acid</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2'-azobis(isobutyric nitrile)</td>
</tr>
<tr>
<td>AMA</td>
<td>allyl methacrylate</td>
</tr>
<tr>
<td>ATMS</td>
<td>allyltrimethylsilane</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerization</td>
</tr>
<tr>
<td>BA</td>
<td>butyl acrylate</td>
</tr>
<tr>
<td>BPO</td>
<td>benzoyl peroxide</td>
</tr>
<tr>
<td>BS</td>
<td>p-tert-butoxystyrene</td>
</tr>
<tr>
<td>CBZ</td>
<td>2-benzimidazole cabamate</td>
</tr>
<tr>
<td>CRP</td>
<td>controlled radical polymerization</td>
</tr>
<tr>
<td>CTA</td>
<td>chain transfer agent</td>
</tr>
<tr>
<td>DIB</td>
<td>1,3-diisopropenylbenzene</td>
</tr>
<tr>
<td>DMA</td>
<td>N,N-dimethyl acetamide</td>
</tr>
<tr>
<td>DMAA</td>
<td>N,N-dimethyl acrylamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>degree of polymerization</td>
</tr>
<tr>
<td>DPE</td>
<td>1,1-diphenylethylene</td>
</tr>
<tr>
<td>2-EBP</td>
<td>ethyl 2-bromopropionate</td>
</tr>
<tr>
<td>EVA</td>
<td>ethylene vinyl acetate copolymer</td>
</tr>
<tr>
<td>EVOH</td>
<td>ethylene vinyl alcohol copolymer</td>
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<tr>
<td>HDPE</td>
<td>high density polyethylene</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>IB</td>
<td>isobutylene</td>
</tr>
<tr>
<td>IBVE</td>
<td>isobutyl vinyl ether</td>
</tr>
<tr>
<td>Iniferter</td>
<td>initiator-transfer agent terminator</td>
</tr>
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<td>LDPE</td>
<td>low density polyethylene</td>
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<tr>
<td>MA</td>
<td>methyl acrylate</td>
</tr>
<tr>
<td>MAH</td>
<td>maleic anhydride</td>
</tr>
<tr>
<td>MB</td>
<td>master batch</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>MEK</td>
<td>methyl ethyl ketone</td>
</tr>
<tr>
<td>$M_n$ and $M_w$</td>
<td>average number and weight molecular weight</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>MWD</td>
<td>molecular weight distribution</td>
</tr>
<tr>
<td>NMP</td>
<td>nitroxide mediated polymerization</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PBS</td>
<td>poly($p$-tert-butoxystyrene)</td>
</tr>
<tr>
<td>PCL</td>
<td>poly(caprolactone)</td>
</tr>
<tr>
<td>PD</td>
<td>polydispersity</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEGMA</td>
<td>poly(ethylene glycol methacrylate)</td>
</tr>
<tr>
<td>PEO</td>
<td>poly(ethylene oxide)</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PEVE</td>
<td>poly(ethyl vinyl ether)</td>
</tr>
<tr>
<td>PHB</td>
<td>poly(3-hydroxybutyrate)</td>
</tr>
<tr>
<td>PIB</td>
<td>poly(isobutylene)</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PVAc</td>
<td>poly(vinyl acetate)</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>PVC</td>
<td>poly(vinyl chloride)</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>tBA</td>
<td>tert-butyl acrylate</td>
</tr>
<tr>
<td>tBMA</td>
<td>tert-butyl methacrylate</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethylpiperidinyl-1-oxy</td>
</tr>
<tr>
<td>TCB</td>
<td>1,2,4-trichlorobenzene</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TPE</td>
<td>thermoplastic elastomer</td>
</tr>
<tr>
<td>TNBT</td>
<td>tetrabutyl titanate</td>
</tr>
<tr>
<td>VAc</td>
<td>vinyl acetate</td>
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Chapter 1.

*General Aspects of the Synthesis of Functional Polymers*
A. Introduction

Polymers become involved as reactants in chemical reactions for a number of reasons and under a wide variety of circumstances. The final form of a macromolecular species may be obtained by a reaction of a polymer or prepolymer. Polymer containing specific functional groups can be prepared either by a polymerization process that introduces the required functional group during polymer formation itself or by chemical modification of precursor polymer. In the polymerization route, different degrees of functionalization can be achieved more readily by various polymerization methods of the functional monomer.

Radical polymerization is industrially the most widespread method to produce polymeric materials such as plastics, rubber and fibers. The advantages of radical polymerizations over ionic or coordination polymerization are numerous: a large variety of vinyl monomers have been polymerized or copolymerized and the required reaction conditions are much less severe than that of ionic or coordination polymerization. Water, as in suspension or emulsion polymerization, or other impurities are well tolerated and the reactions occur at a convenient temperature range, typically from 0 to 100°C. The major drawbacks of conventional radical polymerizations lie in the fact that molecular structure of the produced polymers is difficult to control due to the transfer or termination reactions, and polymers with high molecular weight (MW) and high polydispersity (PD) are generally produced. These features are reflected in the physical and mechanical properties of the produced polymers.

The development of ionic polymerization methods allowed for the preparation of well-defined polymers with controlled chain end functionalities and the synthesis of well-defined block and graft copolymers. However, these polymerizations have to be...
carried out with nearly complete exclusion of impurities and often at very low temperature. Moreover, only a limited number of monomers can be used, and the presence of functionalities in the monomers can cause undesirable side reactions. A relatively new method to synthesize well-defined polymers and copolymers is controlled radical polymerization\textsuperscript{6-9}. In this field, several systems have been applied to control $MW$ and end functionalities: iniferters\textsuperscript{10-11}, nitroxides\textsuperscript{12-17,19}, atom transfer radical polymerization (ATRP)\textsuperscript{33-34}, and most recently the reversible addition fragmentation chain transfer process (RAFT-process)\textsuperscript{29}.

In this study, the nitroxide-mediated radical polymerization was employed to synthesize graft-copolymers with well defined molecular structures. Poly(ethylene-co-vinyl alcohol) (EVOH) was synthesized by saponifying Poly (ethylene-co-vinyl acetate) (EVA) in ethanol/KOH solution in a heterogeneous manner. $\varepsilon$-caprolactone was ring-opening polymerized from EVOH, and the resulting EVOH-g-PCL was used as compatibilizer for PE/biodegradable master batch (MB) blends. Various antimicrobial monomers were designed and synthesized to anchor eventually to PE. Antimicrobial activities were evaluated using the halo zone test.
B. Preparation of Functionalized Polymers

Functional polymers are macromolecules to which chemically functional groups are attached. These polymers have the potential advantages of small molecules with the same functional groups. Their usefulness is related both to the functional groups and to their polymeric nature whose characteristic properties depend mainly on the extraordinarily large size of the molecules.

The attachment of functional polymer groups to a polymer is frequently the first step towards the preparation of functional polymer for a specific use. However the proper choice of the polymer is an important factor for successful application. In addition to the synthetic aliphatic and aromatic polymers, a wide range of natural polymers have also been functionalized and used as reactive materials. Inorganic polymers have also been modified with reactive functional groups and used in processes requiring severe service condition. In principle, the active groups may be part of the polymer backbone or linked to a side chain as a pendant group either directly or via a space groups. A required active functional group can be introduced onto a polymeric support chain, by incorporation during the synthesis of the support itself through polymerization and copolymerization of monomer containing the desired functional groups, chemical modification of a suitably non-functionalized preformed support matrix and by a combination of polymerization and chemical modification. Each of the two approaches has its own advantages and disadvantages, and one approaches may be preferred for the preparation of a particular functional polymer when the other would be totally impractical.
1. Preparation of Functionalized Polymers using Controlled/living free-radical polymerizations

Free-radical polymerizations are preferable to ionic processes on economic grounds. They are easier to perform and much less sensitive to the presence of water and oxygen. In recent years the development of the controlled/living techniques of radical polymerization (CRPs)\textsuperscript{10-17,28,32-34} has enabled synthesis, by well-controlled processes, of narrowly polydispersed polymers. These processes may also be carried out in emulsions and suspensions. CRPs are based on reversible transformations, by thermal, chemical, or photochemical stimuli, of "dormant" species into reactive free-radicals acting as chain propagators. As explained in the Introduction, radical polymerizations are controlled when the fast dynamic equilibrium between "dormant" and active species yields a low stationary concentration of the latter. The probability of terminating encounters and of other side reactions is greatly reduced in such systems. When initiation is faster than chain propagation ($k_i > k_p$), and all polymeric chains start to grow at nearly the same time, narrowly polydispersed polymers are formed. The mechanisms of reversible activation of dormant species may involve dissociation-recombination, atom transfer, or degenerative transfer. CRPs based on dissociation-recombination include polymerizations mediated by nitroxide\textsuperscript{12-17}, by organometallic species and by several other reagents.
1-1. Iniferter

In the early 1980s, Otsu reported a living radical polymerization of alkenes with tetraalkylthiuram disulfide as and described its action as inifer, transfer or iniferter which means that it acted as initiator, transfer agent and terminator\textsuperscript{25}. The systems with thiuram disulfide as iniferter are usually characterized by the initial rapid growth and then a monotonous increase in $MW$ with conversion. In some case $MW$s do not increase linearly with conversion. The polymerization obeys a first order kinetics in monomer, as often observed for stationary state conditions. Molecular weight distribution ($MWD$) remains fairly constant but usually not below $M_w/M_n \leq 2$. Systems initiated with dithiocarbamate derivatives behave differently when initiated thermally and photochemically. Thiuram disulfide is a poor photo chemical initiator and starts to act efficiently only at temperatures above 90°C\textsuperscript{27}.

\[
\begin{align*}
R_2N-C(S)-S-C(S)-NR_2 & \quad 2R_2N-C(S)-S^\cdot \\
R_2N-C(S)-S^\cdot + M & \rightarrow P_1^\cdot \quad \text{(slow)}
\end{align*}
\]

This may be ascribed to low reactivity of the primary radicals $R_2N-C(S)-S^\cdot$. These radicals slowly initiate polymerization and rapidly scavenge growing radicals to form dithiocarbamate and groups which are quite thermally stable but which cleave homolytically in the presence of light:
Growing radicals may also react with dithiocarbamate end groups in two different ways: by a transfer process

\[ R_2N\text{-C(S)-S} - R_2N\text{-C(S)-S-P} + P_n \rightarrow R_2N\text{-C(S)-S-P}_n + P_n \]

and additionally by irreversibly forming head-to-head end groups and producing thiocarbamate radicals of low reactivity. The latter reaction reported by Sigwalt is very important in thermal polymerization of acrylate\(^3,4\)

\[ R_2N\text{-C(S)-S-P}_n + P_m \rightarrow R_2N\text{-C(S)-S-P}_m + P_n \]

Thermal polymerization of acrylate in the presence of benzyl dithiocarbamate is slower than spontaneous thermal polymerization\(^4\). This means that the degradative transfer is the main operating reaction. On the other hand, photochemical cleavage of the NC(S)-S-C bond may provide reversible systems\(^{27}\).

In addition, side reactions such as the evolution of CS\(_2\) were reported and lead to additional complications\(^5\).

\[ R_2N\text{-C(S)-S} - R_2N\text{-CS}_2 \]

Another class of thermal initiators are based on tetraarylethanes\(^{17,18}\) and (phenylazo)triphenylmethane\(^{20}\).
\[
\begin{align*}
\text{Ar}_2\text{OR}-\text{P}_n\text{-RCAr} & \quad \text{Ar}_2\text{OR}-\text{P}_n^+ + \cdot \text{CRAr}_2 \\
\text{Ar}-\text{N}=\text{N-CAr}_3 + n\text{M} & \rightarrow \text{Ar-P}_n\text{-CAr}_3 \quad \text{Ar-P}_n^+ + \cdot \text{CAr}_3
\end{align*}
\]

The bulky \(\text{Ar}_2\text{RC}^+\) or \(\text{Ar}_3\text{C}^-\) species plays a role on scavenging radicals. A good living system should require fast initiation which is usually not fulfilled in these systems. Most studies with these compounds provide PMMA with relatively poor control of \(MWs\) and \(PDs\).

Recently, a new series of initiators, generated from hyponitrite, aryl diazoate or cyanate anions by reaction with electron acceptors such as aryl diazonium ions or activated alkyl halides, have been shown to provide long-lived oxygen-centered radicals\(^{21}\). The "living" nature of these polymerizations was partially demonstrated by a quasi-linear increase in \(DP\) which conversion or by synthesis of block copolymers of the type poly(methacrylate)-poly(butyl acrylate). However, broad \(PDs\) (2.0~3.0) and low conversion were obtained:

\[
\text{nCH}_2=\text{CHCO}_2\text{R} \\
\text{Ar.. ON=NAr} \rightarrow \text{Ar(CH}_2=\text{CHCO}_2\text{R})_n\text{ON=NAr}
\]

This neologistic term is shorthand for initiators-transfer agents-terminators, and is used to describe a group of compounds which under thermal or photon stimuli initiate the polymerization of vinyl monomers, convert reversibly the growing polymers into dormant ones and eventually participate in the termination of the growing chains.

Moreover, iniferters have been used for the preparation of block copolymers\(^{56-59}\), since reversible transformations of growing chains into dormant ones enable the formation of sequences of monomer units during their copolymerization.

The \(MWs\) of the polymers formed with iniferters increase with time. The degrees of conversions are, however, usually rather low. Polymerizations initiated with iniferters are quite slow and may yield polymers with very broad \(PDs\). It has been reported\(^{58},\)
however, for the oligomerization of MMA initiated at 50°C by diethyl 2,3-dicyano-2,3-
diphenyl succinate as iniferter, that the initially broad $PD$ of PMMA decreases with time. All of the photoiniferters described by Otsu et al.\textsuperscript{56,57,59} were based on the readily dissociating $N,N'$-diethyldithiocarbamate group. The prepared polymers had the unstable dithiocarbamate group at their ends. Apparently, they may be stabilized by its removal through a photoinduced transfer to thiol\textsuperscript{60}. In spite of the drawbacks of the iniferter technique, as compared to other living radical polymerization techniques, their use as initiators of radical polymerizations may sometimes be of interest for the introduction of functional end groups and for the controlled surface grafting of oligomers, polymers and copolymers.

Several research groups\textsuperscript{61-63} have recently described the application of iniferter techniques for photografting onto surfaces of polymers, glass or silicon wafers. Such procedures involve covalent bonding of photoiniferters to the surface and subsequent irradiation in the presence of appropriate monomers. A dense layer of a polymer or a block copolymer, of controlled thickness, can thus be grafted onto a surface of endothelial cells.

The grafting of hydrophilic monomers onto the surface of a polyurethane film made it highly wettable by water. Moreover, it minimized the adsorption of platelets onto the surface of the thus treated polyurethane film. The procedure used by Lee and Matsuda\textsuperscript{62} was as follows. After chloromethylation of the surface, which enabled attachment of a dithiocarbamate, the sample was immersed in a solution of poly(ethylene glycol) methacrylate (PEGMA) and irradiated with UV light. Subsequent immersion in a solution of DMAA ($N,N$-dimethylacryl amide) followed by irradiation yielded a dense layer of the block copolymer. The effect of grafting, by the iniferter technique, of various monomers onto the surface of PET was investigated by Matsuda \textit{et al.}\textsuperscript{63}. These researchers activated PET by coating it with a photosensitive layer of
styrene-co-vinylbenzyl-N,N-diethylthiocarbamate and subsequently grafted onto it HEMA and other monomers. They investigated the effect of such treatment on the adhesion of endothelial cells and found that the adhesion was significantly reduced on a layer of PHEMA or poly(dimethylacrylamide), but it was enhanced on a layer of PMA or poly{[N-3(dimethylamino) propyl]acrylamide methoxide}. A monolayer of a photoiniferter, covalently bonded to the surface of silicon wafers or to glass, was formed by immersion of a very carefully purified surface in a toluene solution of dithiocarbamate attached to benzyl(trimethoxy) silane.

1-2. Nitroxide-mediated polymerizations (NMPs)

The concept of the thermodynamically neutral degenerative transfer has not been intentionally used yet. In fact, it is very similar to the inifer system but the species are not initiator perse and require the use of true radical initiators. These initiators can be added in controlled amounts like in the polymerization with alkoxyamines as transfer agents. The role of the initiator may be also played by impurities or even by the product of decomposition of transfer agents (alkyl dithiocarbamates).

Some of the best controlled polymers obtained by radical polymerization are prepared with preformed alkoxyamines or even those prepared in situ. Alkoxyamines alone are inefficient initiators, unless at high temperatures, but they might react easily with radicals. Thus radical polymerization initiated by classic initiator (AIBN, peroxides, etc.) in the presence of alkoxyamines provides polymers with MWs determined by the number of alkoxyamines and rates determined by the stationary concentration of growing free radicals. This is possible when a macromolecular radical (Pn·) attacks alkoxyamine selectively at the oxygen atom, forming a macromolecular alkoxyamine, and releases a radical R· capable of initiation of new chains:

This is probably the main reaction responsible for the formation of well-defined polymers.
in these systems. Indeed, successful polymerization with TEMPO and alkoxyamines require an excess of radical initiator. As discussed previously, dithiocarbamates are poor thermal initiators because they initiate slowly, do not reversibly form radicals and participate in the degradative rather than in the degenerative transfer. According to the results of Sigwait\textsuperscript{3,4}. Alkyl dithiocarbamate reduces the rate of spontaneous thermal polymerization of butyl acrylate but allows some control of MWs. This has been explained by the degradative transfer.

This type of transfer may also lead to the macromolecular formation of block copolymers with the macromolecular dithiocarbamate. Thus block copolymers may not be formed via a typical chain extension process but rather via coupling of a growing polyB with a polyA terminated with a dithiocarbamate moiety. The synthesis of well-defined polymers will require very high chemoselectivity of the degenerative transfer and a very small contribution of degradative transfer.

NMPs may be started by conventional free-radical initiators in the presence of stable nitroxide radicals, and/or by dissociation of so-called "unimolecular initiators" (alkoxyamines) which decompose into a stable nitroxide radical, acting as mediator, and an active free-radical initiator. Subsequent polymerizations involve reversible attachment of the mediating compounds to the growing chains.

Following the pioneering work of Rizzardo \textit{et al.}\textsuperscript{29} and of Georges \textit{et al.}\textsuperscript{14}, who showed that TEMPO can act as a mediator of the CRP of styrene, many other nitroxides, as well as related alkoxyamines, have been used. The structure of the nitroxides strongly affects their ability to efficiently mediate CRPs of various monomers. The synthesis, structure and efficiency of various alkoxyamines have recently been discussed by Hawker \textit{et al.}\textsuperscript{64-66}. The MWDs of styrene-based polymers and copolymers mediated by TEMPO, or in the presence of TEMPO-derived alkoxyamines, are usually in the range 1.2~1.4. $M_w/M_n=1.10$ may, however, be obtained\textsuperscript{67} if the polymerization of styrene at
130°C is mediated by imidazolidone nitroxides. It has recently been reported\textsuperscript{65} that much faster rates of polymerization and $\frac{M_w}{M_n}$ in the range 1.07~1.11 are obtained when acyclic-phosphonylated nitroxides are used as mediators. The relatively fast polymerization may apparently be attributed to the fact that the equilibrium constant of the dissociation of the dormant polymer into free radicals in nearly three orders of magnitude higher for 10 than for TEMPO, while both association and dissociation rates are also faster than with TEMPO. Functionalized alkoxy amines can be used for the preparation of end-functionalized polymers and block copolymers of accurate $MW$ and low $PD$\textsuperscript{64-65,68}.

1-3. Atom transfer radical polymerization (ATRP)

ATRP is a convenient way to prepare functional polymers. Various functional monomers including styrenes, (meth)acrylates and others were (co)polymerized in a controlled fashion, resulting in well-defined polymers with a good control over $MW$ and low $PD$s. To insert functional end groups, alkyl halides containing functional groups were used to initiate ATRP. The resulting polymer contains the functionality at one end and a halogen at the other end. The halogen end groups were converted to other functional groups using either nucleophilic substitution reactions, electrophilic or radical addition reactions. This process has also been used for di- and multifunctional initiators as well as for hyperbranched polymers. Alternatively, polymers with two or several end functionalities could be prepared by a chain coupling process.

The control over radical polymerization is based on two principles\textsuperscript{44-47}. First, initiation
should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect\(^{48-50}\), the majority of these growing polymer chains are dormant species that still preserve the ability to grow because a dynamic equilibrium between dormant species and growing radicals is established. By keeping the concentration of active species or propagating radicals sufficiently low throughout the polymerization, termination is suppressed.

ATRP is another promising CRP technique. It is based on the transfer of an atom (usually a halogen) from a `dormant' initiator or polymeric chain to a transition metal salt. A ligated salt catalyzes this transfer. The transition metal is oxidized when the halogen atom is transferred and a free radical is generated. Polymerization is propagated by the addition of monomer molecules to the thus generated free radicals. The catalyst is regenerated by reduction of the oxidized transition metal complex, while the growing polymeric chain is converted into a dormant one. ATRP proved to be applicable to a broad range of vinyl monomers\(^{69-74}\). The MWDs of the thus prepared polymers can be as low as 1.07, but are usually in the range 1.2~1.4. Various transition metals, such as Cu(I), Ni(II), and Ru(II), have been used as catalysts for ATRP. Copper-based catalysts seem to be the most versatile and inexpensive. Triphenyl phosphine has usually been used as the ligand for nickel and ruthenium, and 2,2'-dipyridine and its derivatives for cuprous halides. It has been reported that CuBr complexed by tris[2-dimethylamino)ethyl]amine or MA6-TREN acts as an effective catalyst for acrylates, in conjunction with ethyl 2-bromopropionate (2-EBP) as initiator. When methyl and butyl acrylate (MA and BA) were polymerized for 1hr at 22°C at [CuBr-Me6TREN]$_0$/[2-EBP]$_0$=0.2 and [MA]$_0$/[2-EBP]$_0$=232 or [BA]$_0$/[2-EBP]$_0$=156, polymers with $M_n$~15,000 and $M_w/M_n$~1.1 were obtained with ~50% conversion.

It has been claimed by Liou et al.\(^{69}\) that a polymeric ligand of copper, developed by them, may prevent contamination of polymers prepared by ATRP while improving the
conversion yield of the process.

ATRP is a radical process\textsuperscript{51} that fulfills these requirements by using a transition metal, in combination with a suitable ligand\textsuperscript{30,31,40,52-55}. The catalyst complex establishes a reversible equilibrium between growing radicals and dormant species (the proposed mechanism for ATRP is shown in Scheme 1). The equilibrium is attenuated by the choice of the ligand and the ligand also increases the solubility of the catalyst complex in the polymerization medium. Additionally, when the concentration of propagating radicals is sufficiently low in comparison with dormant chains, the proportion of termination chains, $P_{m+cv}$, can be often neglected (<5%). This may enable the preparation of highly functional polymers (>95%).

In homogeneous systems, the rate of ATRP has been shown to be first order with respect to the monomer and initiator\textsuperscript{34}. The rate of the polymerization is also influenced by the ratio of concentrations of the activator to deactivator, although this may change during polymerization.

The opportunity to incorporate a functional end group in a linear polymer chain is available by varying the initiator, i.e. a low $MW$ organic compound RX, containing an activated halogen X. After initiation has occurred, the initiator fragment R is present at one end of the chain while the halogen at the other end can be further transformed to various functionalities by means of standard organic procedures. This controlled radical polymerization allows for the polymerization of a wide range of monomers such as styrene\textsuperscript{34-36}, acrylates\textsuperscript{37-38} and methacrylates\textsuperscript{39-40} including a variety of functional monomers.

Since ATRP is a controlled/"living" radical polymerization, well-defined polymers with $MW$ determined by the ratio of consumed monomer to introduced initiator are obtained, $DP_n = \Delta [M]/[I]_0$, the PDs are generally low ($M_w/M_n < 1.3$). Because of its mechanism, ATRP allows for the preparation of more precisely controlled polymers and many new
materials have been synthesized\textsuperscript{41}. New materials are made by varying the topology of the polymer (linear, branched, hyperbranched, stars, etc.) and/or the composition of the polymeric chains (statistical/gradient copolymers, block copolymers, grafts, etc.). Moreover, with this process, the end groups of the polymers are well-defined as they derive from the initiator used. As a variety of initiators can be used, including initiators containing functional groups, end functionalities can easily be incorporated\textsuperscript{42-43}. The produced polymer can further be used to obtain block copolymers because of 'livingness' of the radical process.

1-4. Reversible Addition Fragmentation Chain Transfer process (RAFT)

A much more effective and versatile version of the exchanging radical polymerization was described by Chefari \textit{et al.}\textsuperscript{75}, who patented the RAFT process, based on reversible addition-fragmentation chain transfer. Thermally, or otherwise, generated free radicals start to grow and when they encounter a dithiomolecule, which acts as a chain transfer
agent (CTA), they add to it in a reversible fashion. They are subsequently replaced by longer polymeric residues and grow, after release, until the next encounter with a CTA. A judicious choice of the substituents on the CTA molecule is very important. Substituent Z should activate the C=S double bond towards radical addition, while R should be a good free-radical living group, such as cumyl or cyanoisopropyl, which is capable of effectively reinitiating the free-radical polymerization. A wide range of monomers, which may contain hydroxy, amino or acidic groups, can be polymerized and copolymerized in a controlled fashion by this technique. The RAFT process\textsuperscript{76-77} has been used for the synthesis of polymers and block copolymers with end- and side-chain functionalities. RAFT has also yielded products with PDs ranging from 1.04 to 1.25.

The polymerization of MMA in benzene was initiated by AIBN, and the emulsion polymerization of butyl methacrylate (BMA) was initiated by 4,4'-azobis(4-cyanopentanoic acid). Block copolymers of ethylene oxide (EO) with benzyl methacrylate and of MMA with HEMA have been synthesized with CTAs respectively. The two blocks of the BzMA-\textit{b}-EO block copolymer had the following characteristics: $M_w/M_n=1.04$ and $M_n=750$ of the EO block; $M_w/M_n=1.10$ and $M_n=10,800$ of the BzMA block. For the block copolymer of MMA with HEMA, $M_w/M_n=1.16$ and $M_n=23,000$ were obtained for the MMA block, while $M_w/M_n=1.18$ and $M_n=28,500$ were obtained for the HEMA block\textsuperscript{76}. ABA block copolymers have been prepared\textsuperscript{77} in two steps by the RAFT copolymerization of styrene with MMA, while trithiocarbonates acted as CTAs.

2. Chemical Functionalization of Synthetic Polymers

The preparation of functional polymers by chemical modification is an important technique which has been used extensively both industrially to modify the properties of
polymers for various technological applications and in the area of polymer-supported chemistry to prepare chemically reactive polymers

The application of chemical modification processes to polymers make it possible to create new classes of polymers which cannot be prepared by direct polymerization of the monomers owing to their instability or unreactivity and to modify the structure and physical properties of other commercial polymers to make them suitable for specific applications. The chemical modification of polymers is aimed not only at broadening the spectrum of the properties of conventional polymers but also to prepare polymers for specific purpose such as selectively permeable membrane, media of information storage, energy transducers, etc.

Polymers may be chemically modified to introduce reactive or catalytic groups to enable them to function as polymeric reagents and catalysts. Other polymers may be similarly modified with ligands to function as affinity supports in the isolation and purification of enzymes and species involved in immuno interactions. Indeed such modified polymers can be used directly in immunodiagnostic systems. Alternatively, the ligands introduced may be designed specifically to clelate metal ions for application in water treatment, hydrometallurgy, or analytical chemistry.

2-1. Functionalization of PS
Linear PS and cross-linked styrene-divinylbenzene resins has been subject to more chemical transformation than any other group of polymers because they form the basis of water-treatment resins and have attracted wide interest as heterogeneous supports for regents and catalysts. PS, chloromethylated PS and ring-lithiated PS are used in the chemical modification of styrene resins for the preparation of new functional polymers because they provide a method of attaching a wide variety of both electrophilic and nucleophilic species.

2-2. Functionalization of condensation polymers
Although the mechanical properties of condensation polymers are often superior to those exhibited by PS, little work has been done on the introduction of functional groups by chemical modification of condensation polymers. Chloro methylation of polymers containing oxyphenyl repeat units with chloromethylethyl ether at room temperature in the presence of SnCl₄ has been reported⁸⁸.

The lithiation of condensation polymers with the aid of $n$-butyllithium has also been reported⁸⁹. Poly(2,6-dimethyl-1,4-phenyl ether) was metallated to give both the ring(20%) and the alkyl group(80%) lithium product.
2-3. Chemical modification under phase transfer catalysis

A large number of functional polymers have been prepared by chemical modification under classical conditions. However, many of these reactions carried out on crosslinked polymers proceed very slowly and produce a low degree of functionalization because of hindered diffusion of the regents through the swollen gel and, in many cases, the heterogeneous nature of the reaction system. These difficulties may be alleviated by using specific solvents and/or catalysts.

Recently, phase transfer catalysis has been found to be a valuable tool in the preparation of crosslinked and linear polymers containing various functionalities. The application of phase transfer catalysis to polymer functionalization involves the chemical modification of functional polymers in a two- or three-phase system. These reactions involve mainly nucleophilic displacements on PS derivatives or reactions of polymers that have a reactive nucleophilic pendant group with various electrophiles. In addition to the ease of reaction and work up, it has generally been found that the phase-transfer-catalysed reactions afford better results than those carried out under classical conditions in terms of both polymer purity and functional yields. These simple, mild and economical methods have been used for the synthesis of functional polymers through, chemical modifications of pendant chloromethyl groups in poly(chloromethyl styrene) by reaction with several inorganic salts as well as the salts of organic compound in the presence of typical phase transfer agent.
2-4. Functionalization by grafting

A graft copolymer is a branched polymer in which the main backbone is chemically different from the side branches. The grafting technique has been successfully used for modifying the physical and chemical properties of various polymers by several methods.

2-4-1. Radical chain transfer grafting
The radical chain transfer effect is more pronounced with polymer chains that contain labile atoms that are easily abstracted by the attacking free radical. Heating or irradiating a mixture of a linear polymer dissolved in an appropriate monomer and initiator results in transfer between the polymer chain and the radical formed from the initiator. A polymer radical can initiate polymerization of the monomer. The amount of grafting achieved by this effect is usually small and depends on the magnitude of the chain transfer constant of the polymer which is usually small. Thus, this method of grafting leads to a mixture of linear polymer and graft copolymer.

2-4-2. Chemical reaction grafting
Chemical reaction grafting is formed by attaching polymers with functional groups at the chain ends onto other polymers with the aid of reactive functional groups present along the polymer chain.

2-4-3. Macroinitiator grafting
Macroinitiator (polymeric initiator) grafting involves the creation of initiator radicals, peroxide, halogen or azo groups in the polymer chain followed by polymerization of the
monomer to be grafted to give the graft copolymer. Polymeric chains with halogen end groups by an ATRP-catalyst system it can be used as macroinitiators. In this respect, block and graft copolymers have been synthesized using ATRP. Not only polymers prepared by ATRP, but also commercially available polymers or polymers obtained by other polymerization techniques have been used as macroinitiators. PSs with chlorine chain end, polymerized cationically, was further used to prepare an AB-type block copolymer with a B-segment PMA\textsuperscript{80-81}. Also, difunctional poly(isobutene) capped with a few units of styrene, was shown to be an effective initiator for styrene, MA and MMA yielding well-defined triblock copolymers\textsuperscript{42,78,82}. Multifunctional macroinitiators have also been used in the synthesis of various graft copolymers\textsuperscript{82}.

Commercially available difunctional poly(dimethylsiloxane) (PDMS) was modified by attaching benzyl chloride to the chain ends. This polymer was subsequently used to make triblock copolymers consisting of a PDMS center block and PS terminal blocks yielding a thermoplastic elastomer\textsuperscript{83-85}. Similarly, PDMS with pendant benzyl chloride groups was used to prepare graft copolymers\textsuperscript{79}.

2-4-4. Radiation grafting

Radiation grafting using a simultaneous method is a convenient one-step procedure for modifying polymers\textsuperscript{94}. It is useful in particular for imparting wettability to hydrophobic polymer using hydrophilic monomers. \textit{p}-styryldiphenyl phosphine has been grafted to poly(vinyl chloride) (PVC), PP and crosslinked PS beads at radiation dose levels that do not affect the properties of the resulting copolymer\textsuperscript{94-95}. This technique is valuable for monomers and polymers that are radiation sensitive to achieve the required grafting. The most commonly used energy sources are ionizing
radiation, plasma gas discharge and ultraviolet light sources in the presence of photosensitizer\textsuperscript{96-97}.

The technique involves irradiating a solution of polymer in monomer with radiation that results in radical formation on the primary polymer chain. The sites of radical formation become the points of initiation for the side chains. At the same time, the radiation initiates polymerization of the monomer and thus a mixture of graft copolymer and homopolymer is obtained. The predominant variables which influence the grafting yield include the radiation dose and dose rate(time), the concentration of monomer and sensitizer in the solvent and the structure of both monomer and base polymer.
C. Application of Functionalized Polymers

1. Blends of biodegradable and non-biodegradable polymers

The blending of biodegradable polymers, such as starch, with inert polymers, such as PE, has received a considerable amount of attention for possible applications in the waste disposal of plastics. The reasoning behind this approach is that, in principal, if the biodegradable component is present in sufficient amounts and if it is removed by microorganisms in the waste disposal environment, the plastic or film containing the remaining inert component should lose its integrity, disintegrate and disappear. This concept has found its principal application in blends of minor amounts of starch with PE in which the latter constitutes the continuous phase so that the blend can be melt processed to form films or plastics with PE-like properties\textsuperscript{98}.

Granular starch, either in its virgin form or chemically modified on the granule surface to increase its compatibility with the matrix polymer, has been used to form these types of blends\textsuperscript{99-102}. In a biologically active environment containing microorganisms that secrete amylases, the exposed starch granules on the surface of the sample and those granules within the sample which are in direct contact with the surface granules, can be enzymatically hydrolyzed and completely removed to create pits or voids. When a sufficient amount of the starch present in the blend is degraded and removed in that manner, the sample should lose its strength and or continuity and disintegrate. However,
this effect occurs only for samples containing fairly large amounts of starch, of the order of 30% by volume, and PE plastics and films containing so much granular starch have substantially decreased tensile, tear and impact strengths. That is, the effective connectivity and accessibility of the starch granules, which is required for extensive enzymatic hydrolysis and removal, is achieved only at relatively high starch contents. At lower starch contents, with blend compositions much below the threshold level for the connectivity of granules, very little effect on mechanical properties results from the biodegradation of the accessible starch component\textsuperscript{101-104}.

Graft copolymerization of thermoplastic polymers onto starch provides another method for preparing starch-polymer composites. An important advantage of graft copolymerization is the fact that starch and synthetic polymers are held together by chemical bonding rather than existing merely as physical mixtures. The two dissimilar polymers therefore tend to be more intimately associated, and separation of the two polymer phases is less likely to occur. Fanta and Doane\textsuperscript{105} have made an extensive study of the synthesis and properties of starch graft copolymers: in the course of this research, the properties of starch-g-poly(methyl acrylate) (starch-g-PMA) have proven to be especially interesting.

Graft polymerization of MA onto either granular or gelatinized starch takes place readily in water with ceric ammonium nitrate initiation, and graft copolymers containing about 50~60% PMA can be easily prepared with minimal formation of ungrafted homopolymer. The combined properties of the rigid starch matrix and PMA result in the formation of a tough leathery plastic on extrusion processing. Dennenberg \textit{et al.}\textsuperscript{108} showed that the starch portion of these starch-g-PMA extrudates is susceptible to fungal attack.

Patil and Fanta\textsuperscript{106} prepared starch-g-PMA copolymers containing 55~60% PMA from
cornstarch, high amylose cornstarch, and waxy cornstarch with ceric ammonium nitrate initiation. The graft copolymers were characterized with respect to the percentage conversion of monomer to polymer, grafted PMA content, grafting frequency, $MW$ and $MWD$ of the PMA grafts. Variables investigated in the graft copolymerization reaction were nitric acid concentrations, ceric ion-to-starch ratios, reaction times, gelatinization of starch and reactant concentrations in water. At high concentrations, high conversions of MA to grafted PMA could be obtained in less than 0.5hr at 25°C.

Henderson et al.\textsuperscript{107} grafted PMA onto wheat starch by $\gamma$ -irradiation and chemical initiation, respectively. The effect of water on the starch-$g$-PMA extrudate, $MWD$ of the homopolymer, tensile and dynamic mechanical properties of the extrudate and moulded samples of both graft polymers were all reported.

Dennenberg et al.\textsuperscript{108} prepared starch-$g$-PMA copolymers having grafted side chains with $MW$s of less than 500,000. This material can be easily extruded into a film which shows excellent initial tensile strengths and elongations. Tensile strength, however, falls off rapidly after 70hrs of water immersion at 25°C. starch-$g$-PMA films show excellent susceptibility to fungal growth, some samples losing more than 40% of their weight after 22 days of incubation with Aspergillus niger. Tensile tests and SEM of the incubated samples, after being freed of mycelium, indicate substantial biodegradation of the starch portion of the copolymer. This material may have an application as a biodegradable plastic mulch.

Although Dennenberg et al.\textsuperscript{108} confirmed that the starch portion of these graft copolymers is indeed susceptible to fungal attack, PMA is resistant to biodegradation. Enzymes produced by microorganisms can theoretically hydrolyze ester linkages to yield poly(acrylic acid); however, the biodegradation of poly(acrylic acid) is $MW$ dependent,\textsuperscript{109} and high $MW$ polymer apparently remains resistant to microbial attack despite its water solubility.
To enhance the biodegradability of the PMA portion of the graft copolymers, Fanta et al.\textsuperscript{110} introduced PVAc segments into the polymer grafts by copolymerizing VAc with MA during the grafting reaction. Esterases produced by microorganisms will convert PVAc to poly(vinyl alcohol) (PVA). PVA can then undergo further microbial attack to cleave the polymer chain,\textsuperscript{111-112} thus yielding fragments to further degradation in the environment because of their low $MW$s. Bailey et al.\textsuperscript{113} enhanced the biodegradation of synthetic polymers by a similar approach in which degradable polyester segments were introduced into polymer chains via ring-opening polymerization of cyclic keten acetal comonomers.

An alternative approach is to bring about some compatibility of the starch and synthetic polymer by blending starch with polymers containing polar functional groups that can interact with starch. In recent years, several patents have been granted\textsuperscript{106-108} and the Novon division of the pharmaceutical giant Willett\textsuperscript{108} used starch, copolymers of an olefin, and optionally, a poly(mono)olefin or poly(mixed)olefin to make blends that were injection moulded or film blown into commercial articles. An increase in the starch percentage adversely affected the physical properties of the blends.

Yet another economical and commercially viable approach is to form graft or block copolymers in situ during the blend preparation by using polymers containing reactive functional groups. The blending is performed under the conditions that promote the reaction. This method is commonly known as reactive blending. Small amounts of blocks of graft copolymers formed during the blending process, due to reaction between the two components, are generally enough to stabilize the morphology and improve the properties of the blend. Reactive blending is known to improve the compatibility and interfacial adhesion of two immiscible polymers. This technique has been extremely popular in generating polymer blends in the synthetic polymer industry\textsuperscript{109}. Synthetic polymers having functional groups such as carboxylic acid, anhydride, epoxy urethane,
or oxazoline, can react with hydroxyl or carboxyl groups (in modified starch) to form a blend with stable morphology.

Jane et al.\textsuperscript{107} in their patent used starch, oxidized PE, and LDPE to produce films. According to these authors, the carboxy and ketone groups of oxidized PE react with the hydroxyl groups on the starch to form bonds. They also report that as the percentage of starch in the blend is increased, the tensile strength and the percentage elongation decrease.

The reactivity of the functional groups is an important parameter in reactive blending. Most of the blends are commercially prepared in an extruder. The functional groups should react to form the required concentrations of graft or block copolymers in the short residence times typical of extrusion processes. From this point of view a cyclic anhydride group may react more quickly than the carboxylic group because of its higher reactivity. Unlike carboxylic groups, reaction of anhydride with hydroxyl to form an ester is not an equilibrium reaction as no water is produced during the reaction. Anhydride functionality can be incorporated into a polymer by copolymerization or grafting of anhydrides like MAH. MAH can be grafted with relative ease onto many polymers under normal melt processing temperatures\textsuperscript{109}.

Maldas and Kokta\textsuperscript{111} used anhydride functionalized PS to improve the compatibility and adhesion with cellulosic fibres. They reported that the properties of the composites varied with the concentration of MAH, type of wood used, and pulping technique. Maleated high density polyethylene improved the tensile strength of composites containing wood flour with increasing concentration of filler\textsuperscript{112}.

Vaidya and Bhattacharya\textsuperscript{113} studied the properties of blends of starch and synthetic polymers containing anhydride groups. Corn starch was blended with styrene maleic anhydride copolymer, and the corresponding nonfunctional PS and ethylene propylene copolymers. The concentration of starch in the blend was varied between 50 and 80\%
by weight. The torque generated during blending is reported as a function of starch content, mixer speed, and mixing time. Torque increased with increasing starch content for starch/SMA blends; the reverse was true for starch/EPMA blends. The torque was higher for the blends of the anhydride functional polymers compared to blends of the corresponding nonfunctional polymers. Water absorption of the blends increased with an increase in the starch content. Starch/SMA blends made at higher mixer speeds or times were more water sensitive. Blends containing EPMA absorbed less water than SMA blends containing the same weight fraction of starch. The tensile strengths of blends containing functional groups were superior compared to the blends made from nonfunctional polymers. When the starch contents increased from 60 to 70%, the tensile strength remained unchanged for the SMA blend but increased for the EPMA blend. All samples supported the growth of microorganisms, which increased with increasing starch content.

2. Polymeric Biocides

2-1. Biocides

Many natural and some synthetic polymers are subject to attack by biological agents. At some time during its life, a polymer may be a possible source of nutrients for living organisms, a barrier to be penetrated in the search for substance, a substrate subject to enzymatic or chemical attack, or a material for shelter or attachment during the life cycle of certain organisms. Such action depends on the susceptibility of the polymer to penetration and degradation. The degree of susceptibility, the use of the material, costs,
and other factors govern the application of protective treatment. Biologically active chemical compounds used as preservations control degradation in several ways; those that cause the death of the degradative organism are termed biocidal. Many chemical agents may inhibit the reproduction and growth of organisms without causing their death. These may be exemplified in the two common classes of control agents known as bacteriostats and fungisstats. With higher organisms, e.g., some of the mammals, the repellent qualities of a chemical agent may minimize damage. These protective agents make the polymer less susceptible to biological attack and prolong its useful life by preserving its physical properties and appearance.

The more common usage of the term biocide all chemical agents that control or destroy microorganisms. This would encompass materials variously described as bactericides, bacteriostats, mildewcides, fungicides, fungisstats, microbiocides, germicides, preservatives, etc.

The first materials used as biocides included sulfur, copper, mercury and arsenic compounds. Sulfur was used for mildew control, arsenic compounds for insect control. The Bordeaux mixture (slaked lime in a copper sulfate solution) was the principal USA biocide until the 1930s. The era of organic biocides was initiated by the discovery of the fungicidal activity of dithiocarbamates in 1934 and insecticidal properties of phenothiazine (9-thia-10-azaanthracene) in 1935. Since that time, many biocides have been developed and marketed including DDT \([1,1,1\text{-trichloro-2,2-bis}(p\text{-chlorophenyl})\text{ethane}]\), chlordane, dithiocarbamate salts, DDD \([1,1\text{-dichloro-2,2-bis}(p\text{-chlorophenyl})\text{ethane}]\), phenylmercury and a multitude of others.
2-2. Microorganisms

Two types of microorganisms are of particular interest in the biodegradation of natural and synthetic polymers: bacteria and fungi.
2-2-1. Fungi

Eumycetes, or true fungi, are microorganisms of particular importance in causing the degradation of materials. Fungi are nucleated, spore-forming, nonchloro phyllous organisms, which reproduce both sexually and asexually; most of them possess filamentous, somatic structures, and cell walls of chitin and/or cellulose. More than 80,000 species are known.

True fungi are present everywhere. Their importance as deteriorative agents is a result of the production of enzymes which break down nonliving substrates in order to supply nutrient materials present in polymer compositions. Certain environmental conditions are essential for optimum growth and degradative activity. These include an optimal ambient temperature, the presence of nutrient materials, and high humidity.

The group of test fungi that evolved for assay purposes in the field of natural polymers and that were further selected for their utility in assay procedures on synthetic polymers are taxonomically a very heterogeneous group, exhibiting no marked taxonomic similarities among them. Many of them were selected primarily because their reproduction spores are produced asexually and the variation associated with spores resulting from the fusion of sexual element is minimized. The test organisms cited are also, for the most part, the selected organisms from a large number of isolations which have proved their capability for yielding reproducible results repetitively, over long periods of time, under laboratory conditions, and in synthetic or highly controlled and specific culture media.

The most acceptable organisms are characterized by strain or culture collection number. The strain of *Aspergillus niger* is identified by the ATCC Number 9642 or the Quartermaster Number or Mycological Services No. 386.

2-2-2. Bacteria
Schizomycetes, a bacteria, have played an undetermined role in relation to fungi in polymer deterioration. Bacteria can be single-cell rods, cocci, or spirilla; others are chain-like or filamentous. Bacteria can either be aerobic or anaerobic; in contrast, fungi are necessarily aerobic. Some bacteria are motile; bacteria are predominantly nonchlorophyllous. Their degradative action is also chiefly a result of enzyme production and resultant breakdown of the nonliving substrate in order to obtain nutrient materials. Bacteria present in soil are important agents for material degradation. Particularly affected are cellulosic plant life, wood products, and textiles subject to cellulytic degradation.

2-2-3. Enzymes
Enzymes are essentially biological catalysts, with the same action as chemical catalysts. By lowering the activation energy they can induce an increase in reaction rates in an environment otherwise unfavourable for chemical reactions, e.g. water at pH 7 and 30°C. In the presence of enzymes, a rise in reaction rate of $10^{8}$~$10^{20}$ can often be observed. The vast majority of enzymes are proteins having a polypeptide chain with a complex three-dimensional structure. Enzyme activity is closely related to conformational structure.

The three-dimensional structure of enzymes with folds and pockets creates certain regions on the surface with characteristic primary structures which form an active site. At the active site the interaction between the enzyme and substrate takes place leading to a chemical reaction, giving a particular product.

For optimal activity certain enzymes must associate with cofactors which can be metal ions. Organic cofactors are also called coenzymes and they can vary in structure, some are derived from different B-vitamins while others are important compounds in metabolic cycles such as nicotinamide adenine dinucleotide, nicotinamide adenine
dinucleotide phosphate, flavin adenine dinucleotide, adenosine triphosphate, etc. An enzyme plus a cofactor is called a holoenzyme while an enzyme lacking a cofactor is called an apoenzyme.

All enzymes, except those few retaining historically important trivial names (trypsin, pepsin, etc.), are named according to rules adopted by the International Enzyme Commission. The names give the nature of the chemical reaction catalyzed and also describe the substrate. All new enzymes end with the suffix -ase, but shorter names are often used as some enzyme names become very long.

Chemical biocides fulfil a key role in the preservation of products as diverse as cutting fluids, foods, and beverages, cosmetics and pharmaceutical formulations and afford protection against spoilage in a wide range of industrial and environmental applications. Biocides which interact strongly by chemical or electrostatic bonding with their target(s) are generally difficult to neutralize by dilution and will required some form of surrogate compound with which to interact; this is the basis of action for the specific inactivating agents.

By far the most frequently-cited target region is the microbial cytoplasmic membrane. This is not surprising given its fundamental metabolic and structural role within the cell, its large surface area for interaction, and its proximity to the external aqueous environment. A wide range of biocides of different chemical classes will damage the membrane, albeit by different mechanisms. It will be also noted in Table 1 that several agents have plurality of action, often reflecting, a more generalized reactivity. This leads to an alternative classification of biocides by reference to their physicochemical mechanism of interaction with their target (Table 2). This affords some explanation for the target specificity of some agents and the apparent promiscuity of others.
2-4. Biological degradation of synthetic polymers

Synthetic polymers, such as polyolefins, polyesters, or vinyl polymers, are considered for the most part to be resistant to biological attack, except perhaps in specialized environments. Some synthetic polymers, such as the polyester from ε-caprolactone, have been designed to be subject to biological degradation, whereas others may be subject to attack after exposure to the weather. Polymers with hydrolyzable backbones have been found to be susceptible to biodegradation. Almost the only high MW compounds shown to be biodegradable are the aliphatic polyesters. The reason for this is the extremely hydrolyzable backbone found in these polyesters. It was found that polyesters derived from diacids of medium sized monomers (C6~C12) are more readily degraded by fungi (Aspergillus niger and Aspergillus flavus), than those derived from longer or shorter monomers\textsuperscript{120-121}. In order for a synthetic polymer to be biodegradable by enzyme catalysts, the polymer chain must be able to fit into the enzyme’s active site. This is one reason why flexible aliphatic polyesters are degradable and the rigid aromatic polyesters are not\textsuperscript{122-124}.

Poly(glycolic acid) (PGA) is the simplest linear, aliphatic polyester. PGA\textsuperscript{125-128} and poly(glycolic acid-co-lactic acid) (PGA/PL) are used as degradable and absorbable sutures. Their great advantage is their degradability by simple hydrolysis of the ester backbone in aqueous environments such as body fluids. Furthermore, the degradation products are ultimately metabolized to carbon dioxide and water or are excreted via the kidney.

PCL has been thoroughly studied as a substrate for biodegradation\textsuperscript{129-136} and as a matrix in controlled-release systems for drugs\textsuperscript{137-140}. Its degradation in vivo is much slower than that of poly(γ-hydroxy acid)s\textsuperscript{137}. Thus, it is most suitable for controlled-release devices
with longer working lifetimes. PCL is generally prepared from the ring-opening polymerization of ε-caprolactone\textsuperscript{141}. Tokiwa and Suzuki\textsuperscript{142} have discussed the hydrolysis of PCL and biodegradation of PCL by fungi, and have shown that PCL can be degraded enzymatically.

Blends of PCL and polyesters prepared from alkanediols and alkane dicarboxylic acids with natural substances such as tree bark have been moulded into shaped containers for horticultural seeding plantouts\textsuperscript{141}. After three months of soil burial, the PCL containers were found to be embrittled, disintegrated, and biodegraded which suggests that the extracellular enzymes in the soil may cleave the polymer chain prior to the assimilation of the polymer by microorganisms.

Polyesters derived from alkanediols and alkane dicarboxylic acids are readily degraded by biological systems\textsuperscript{143-146} but their applications have been limited because of their relatively low MWs and poor physical strengths.

Although polyamides contain the same amide linkage that is found in polypeptides, their rate of biodegradation is so low that often they are reported to be nondegradable. However, the degradation by enzymes and microorganisms for low MW oligomers has been reported\textsuperscript{147-151}. Even aramid fibre was reported to be attacked by Aspergillus fungi\textsuperscript{282}. The introduction of substituents such as benzyl, hydroxy and methyl greatly improve the biodegradation.

The higher crystallinity of polyamides due to strong interchain interactions is behind the observed lower rates of biodegradation. Copolymers with both amide and ester groups are generally found to be readily degraded\textsuperscript{153-155}. As expected, the rate of degradation increases with increasing ester content.

Natural proteins seldom contain repeating units. As a result, there is less tendency for them to pack into highly ordered morphologies. Therefore, they are generally accessible to enzyme attack. On the other hand, synthetic polyamides have short and regular
repeating units. Their higher symmetries and strong interchain hydrogen bonding result in highly ordered crystalline morphologies, which, in turn, limits the accessibility to enzyme attack. Poly(amide-ester)s and poly(amide-urethane)s with long repeating chains have been found to be degraded at rates somewhat in between those of proteins and synthetic polyamides\textsuperscript{153}.

Polyurethanes can be considered to have both the structural characteristics of polyesters and polyamides, whereas polyureas might be viewed as poly(diamide)s. Their susceptibility to biodegradation can be expected to be similar to that of polyesters and polyamides, with differences in rates. In general the biodegradability of polyurethanes was shown to be dependent on whether the prepolymer is a polyester or a polyether\textsuperscript{159}. The polyether-based polyurethanes are resistant to biodegradation whereas the polyester polyurethanes are readily attacked. Many microorganisms (\textit{Aspergillus niger}, \textit{Aspergillus fumigatus}, \textit{Fusarium solanii}, \textit{Cryptococcus lacirentii}, etc.) and enzymes (\textit{papain}, \textit{subtilisin}, etc.) are effective in degrading polyurethanes. A series of polyurethanes derived from poly(caprolactone diol)s of various \(MW\)s, and aliphatic or aromatic diisocyanates were treated with various organisms. It was found that the degradation rate increases with increasing polyester segment length. It was also observed that polyurethanes derived from aliphatic diisocyanates are degraded faster than those derived from aromatic diisocyanates\textsuperscript{160}.

Polyanhydrides are a group of polymers with two sites in the repeating unit susceptible to hydrolysis. These are interesting materials due to their good biocompatibilities\textsuperscript{161}. These are fibre-forming polymers that are very susceptible to hydrolysis\textsuperscript{162}. Langer \textit{et al.}\textsuperscript{163} synthesized aliphatic-aromatic polyanhydrides for slow release formulations. The bioerodible polymers, especially polyanhydrides, are useful materials for drug delivery. The degradation rates can be altered with changes in the polymer backbone. Aliphatic polyanhydrides degrade within a few days while aromatic polyanhydrides can degrade
slowly over a period of several years\textsuperscript{164}. Recently, a new synthetic route for producing linear poly(adipic anhydride)s by use of ketene gas has been presented\textsuperscript{165}. This synthetic route has the advantage of avoiding formation of acetic acid, which can drive the reaction backwards. Polyanhydrides are useful in biomedical applications due to their fibre-forming properties. An increase in the aliphatic chain length between the acid groups not only increases their $MW$ but also notably improves their hydrolytic stability\textsuperscript{166-167}.

Vinyl polymers, with few exceptions, are generally not susceptible to hydrolysis. Their biodegradation, if it occurs at all, requires an oxidation process, and most of the biodegradable vinyl polymers contain an easily oxidisable functional group. Approaches to improve the biodegradability of vinyl polymers often include the addition of catalysts to promote their oxidation or photooxidation, or both. The incorporation of photosensitive groups, e.g. ketones, into these polymers has also been attempted.

PVA is the most readily biodegradable of vinyl polymers. It is readily degraded in waste-water-activated sludges\textsuperscript{168}. The microbial degradation of PVA has been studied, as well as its enzymatic degradation by secondary alcohol peroxidases isolated from soil bacteria of the Pseudomonas strain\textsuperscript{169-170}. It was concluded that the initial biodegradation step involves the enzymatic oxidation of the secondary alcohol groups in PVA to ketone groups. Hydrolysis of the ketone groups results in chain cleavage. Other bacterial strains, such as Flavobacterium\textsuperscript{172} and Acinetobacter\textsuperscript{173} were also effective in degrading PVA. The controlled chemical oxidation of PVA was carried out to yield poly(enol-ketone) (PEK), which has a similar structure to the intermediate formed as PVA is biodegraded\textsuperscript{157}.

PVAc reportedly undergoes biodegradation more slowly\textsuperscript{174-175}. Copolymers of ethylene and VAc were susceptible to slow degradation in soil-burial tests\textsuperscript{176}. The weight loss in a 120-day period increased with increasing acetate content. Because PVA is obtained
from the hydrolysis of PVAc, which can be controlled easily in terms of the extent of hydrolysis and the sequence of PVAc and PVA, a controlled hydrolysis of PVAc followed by controlled oxidation should provide degradation materials having a wide range of properties and degradability.

PVA can form complexes with a number of compounds and has been used in the detoxification of organisms. When it is used in a low-MW form, i.e. below 15,000, it can be eliminated from organisms by glomerular filtration. PVA has also been used as a polymer carrier for pesticides and herbicides\textsuperscript{178-179}.

The plasticizer type is important\textsuperscript{180}. PVA is almost completely resistant to fungi and bacteria in dry state. Aqueous solutions are susceptible to microbial degradation.

Synthetic polymers are seldom used alone but are frequently mixed with plasticizers, lubricants, stabilizers, fillers\textsuperscript{114-117}, and other materials that usually change the biological resistance of the polymer and the finished composition. Such materials may be vulnerable to biological attack. Reports on plasticizers\textsuperscript{180} indicate that a particular choice can affect the durability of a product owing to the destruction of the plasticizer by bacteria and/or fungi. Most plasticizers are susceptible to microbial attack (Table 3). Not all additives increase product or polymer susceptibility to attack by biological agents. Some may even increase bioresistance, certain organometallic stabilizers, which increase fungal resistance.
Table 3. Susceptibility of common plasticizers to microbial attack\textsuperscript{118-119}
<table>
<thead>
<tr>
<th>Type of plasticizer</th>
<th>Susceptibility</th>
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<tr>
<td>abietic acid derivatives</td>
<td>susceptible</td>
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<tr>
<td>adipic acid derivatives</td>
<td>susceptible</td>
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<tr>
<td>aliphatic alcohols</td>
<td>susceptible</td>
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<tr>
<td>azelaic acid derivatives</td>
<td>susceptible</td>
</tr>
<tr>
<td>chlorinated hydrocarbons</td>
<td>resistant</td>
</tr>
<tr>
<td>citric acid derivatives</td>
<td>variable</td>
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<tr>
<td>dibutyl tartrate</td>
<td>variable</td>
</tr>
<tr>
<td>epoxidized oils</td>
<td>susceptible</td>
</tr>
<tr>
<td>epoxidized octyl tallate</td>
<td>susceptible</td>
</tr>
<tr>
<td>4,5-epoxytetrahydrophthalates</td>
<td>resistant</td>
</tr>
<tr>
<td>glycercyl esters</td>
<td>variable</td>
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<tr>
<td>glycolates</td>
<td>susceptible</td>
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<tr>
<td>laurates</td>
<td>susceptible</td>
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<tr>
<td>oleates</td>
<td>susceptible</td>
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<tr>
<td>phosphoric acid derivatives</td>
<td>variable</td>
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<td>phthalic acid derivatives</td>
<td>susceptible</td>
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<td>stearates</td>
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<td>succinic acid derivatives</td>
<td>susceptible</td>
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<tr>
<td>vegetable oils</td>
<td>susceptible</td>
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</table>
2-5. Polymeric biocides

Polymeric biocides after great promise for enhancing the efficacy of some existing biocides as well as reducing the environmental problems associated with others. Polymeric biocides can significantly reduce losses associated with volatilization, photolytic decomposition, dissolution, and transport. Moreover, increased efficiency, selectivity, and handling safety are additional benefits which may be realized. Many attempts have been made in polymeric drugs utilizing characteristic like polymeric biocides, especially, polymeric antitumors, but few works are reported on polymeric biocides.

Pentachlorophenol, a well known biocide, has been chemically anchored to polymers by copolymerizing pentachlorophenol methacrylate with MMA by Akagane and Matsuura. Pittman copolymerized pentachloro phenyl acrylate with both VAc and ethyl acrylate. Pittman's copolymers retarded or prevented growth of *Aspergillus sp.*, *Pseudomonas sp.*, *Alternaria sp.* or *Aureobasidium pullulans* significantly.

Nonaka and coworkers introduced phenolic hydroxy moiety by treating amine-functionalized resins with p-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid and 3,4,5-trihydroxybenzoic acid. Antibacterial activities increased in the order of increasing number of hydroxy groups.

Ikeda and coworkers evaluated the antibacterial activities of trialkyl-vinyl benzyl ammonium chloride monomers and their polymers by the conventional spread plate method and the viable counting method. The compounds with dodecyl chain exhibited particularly high activity. They also found that the polymers were more active than the corresponding monomers, due to possibly their favored adsorption onto the bacterial cell surface and the cytoplasmic membrane with subsequent disruption of its integrity.

Polycationic biocides with phosphonium salt were immobilized on PP surface through surface photografting to show high antibacterial activity. The bacterial cells in contact
with the immobilized polycationic biocides were observed by SEM to be significantly shrunken and deformed\textsuperscript{185}.

Sun and coworkers modified PS by chemically attaching a hydantoin derivatives\textsuperscript{186} and a chlorinated triazinedione moiety\textsuperscript{187}. These polymeric biocides are water insoluble so that toxicological evaluation would not be required when used for disinfecting potable water. \textit{N}-halamine polymeric disinfectants were synthesized and tested for efficacy on inactivating bacteria\textsuperscript{188}. Polymeric \textit{N}-halamine has an advantage in that it needs short contact time to kill microorganisms and its biocidal activity can be regenerated once exhausted by simply flowing an aqueous solution of free halogen through it. \textit{N}-halamine precursor monomers were copolymerized with other monomers in water with the aid of a surfactant to produce latexes, which could be used in numerous coating applications\textsuperscript{189}.

Oh and coworkers synthesized 2,4,4'-trichloro-2'-acyrloyloxydiphenyl ether, its homopolymer and its copolymer with styrene. The bactericidal activities decreased in the order of monomer > homopolymer > copolymer\textsuperscript{190}.

Methyl 2-benzimidazolecarbamate(carbendazim, CBZ), which has been used since 1960's as various pesticides, has relatively low toxicity(\textit{LD}_{50}=6,400\text{mg/kg for rat}). Recently it has been discovered that CBZ inhibits growth of fungi very efficiently\textsuperscript{191}.

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Chapter 2.

*Synthesis and Properties of Polyethylene with Environmentally Benign Characteristics*
A. Modification of polyethylene through nitroxide mediated living radical polymerization

1. Grafting of polystyrene branches to polyethylene and polypropylene

1-1. Introduction

Polyolefins have been used for various applications for human daily life. However few polymers are compatible with polyolefins due to the absence of any interaction groups in polyolefins. PE, PP and PS are major constituents in commingled waste plastics. Hence substances compatibilizing the three polymers with each other would be helpful to the recycling of commingled waste plastics without resort to the tedious and expensive sorting processes. PE-g-PS and PP-g-PS could be effective candidates for the compatibilizer\(^1,2\).

In general, polyolefin-grafted copolymers are synthesized by the post-polymerization methods. PE-g-PS copolymers have been synthesized by polymerization of styrene in the presence of PE with photoinitiation or with thermally dissociative initiation\(^3,5\). However a systematic study on the effects of molecular structure on the compatibilization with thus synthesized copolymers would be difficult to carry out, because graft density and graft length were hardly possible to control. Moreover crosslinking reactions often took place concomitantly.
In this study, PE-TEMPO and PP-TEMPO macroinitiators were synthesized respectively by reacting PE and PP with BPO and TEMPO. Styrene bulk polymerization with the macroinitiators produced PE-g-PS and PP-g-PS whose molecular structures could be characterized from the concentration of the TEMPO-dormant sites on the macroinitiators\textsuperscript{6-10}. The grafting copolymerization was also helpful to investigate the side reactions such as the chain transfer reactions because PS homopolymer by-product could be easily separated from the copolymers.

1-2. Experimental

Materials

Styrene (Junsei) was purified by two times of vacuum distillation. BPO (Acros organics) was purified by precipitation from chloroform into methanol, and recrystallized in methanol at 0°C. TEMPO (Aldrich) was used as received. LDPE ($M_w$ 482,000) and PP ($M_w$ 1,850,000) were donated by Hanwha (Korea) and Korea Petrochemical respectively. PS ($M_w$ 200,000) was received by Hannam Chemical (Korea).

Synthesis of macroinitiator

The LDPE was first dissolved in TCB at 170°C and kept under N\textsubscript{2} blanket to prevent oxidation. After stirring for 30 min, the chloroform solution of BPO (1M) was then quickly added to the hot solution and stirred for 2 min. The reaction was terminated with excess quantity of TCB solution of TEMPO (2M). The product was precipitated in methanol and dried \textit{in vacuo} followed by soxhlet-extraction with boiling methanol for 2 days to remove the unreacted TEMPO.

Grafting copolymerization
Styrene was bulk polymerized in the presence of the macroinitiator at 120°C. The product was precipitated in chloroform and dried in vacuo followed by soxhlet-extraction with boiling chloroform for 2 days to remove PS homopolymer formed during the copolymerization.

**Instrumentation**

$MW$ and its distribution were measured using GPC (Waters model 150C, TCB eluent, 1.0 $ml/min$, 145°C, column (porosity: 10 $\mu m$, Stragel® HT6E, HT5, HT3)) employing PS (Showadenko SL-105) as a standard. The thermal properties of the polymers were determined by DSC (Perkin Elmer DSC 7). Thermal history of the products was removed by scanning to 200°C with the heating rate of 20°C/min. After cooling down the sample at the rate of 5°C/min to room temperature, it was reheated at 20°C/min to 200°C and the DSC thermograms were obtained.

Graft copolymers were characterized by $^1H$-NMR spectra recorded at 120°C on a Bruker AC-250 FT-NMR spectrometer.

**Polymer blending**

The LDPE/PP/PS mixture was fed into the cam-type mixing head of BRABENDER Plasti-Corder(Western Germany, Type : 810602) set at 180°C. The rotor speed was maintained at 60 rpm and the blending was continued for 10min in the closed mixer. Blend sheets were made by hot pressing at 200°C for 5 min under 1.55 atm, and quickly immersed into ice water. PS sheets were prepared on a hot press at 180°C for 5 min under 1.21 atm and then immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the film were determined with a tensile test machine (Instron 4462) at a cross
head speed of 5 mm/min according to ASTM D 638 at 20 ± 1°C.

The film was fractured while immersed in liquid nitrogen and then etched with boiling chloroform to dissolve out the PS domains. SEM (Hitach S-4200) was used to observed the fractured surface morphology.

1-3. Results and Discussion

_Synthesis of PE-TEMPO and PP-TEMPO macroinitiators_

LDPE and PP were reacted with BPO and TEMPO to produce PE-TEMPO and PP-TEMPO respectively whose $^1$H-NMR spectra were shown in Fig. 1-1. Dokolas et al. investigated the chemistry of free radical graft copolymerization, initiated with $t$-butoxy radicals. They provided evidences that grafting on LLDPE occurred most frequently from the secondary C-H reaction sites, while grafting on PP took place predominantly at the tertiary C-H sites.

Comparing the $^1$H-NMR signals of LDPE and PP to those of PE-TEMPO and PP-TEMPO respectively, it can be perceived that a new peak appeared at 0.37 ppm due to the introduction of TEMPO into the polymers. A clear explanation has not been provided yet why the signal from the tetramethyl protons of TEMPO, whose $^1$H-NMR peaks usually appeared at 0.8–0.9 ppm moved upfield as far as to 0.37 ppm.

Yoshida and Fujii performed radical polymerization of methyl styrene using BPO in the presence of 4 methoxy-2,2',6,6'-tetramethyl-1-piperidinyl-1-oxyl (MTMPO). The tetramethyl protons from MTMPO on the polymer exhibited their $^1$H-NMR peaks at 0.30, 0.45, 1.00 and 1.15 ppm.

$^1$H-NMR spectra for both LDPE and PP homopolymers also exhibited small peaks at 0.8–0.9 ppm. Therefore the peaks at 0.8–0.9 ppm appearing in the spectra of PE-TEMPO and PP-TEMPO in Fig. 1-1
were thought to be due not only to the protons of TEMPO but also to those of LDPE and PP themselves. Contents of the TEMPO units in the macroinitiators were determined from the peaks at 0.37 ppm and 0.8–0.9 ppm, taking into consideration the contribution of LDPE and PP homopolymers to the peaks at 0.8–0.9 ppm, by assuming that the peak intensity of the methylene protons of LDPE and that of the methine protons of PP were the same as that corresponding to PE-TEMPO and to PP-TEMPO respectively.

Average number of TEMPO units per macroinitiator molecule, θ, was determined from average number of TEMPO units of the macroinitiator molecules, θ', using Eq. (1).

\[ \theta = \frac{\theta'}{1 + \theta'} \mu_w \]  

(1)

where \( \mu_w \) is the weight average degree of polymerization. \( \theta' \) was calculated, in turn, from the weight unit

\[ \overline{M_w} = M_1 \left( \mu_w - \frac{\theta'}{1 + \theta'} \mu_w \right) + M_2 \frac{\theta'}{1 + \theta'} \mu_w \]  

(2)

of the backbone polyolefin \( M_w \) using Eq(2)

Where \( M_1 \) and \( M_2 \) are molar mass of the repeating and that of the repeating unit holding a TEMPO unit respectively.

On the average, 6.9 TEMPO units and 8.8 TEMPO units were introduced per 1000 repeating units of PE-TEMPO and PP-TEMPO respectively. More TEMPO units were found on PP-TEMPO than on PE-TEMPO because the tertiary hydrogen of PP were more susceptible to be abstracted by the peroxide radicals compared to the hydrogens of LDPE.
On the contrary, Dokolas et al. predicted that PP was less reactive than LLDPE to free radical graft copolymerization initiated with t-butoxy radicals from their experimental results with 2-methyl pentane and 2,4-dimethyl pentane as models for LLDPE and PP respectively.

The $MW$ was decreased and the $PD$ became narrower during the reaction of PP with the BPO/TEMPO system. In contrast, the same reaction increased the $MW$ of LDPE (Table 1-1).

Roover et al. grafted MAH on PP using 1,3-di-t-butyl peroxyisopropyl benzene. They found the $MW$ of PP decreased exponentially with the peroxide concentration independently of the MAH concentration.

**Polymerization of styrene using PE-TEMPO and PP-TEMPO**

Styrene was bulk-polymerized in the presence of PE-TEMPO and PP-TEMPO in an attempt to synthesize PE-g-PS and PP-g-PS respectively, whose $^1$H-NMR spectra were determined in Fig. 1-2. These experiments were designed to measure amount of styrene polymerized as a result of the contribution of the reversible cleavage of the TEMPO-polymeric radical adduct, because styrene could be consumed also by the thermal self initiation and by the radicals produced by the chain transfer reactions. PS homopolymer produced could be easily removed from PE-g-PS and PP-g-PS by using chloroform.

The results of the styrene bulk-polymerization with the PE-TEMPO and PP-TEMPO were collected in Table 1-2 and 1-3 respectively.

When the weight increase was plotted as a function of polymerization time for the above two styrene polymerizations, it increased up to 20 hrs and then leveled off (Fig. 1-3). The plateauing behavior is also seen in the plot of grafting conversion as a function of total conversion (Fig. 1-4). This substantiates the fact that the chain transfer and the thermal self initiation took place in addition to the reversible cleavage of the TEMPO-polymeric radical adduct, because in the absence of the chain transfer or the thermal self initiation the weight increase would rise linearly with conversion.
Table 1-2 and 1-3 demonstrate that a huge amount of PS homopolymer was formed as by-product.

Greszta and Matyjaszewski incorporated the transfer to the Mayo dimer into their model, which was 20 times faster than the transfer to styrene, and their model fit accurately both the kinetic data and $MW$ of the thermal self initiated styrene homopolymerization.

The alkoxyamines could also be irreversibly decompose to the hydroxylamine and the macromolecular species.

Admitting that the rate of transfer to polymer is much slower than the other transfer reactions, the PE-g-PS and PP-g-PS should cease to grow once the chain breaking reactions took place.

At the polymerization temperature (120°C), the polymer radicals and the free TEMPO molecules are in equilibrium with the TEMPO-dormant site with equilibrium constant of $10^{11}$ l/mole.

While the free TEMPO molecules, which are approximately 0.1% based on the initial concentration of the alkoxyamine, are cleaved off from the alkoxyamine dormant site, propagation takes place by the radicals on the copolymer molecules.

Protection of the radicals on the copolymer molecules by the free TEMPO molecules becomes less probable and more susceptible to the chain breaking reactions, because radicals are continuously generated in styrene monomer moiety and share the TEMPO molecules with the radicals on the copolymer molecules.

The macroinitiators being used on an equal weight basis, molar concentration of TEMPO dormant sites of PE-TEMPO was 1.2 times higher than that of PP-TEMPO. However this does not provide full explanations for the curious fact that the weight increase in the polymerization with PE-TEMPO was much greater than that with PP-TEMPO.

Aside from the TEMPO dormant sites, the copolymer molecules could also became active for styrene polymerization once radicals were transferred from the styrene moiety to the copolymer molecules. We do not have at present any logical reasoning why the radicals are more easily transferred to PE-g-PS than to
PP-g-PS, or why the TEMPO-polymer radical intermediates in the PP-g-PS are more susceptible to the chain breaking reactions than those in PE-g-PS.

The MW of the PS homopolymer in Table 1-2 and 1-3 was much higher than that of PS produced during the styrene polymerization with TEMPO/BPO system.

Hui and Hamielec reported that molecular weight of PS produced by thermal self initiation decreased slightly or remained almost constant depending on polymerization temperature as the conversion rose. In direct contrast, MW of PS homopolymer in Table 1-2 and 1-3 increased with the conversion. This implies that some radicals on PS homopolymer molecules were protected by the free TEMPO molecules from the chain breaking reactions.

The glass transition temperature of PP-g-PS appeared at 105°C irrespectively of the copolymer composition indicating that PS and PP moieties in the copolymer were separated from each other, because the glass transition temperature was the same as that of PS homopolymer. The glass transition temperature of the PS phase in PE-g-PS was covered up by the melting peak of the PE phase.

It is to be note that the melting temperature of both PE-g-PS and PP-g-PS decreased as the PS content (Table 1-4) increased, which was ascribed to the fact that the PS moieties seized hold of the crystallizable PE and PP parts to reduce the crystallization rate of the latter.

Chung et al. also observed that the melting temperature of PE-g-PS synthesized by an anionic polymerization decreased with increase of the PS content.

**Compatibilizing effect of PE-g-PS and PP-g-PS**

PE-g-PS03 and PP-g-PS03 were compounded with the incompatible PP/PE/PS, PP/PS and PE/PS blend systems, and the results were collected in Table 1-3. The glass transition peak of the PS phase, the melting peaks of the PE and PP phase, and the crystallization peaks appeared well separated from each other,
except that $T_c$ of the PS phase was masked by the melting peak of the blends containing PE moiety.

Incorporation of the graft copolymers enhanced significantly the mechanical properties of the blends such as the maximum stress and the elongation at break (Table 1-5), in spite of the fact that the SEM photography in Fig. 1-5 did not show any clear indication of improved adhesion between the separated phases. However the domain size of the dispersed phase was reduced in the presence of the graft copolymers.

The crystallization temperatures (Table 1-3) were obtained during cooling at -5°C/min from the melt state. Hence the higher the crystallization temperature, the more easily the crystallization takes place. It is interesting to observe that the addition of the graft copolymer rendered the blends more crystallizable, which should be at least partly ascribed to the increased interfacial area for the crystal nucleation sites.
1-4. Reference


9. E. Yoshida, T. Ishizone, A. Hirao, S. Nakahama, T. Takata, T. Endo,


Fig 1-1. The $^1$H-NMR spectra of (a) PE-TEMPO (b) PP-TEMPO
Fig 1-2. $^1$H-NMR spectra of (a) PE-g-PS(PE-g-PS03) and (b) PP-g-PS (PP-g-PS03)
Fig 1-3. Weight increase as a function of polymerization time for bulk polymerization of styrene using PE-TEMPO(σ) and PP-TEMPO(τ) at 120°C.
Fig 1-4. Grafting of poly styrene to PE-TEMPO(σ) and PP-TEMPO(τ)

Total conversion :
(weight increase of the copolymer + weight of homopolymer)/
(initial weight of styrene)

Graft conversion :
(weight increase of the copolymer)/(initial weight of styrene)
Fig 1-5. Scanning electron photomicrographs of the fractured surface
2. Living radical copolymerization of styrene/maleic anhydride

2.1. Introduction

The ability to synthesize macromolecules with complex and controlled architecture is becoming an increasingly important aspect of polymer science. Traditionally, control of polymer $MW$ distribution and structure has been achieved using living polymerization techniques such as anionic or cationic polymerization.

Recent studies reported that narrow $PD$ resins could be synthesized by a stable free-radical polymerization (SFRP) process by using nitroxide free radicals such as TEMPO. Subsequently a large number of publications have appeared confirming the "living" nature of this new technique and demonstrating the preparation of well-defined macromolecular architecture. However, long reaction time and low $MW$ limited the usefulness of this reaction for industrial applications.

It has been reported that the rate of the SFRP could be enhanced by performing the reaction in the presence of polar additives, such as camphorsulfonic acid, 2-fluoro-1-methylpyridinium $p$-toluenesulfonate (FMPTS) and acetic anhydride. The strong organic acids have been known to reduce the autopolymerization of styrene, which took place concomitantly with the SFRP at high temperatures.

Benoit et al. performed the SFRP using a new type of nitroxide, 2,2,5-trimethyl-4-phenyl-3-azahexane-3- oxy and obtained polysisoprene and poly(1,3-butadiene) with low $PD$.

A series of styrene/MAH copolymerizations were performed, using BPO and TEMPO with varying amounts of MAH. Interestingly enough, MAH boosted up the rate of the SFRP significantly and made the SFRP realizable even below 110°C. In this paper, effects of MAH concentration on the SFRP for styrene/MAH copolymerization are reported.
2-2. Experimental

Styrene (Junsei) was purified by two times of vacuum distillation. BPO (Acros organics) was purified by precipitation from chloroform into methanol, and recrystallized in methanol at 0°C. TEMPO (Aldrich) and MAH (Showa Chemical Inc.) was used as received.

Styrene was copolymerized with MAH in the presence of TEMPO and BPO ([TEMPO]/[BPO]=1.8) at 120°C. The product was precipitated in methanol and dried in vacuum oven at 60°C until constant weight was attained.

MW and MWD were measured using GPC (Waters 410, RI detector, THF eluent, 1.0 ml/min, 30°C, column (porosity : 10μm, Stragel® HR 1, HR 2, HR 4, Linear)) employing PS (Showadenko SL-105) as a standard.

The thermal properties of the polymers were determined by DSC (Perkin Elmer DSC 7). Thermal history of the products was removed by scanning to 200°C with the heating rate of 20°C/min. After cooling down the sample at the rate of 20°C/min to room temperature, it was reheated at 20°C/min to 200°C and the second scan DSC thermogram was obtained.

Styrene/MAH copolymer was characterized by ¹H-NMR spectra recorded at room temperature on a Bruker AC-250 FT-NMR spectrometer. 10 mg of the copolymer was dissolved in 0.5 ml of CDCl₃ (20 wt/vol%) and was subjected to the ¹H-NMR measurements.

2-3. Results and Discussion

Styrene/MAH copolymers produced from the reaction medium containing 0.2 mole % of MAH and 17.5 mol% of MAH by BPO/TEMPO at 120°C exhibited ¹H-NMR spectra as shown respectively in Fig. 2-1 (a)
and Fig. 2-1 (b). The peak at 0.8 ppm in Fig. 2-1 (a) is ascribed to the methyl protons in TEMPO.

As the MAH concentration in the reaction increased to 17.5 mol%, methine peaks of MAH units in the copolymer were observed at 3.0~3.7 ppm as in Fig. 2-1 (b).

Conversion, $MW$ and $MWD$ are collected in Table 2-1 for copolymers synthesized from the reaction medium composed of 0.2~17.5 mol of MAH with $[\text{TEMPO}]/[\text{BPO}]$ fixed at 1.8, where the conversion was defined as weight of the produced copolymers divided by weight of the initial monomers.

Bulk polymerization of styrene for 20 hrs reached 42% of conversion with weight average $MW$ of 9,100. In comparison, conversions after 20 hrs copolymerization of reaction medium containing 2.6, 3.8 and 5.0 mol% of MAH in styrene increased respectively to 82, 86 and 91%. Thereafter a further increase in MAH concentration did not increase the rate of copolymerization considerably. Similarly $MW$ of the copolymers increased with MAH concentration up to 5.0 mole % and then leveled off. $MWD$ broadened to $M_w/M_n$ of 1.6 as the MAH content in the reaction medium increased to 17.5 mol%.

Table 2-2 and Table 2-3 lists conversion, $MW$ and $MWD$ of copolymers synthesized at different temperatures with $[\text{TEMPO}]/[\text{BPO}]$ of 1.8 and MAH concentration of 2.6 mol%. Contrary to the conventional radical copolymerization, $MW$ increased as the copolymerization temperature went up.

Fig. 2-2 shows good linear relationship between $\ln\{\ln(1-x)\}^1$ and $1/T$ for styrene homo-polymerization with an activation energy of 82.4 kJ/mole indicating that styrene homo-polymerization by BPO/TEMPO follows the 1st-order kinetics.

For copolymerization, the kinetics appears to be quite complicated due to different reaction rate constants and cross terminations. However $\ln\{\ln(1-x)\}^1$ vs $1/T$ plot appeared to be linear for styrene/MAH copolymerization by BPO/TEMPO except the copolymerization at 90°C when conversion was defined as previously.

The apparent activation energy was determined to be 64.7 kJ/mole from the slope of the plot. Thus it can
be said that addition of MAH in the reaction medium increased the copolymerization rate, and reduced its temperature dependence.

Polymer was not produced at all below 110°C for styrene homopolymerization. However, curiously enough, copolymer was formed from styrene/MAH (97.4 mol% /2.6 mole%) mixture at 90°C even though reaction temperature should be higher than 110°C in order to reactivate the bond blocked by TEMPO. Malmstrom et al.12 also observed that addition of a small amount of acetic anhydride accelerated greatly the nitroxide-mediated free radical polymerization. They suggested acylation of the alkoxyamine nitrogen leading to an increase in the liability of the C-ON bond as a possible explanation for the effect.

It has been reported10 that styrene/MAH copolymerization above 80°C proceeds randomly rather than in alternating manner, because the charge-transfer complex of styrene and MAH could not be formed. In this study, copolymerization of styrene/MAH was carried out well above 90°C, excluding the possibility of the copolymerization in the form of the styrene-MAH charge-transfer complex.

In Fig. 2-3 the initial slope of the plots for ln(1-x)1 vs time goes up with increase in MAH concentration. Random copolymerization of styrene/MAH took place in the initial stage of the reaction followed by polymerization of practically pure styrene after almost complete exhaustion of MAH molecules in the reaction medium (in this stage the polymerization rate fell sharply as in Fig. 2-3) to produce copolymers with styrene-co-MAH block and styrene-rich block.

Fig. 2-4 (a) and Fig. 2-4 (b) correspond DSC thermograms respectively for TPSM06 (MAH 9.6 mol%) and TPSM07 (MAH 17.5 mol%). $T_g$ of TPSM06 was 105.1°C which was slightly higher than that of PS homopolymer (100°C). On the other hand, two $T_g$'s appeared on DSC thermogram of TPSM07 at 105.1°C and 178.2°C respectively. As the copolymer was soxhlet extracted with boiling cyclohexane for 24 hrs, residual PS homopolymer in the copolymer would not exhibit any detectable glass transition.
A literature\textsuperscript{1} reports $T_g$'s of styrene/MAH copolymers containing 5.0 mol % of MAH and 33 mol % of MAH were 106°C and 155°C respectively. Therefore it can be said that the results in Fig. 2-4 (a) and Fig. 2-4 (b) supports the conclusion that TPSM07 is composed of styrene-co-MAH block and styrene rich block.

It should be noted that the high $T_g$ of TPSM07 (178.2°C) is much higher than $T_g$ of styrene/MAH copolymers having 33 mol% of MAH made by the conventional radical copolymerization(155°C). This is because MAH reacts with styrene-ended radical faster than styrene. Addition of MAH to MAH-ended radical should be difficult due to the steric hinderance of MAH. Hence MAH molecules wait until another styrene molecules react with MAH-ended radical. Therefore it can be said that styrene-co-MAH block in TPSM07 resembles styrene-alt-MAH rather than styrene-ran-MAH.

Fig. 2-5 shows $M_n$ and $M_w$ as a function of conversion. As was previously reported\textsuperscript{6} $M_n$ and $M_w$ of styrene homopolymer follow a good linear relationship with respect to conversion. When styrene/MAH concentration was carried out isothermally $M_n$ and $M_w$ of styrene/ MAH copolymer also increased linearly with conversion. However $M_n$ and $M_w$ of styrene/MAH copolymer produced at different temperatures deviated considerably from the linear relationship indicating that the copolymerization was not a perfect living system.

2-4. Reference


14. C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao, and W. Devonport,
Table 2-1. Effect of MAH concentration on the behavior of the styrene-MAH copolymerization
### Table 2-2. Effect of polymerization temperature on the behavior of the styrene-MAH copolymerization

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Polymerization time (hours)</th>
<th>[MA] (mol%)</th>
<th>Conversion (%)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
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Polymerization temperature: 120°C, [BPO]=0.033M, [TEMPO]/[BPO]=1.8
Table 2-3. Effect of polymerization time on the behavior of the styrene-MAH concentration

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<tr>
<th>Sample code</th>
<th>Polymerization temperature (°C)</th>
<th>Conversion (%)</th>
<th>$M_n$</th>
<th>$M_w$</th>
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<td>21,900</td>
<td>31,400</td>
<td>1.43</td>
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</table>

Polymerization time: 20 hrs, [BPO]=0.033M, [TEMPO]/[BPO]=1.8, [MA]=2.6 mol%,
[ST]=0.48mol, Polymerization temperature : 120°C, [TEMPO]/[BPO]=1.8, [MA]=5.0mol%

<table>
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<th>Sample code</th>
<th>Polymerization time(hrs)</th>
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<th>$M_w$</th>
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Fig 2-1. $^1$H-NMR spectra of copolymer (a) TPSM01 and (b) TPSM07
Fig 2-2. Relationship between $\ln\{\ln(1-x)\}$ and $1/T$ for styrene/MAH copolymerization by BPO/TEMPO system.

$\nu$ : styrene/MAH copolymerization
$\lambda$ : styrene homopolymerization
Fig 2-3. Representation of the copolymerization of styrene/MAH by the 1st-order kinetics

\[ [MA] = 5.0 \text{ mol\%} : \sigma, \ [MA] = 2.6 \text{ mol\%} : \tau \]

\[ [MA] = 0.2 \text{ mol\%} : \nu, \ [MA] = 0.0 \text{ mol\%} : \lambda \]
Fig 2.4. DSC thermograms of poly(styrene-co-MAH)

(a) Styrene/MAH copolymer produced from a reaction medium containing 90.4 mol% of styrene and 9.6 mol% of MAH (TPSM06)
(b) Styrene/MAH copolymer produced from a reaction medium containing 82.5 mol% of styrene and 17.5 mol% of MAH (TPSM07)
Fig 2-5. Molecular weight as a function of conversion for styrene homo-polymerization and for styrene/MAH copolymerization

- △, ▽: Mn and Mw for isothermal polymerization of styrene
- ○, ★: Mn and Mw for isothermal copolymerization of styrene and MAH
- □, ■: Mn and Mw for copolymerization of styrene and MAH at different temperatures
3. Synthesis of polyethylene-g-(styrene-co-maleic anhydride) and its compatibilizing effects on polyethylene/starch blends

3-1. Introduction

Introduction of functional groups onto polyolefins has been investigated to improve the compatibility of polyolefins with other synthetic polymers\(^1\text{,}^2\). Graft polymerization is often employed for the functionalization of polyolefins. The conventional graft polymerization on polyolefins using thermal and photoinitiators cannot control graft density and graft length effectively and sometimes crosslinking or chain scission takes place.

A TEMPO-bound macroinitiator\(^3\text{-}^5\) could synthesize various block copolymers such as PS-\(b\)-PCL\(^6\), PE-\(b\)-poly(\(p\)-styrene sulfonate)\(^7\) and PS-\(b\)-poly(\(p\)-bromostyrene)\(^8\), using the living character of the radical polymerization.

In this study, graft copolymerization of styrene and MAH was carried out using PE-TEMPO as a macroinitiator.

Styrene homopolymerization with PE-TEMPO proceeded very slowly and produced a large amount of PS homopolymer by-product. A negligible amount of MAH was grafted by PE-TEMPO when MAH was homopolymerized. However the graft copolymerization became fast in the presence of styrene/MAH mixture. The amount of MAH units in the produced PE-\(g\)-(styrene-\(\alpha\)-MAH) was much larger than that of MAH grafted on PE by using the conventional grafting method with thermal or photoinitiators.

Compatibilizing effect of PE-\(g\)-(styrene-\(\alpha\)-MAH) was investigated on PE/starch blend.

3-2. Experimental
Materials

Styrene (Junsei, Japan) was purified by two times of vacuum distillation. BPO (Acros organics, USA) was purified by precipitation from chloroform into methanol, and recrystallized in methanol at 0°C. TEMPO (Aldrich, USA) was used as received. LDPE (MI=5, Mw 482,000) were donated by Hanwha (Korea). Corn starch was received by Samyang (Korea). Other chemical compounds were of reagent grade and were used as received.

Synthesis of macroinitiator

LDPE was first dissolved in TCB at 170°C and kept under N₂ blanket to prevent oxidation. After stirring for 30 min, the chloroform solution of BPO (1M) was then quickly added to the hot solution and stirred for 2 min. The reaction was terminated with excess quantity of TCB solution of TEMPO. The product was precipitated in methanol and dried in vacuo followed by the soxhlet-extraction with boiling methanol for 2 days to remove the unreacted TEMPO.

Grafting copolymerization

Styrene and MAH was copolymerized in the presence of the macroinitiator, PE-TEMPO, at 120°C. The product was precipitated in chloroform and dried in vacuo followed by the soxhlet-extraction with boiling chloroform for 2 days to remove ungrafted poly(styrene-co-MAH) formed during the copolymerization.

Instrumentation

MW and MWD were measured using GPC (Waters model 150C, TCB eluent, 1.0 ml/min, 145°C, column
(porosity : 10μm, Stragel® HT6E, HT5, HT3)) employing PS (Showadenko SL-105) as a standard.

The thermal properties of the polymers were determined by DSC (Perkin Elmer DSC 7). Thermal history of the products was removed by scanning to 200°C with the heating rate of 20°C/min. After cooling down the sample at the rate of 5°C/min to room temperature, it was reheated at 20°C/min to 200°C and the DSC thermograms were obtained.

Graft copolymers were characterized by 'H-NMR spectra recorded at 120°C on a Bruker AC-250 FT-NMR spectrometer. 10mg of the copolymer was dissolved in 0.5 ml of 1,2-dichlorobenzene(20 wt/vol%) and was subjected to the 'H-NMR measurements.

**Polymer blending**

The PE-g-(styrene-co-MAH) mixture was first dissolved in TCB at 140°C and kept under N₂ atmosphere. After stirring for 30 min, starch was then added to the hot solution and stirred for 20min. The product was precipitated in methanol and dried \textit{in vacuo} at 60°C.

Blend sheets were made by hot pressing at 200°C for 5 min under 1.55 atm, and quickly immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the film were determined with a tensile test machine (Instron Model No. 4200) at a cross head speed of 50mm/min according to ASTM D 638 at 20°C, RH 65%.

The film was fractured while immersed in liquid nitrogen. SEM (Hitach S-4200) was used to observed the fractured surface morphology.

**3-3. Results and discussion**

Fig. 3-1 (a) shows 'H-NMR spectra of PE-TEMPO. The protons of the tetramethyl groups of the
TEMPO units showed their peak at 0.8~0.9 ppm and 0.37 ppm. Since PE homopolymer also exhibited small peaks at 0.8~0.9, the contribution of the tetramethyl protons of the TEMPO units in the peak at 0.8~0.9 ppm was calculated by assuming that the number of methylene protons of PE homopolymer, whose peaks appeared at 1.2~1.4 ppm, was the same as that of methylene protons of PE-TEMPO. Styrene bulk polymerization using PE-TEMPO as a macroinitiator proceeded slowly and produced a large amount of PS homopolymer as by-product, indicating that a thermal initiation of styrene took place significantly. A possible radical chain transfer from PE-TEMPO to styrene should contribute in part to the PS homopolymer production. However styrene/MAH copolymerization with the PE-TEMPO progressed much more rapidly than styrene homopolymerization did. And the amount of PS homopolymer by-product decreased as the mole fraction of MAH increased in the reaction medium. Fig. 3-1 (b) exhibits 1H-NMR spectra of styrene/MAH copolymers produced over the PE-TEMPO. The styrene/MAH copolymers should be graft-copolymers because the PE-TEMPO contained 6.9 TEMPO units per 1000 repeating units. Methylene protons of ethylene and those of styrene units exhibit their peaks at 1.2~1.4 ppm and 1.7~2.0 ppm respectively. Phenyl ring protons of styrene units appeared at 6.6~7.4 ppm. The peaks at 2.4~3.4 ppm correspond to the methine protons of MAH units. Table 3-1 demonstrates the results of styrene/MAH copolymerization with the PE-TEMPO. The copolymerization was carried out in bulk state, but xylene solution polymerization was employed for the copolymerization when MAH concentration was higher than 2.5 M where MAH began to be insoluble in styrene. Since the formation of styrene/MAH charge transfer complex became a rare event above 80°C, styrene/MAH copolymerization at 120°C or higher should proceed randomly rather than in an alternating manner.
MAH content in the copolymer was determined from the FTIR spectra using the peak intensity at 1780cm⁻¹ (stretching of carbonyl group of MAH) and that at 719cm⁻¹ (C-H stretching of ethylene units). As the MAH anhydride ring could be opened during the copolymerization, the copolymer was heated at 180°C for 4 hrs under vacuum before the FTIR measurements. MAH content thus obtained was lower than that determined from ¹H-NMR spectra. We place more confidence in the FTIR results than in the ¹H-NMR ones, because ¹H-NMR peaks of MAH units were poorly resolved.

Fig. 3-2 shows conversion of styrene/MAH copolymerization as a function of styrene mole fraction in the reaction medium. The copolymerization time was fixed to be 20 hrs.

It is immediately evident that the copolymerization became faster as the concentration of styrene and that of MAH became equimolar.

Melting point of PE moiety in PE-g-(styrene-co-MAH) decreased, and crystallization peak, observed during cooling at -5°C/min on DSC, appeared at a lower temperature, as the amount of the grafted styrene/MAH copolymer increased, indicating that the grafted copolymer reduced the crystallization rate of the PE phase (Table 3-1).

Table 3-2 demonstrates the tensile properties of PE/starch/PE-g-(styrene-co-MAH) blends. Average of at least 5 measurements was taken. Addition of PE-g-(styrene-co-MAH) increased the elongation at break of the blends to a slight extent.

Fig. 3-3 exhibits FTIR spectra of PE-g-(styrene-co-MAH)(a), PE/starch/PE-g-(styrene-co-MAH)(b) and PE/starch blends(c). The stretching vibration peak of carbonyl group of MAH appears at 1790cm⁻¹ and 1865cm⁻¹. The peak at 1730cm⁻¹ corresponds to stretching of carbonyl groups in the ester groups. Carboxylic groups of MAH exhibits its peak at 1710cm⁻¹. The intensity of the peak at 1650cm⁻¹ due to the absorbed water decreased after the blending process.

PE-g-(styrene-co-MAH) showed peaks not only at 1730, 1790, and 1865cm⁻¹ but also at 1710cm⁻¹ as a
shoulder. It can be perceived from Fig. 3-3 that decrease of the peak intensity corresponding to the anhydride carbonyl of MAH or increase of the peak height of the ester carbonyl groups was not discernible after the blending, saying that the esterification reaction between MAH and starch did not take place appreciably. Morphology of the fractured surface of the blends demonstrated in Fig. 3-4 does not provide any clear evidence of enhanced interfacial adhesion owing to PE-g-(styrene-co-MAH).

Tetrabutyl titanate (TNBT, Ti[O(CH₂)₃CH₃]₄; 0.01g/g of polymer) was added to TCB solution of PE/Starch/PE-g-(styrene-co-MAH)(64/26/10), and the solution was kept at 170°C for 20 min and then was precipitated quickly in methanol. The specimens prepared by hot pressing the precipitated solid after drying were subjected to the measurements of the tensile properties, and the results are shown in Table 3-2. Morphology of fractured surface of PE/starch/PE-g-(styrene-co-MAH) specimens (64/26/10) prepared by compounding in the absence of TNBT (Fig. 3-4 (c)) shows that many starch particles protruded on the fractured surface, which is an evidence that weak points were concentrated at the interface, and that cracks were propagated mainly through the interface. In sharp contrast, Fig. 4-e exhibits that the number of starch particles protruded on the fractured surface of the same blend but prepared in the presence of TNBT decreased significantly compared to that in Fig 3-4 (c). This clearly substantiates that the weak points concentration at the interface was mitigated by enhancing the interfacial adhesion through the esterification reaction between MAH and starch catalyzed by TNBT. Improvement of elongation at break of PE/Starch/PE-g-(styrene-co-MAH)-TNBT compared to that of the same blend but without TNBT, as shown in Table 3-2, should also be ascribed to the enhanced interfacial adhesion.

3-4. Reference


4. R. P. N. Veregin, M. K. Georges, P. M. Kazmaier and G. K. Hamer, 
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5. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer and M. Saban, 


Fig 3-1. $^1$H-NMR spectra of (a) PE-TEMPO and (b) TPESTMA03
Fig 3-2. Conversion of the copolymerization in the presence of PE-TEMPO as a function of [ST]/([ST]+[MA]).
Fig 3-3. FTIR spectrum of blend system

\[
\begin{align*}
\text{PE/Starch} & \quad \text{PE/Starch/TPEMAST05} \\
\text{TPEMAST05} & \quad \\
\end{align*}
\]
4. Synthesis of PVAc-g-PS and its Compatibilizing Effect on PS/PVAc Blends

4-1. Introduction

Aside from the anionic 'living' polymerization system, 'living' stable free radical polymerization using TEMPO produces PS of narrow MWD. Various block copolymers of styrene and other monomers have been synthesized by 'living' stable free-radical polymerization such as PS-b-PCL, PS-b-Poly(styrene sulfonic acid), PS-b-Poly(p-bromostyrene). Yosida and Fujii used a 4-methoxy derivative of TEMPO to polymerize methylstyrene in accordance with the 'living' mechanism.

In this study we attempted to synthesize block copolymers composed of PVAc and PS blocks. Copolymerization of VAc in the presence of the PS-TEMPO macroinitiators, which was made by styrene homopolymerization using BPO and TEMPO, was unsuccessful because the monomer without stabilizing substituents (VAc), would self propagate rather than copolymerize with the monomer with stabilizing substituent (styrene), and because the reaction temperature (120°C) to make the dormant species active enough was well above the boiling point of VAc (72°C).

This article describes the copolymerization behavior of styrene using PVAc-TEMPO macroinitiator and compatibilizing effect of the resulting copolymer on the incompatible PS/PVAc blends.

4-2. Materials and Method
**Materials**

VAc (Aldrich) and styrene (Junsei) was purified by three times of vacuum distillation and TEMPO (Aldrich) was used as received. PS ($M_w$ 200,000) and PVAc ($M_w$ 280,000) for blending were donated by Hannam Chemical Co. and Orient Chemical Co. respectively.

**PVAc-TEMPO Macroinitiator**

VAc was bulk-polymerized with different amount of BPO at 60°C and terminated with excess quantity of TEMPO. The product was precipitated into $n$-hexane and was soxhlet-extracted with boiling $n$-hexane for 2 days to remove the unbound TEMPO, and finally dried in vacuo to attain constant weight.

**PVAc-g-PS**

PVAc-TEMPO macroinitiator was soluble in styrene and styrene was bulk polymerized in the presence of the macroinitiator at 120°C. The product was precipitated in methanol and dried in vacuo followed by soxhlet-extraction with boiling methanol and boiling cyclohexane in sequence each for 2 days to remove unreacted PVAc-TEMPO macroinitiator and PS homopolymer formed during the copolymerization.

**Instrumentation**

$M_W$ and $M_W$ were measured with GPC (Waters 410, RI detector, THF eluent, 1.0 ml/min, 30°C, column (porosity: $10\mu m$, Stragel® HR 1, HR 2, HR 4, Linear)). Narrow molar mass PS standards (Showadenko SL-105) were used for the universal calibration. Copolymer composition was analyzed with NMR (Bruker DPX250). A polarizing microscope (Nikon, OPTIPHOT 2-POL) was used to obtain the optical micrographs of the copolymer films of 0.05μm thick made by chloroform solution casting.
tan δ of the film (30×4×0.5 mm) was measured using Rheovibron (DDV-II-C) at a fixed frequency of 110 Hz while heating the sample from -50°C to 150°C at a heating rate of 20°C/min.

Mechanical properties of the film were determined with a tensile test machine (Instron 4462) at a cross head speed of 5 mm/min according to ASTM D638 at 15 ± 1°C.

The film was fractured while immersed in liquid nitrogen and then etched with methanol to dissolve out PVAc domains. A SEM (Hitach S-4200) was used to observed the fructured surface morphology.

**Peel test**

Copolymer films and PVAc sheet were made by hot pressing at 140°C for 4 min under 4–8 atm, and quickly immersed into ice water. PS sheets were prepared on a hot press at 180°C for 5 min under 12.1 atm and then immersed into ice water. The film thus formed was free from any distortion problems.

Copolymer films (0.05±0.02 mm thick) were put in between PS sheet (0.3±0.1 mm thick) and PVAc sheet (0.3±0.1 mm thick) and then compacted by hot pressing at 140°C for 5 min under 3.1 atm. Specimens of 15×2.5×0.6 mm were prepared according to ASTM D3870. The PS sheet and the PVAc sheet were peeled apart at 5 mm/min. Temperature for the peel test was controlled to be 15±1°C well below the softening point of PVAc.

**4-3. Result and Discussion**

Molecular characteristics of PVAc-g-PS copolymer are summarized in Table 4-1. TP in the sample code means TEMPO-terminated PVAc, and the figures after TP correspond to $M_i \times 10^3$ of the macroinitiator.
(PVAc-TEMPO). The figures following PS signify $M_r \times 10^3$ of the PVAc-g-PS copolymers. Hence PS124TP115 corresponds to the PVAc-g-PS copolymer having $M_r$ of 124,000 synthesized by copolymerization of styrene in the presence of the macroinitiator whose $M_n$ was 115,000.

$\theta$ (number of branch sites/mole of VAc units) was assumed to be average number of TEMPO molecules in the PVAc-TEMPO macroinitiator, measured from the $^1$H-NMR spectra. The $MW$ of the PVAc-g-PS copolymers analyzed by GPC did not increase significantly compared to the $MW$ of the corresponding macroinitiator. However the average $M_n$ of the PVAc-g-PS copolymers was much higher than the GPC results when calculated from the ratio of $^1$H-NMR peaks for styrene units to those of VAc units as shown in Table 4-1. Therefore it can be said that copolymerization of styrene in the presence of the macroinitiator did not yield PVAc-$b$-PS block copolymers but produced PVAc-g-PS graft copolymers with PVAc Backbone chain grafted with PS chains. The number of the nitroxide bonds per macroinitiator far greater than 1.0 supports this point of view. The hydrodynamic volume of the copolymer did not increase in proportion to the grafting content of PS chains. It has been known that bulk polymerized PVAc has many branches due to the chain transfer to polymer occurring mainly on the hydrogen atoms of the acetyl group. The radical formed in the chain transfer reaction is stabilized by the neighboring carbonyl group and continues VAc chain propagation$^{12}$. The values of the chain transfer constant, $C_P$, was determined to be $1.8 \times 10^{-4}$ from viscosity, light-scattering and osmotic pressure measurements$^{13}$. According to Flory the branching density $\rho$ (number of branches per monomer molecules polymerized) can be expressed as $\rho = C_p/[1+(1/p)\ln(1-p)]$ where $p$ is the extent of reaction.

The branching density thus calculated was in range $1.28 \sim 9.49 \times 10^{-5}$ which was far below the corresponding values in Table 4-1. It is possible that the nitroxide bonds in the macroinitiator do not participate in the
ramification. Instead, they can be transferred to form PS-TEMPO by combining with styrenic radicals. Therefore, the actual number of branching sites should be less than that of the nitroxide bonds on the macroinitiator. However, the $C_p$ value of $1.8 \times 10^{-4}$ seems to be underestimated, because the copolymerization produced only an insignificant amount of PS homopolymer.

The temperature dispersions of tan $\delta$ of the copolymer in Fig. 4-1 exhibited two dispersion peaks indicating that the PVAc-g-PS copolymer had phase-separated morphology. However, both the higher transition peak corresponding to the PS phase and the lower transition peak corresponding to the PVAc phase moved slightly downward as a result of the grafting. Comparing the intensity of the PS phase transition peak with that corresponding to the PVAc phase, it can be confirmed that the content of styrene units in the copolymer was not so low as that predicted from the GPC results.

The optical micrographs of the solution cast film of the copolymer in Fig. 4-2 show the phase-separated morphology. It is interesting to observe that the domains became more distinct, as the content of VAc units in the copolymer increased from 12.1 mol % (Fig 4-2 (d)) to 18.8 mol % (Fig 4-2 (a)), indicating that the phase-separation in the copolymer with higher VAc content was realized more completely. Moreover, both the tan $\delta$ peak of the PS phase and that of the PVAc phase in the copolymer moved to that of the respective parent polymers as the copolymer became richer in VAc units.

The PVAc-g-PS copolymer was used as a compatilizer for PS/PVAc blends. Table 4-2 shows $T_s$ s of the solution-mixed blends determined from the tan $\delta$ peaks by Rheovibron. The PVAc phase and the PS phase in the blends exhibited their respective $T_s$ s, and confirmed the phase separated morphology. However, when the copolymer having the highest content of VAc units, PS124TP115, was added to the PS/PVAc blends, $T_s$ of the PS-phase as well as that of PVAc-phase appeared at a lower temperature than when the other copolymers were used. The pronounced effect of PS124TP115 on the $T_s$ s of the PS/PVAc/PS124TP115 blends was doubted because the amount of the copolymer added was quite limited. However, three times of the $T_s$
measurements gave the identical results.

Table 4-3 lists the tensile properties of the solution-mixed blends. The PS phase formed the continuous phase and the PVAc counterpart formed the dispersed phase in the PS/PVAc 70/30 blend, so that the blend was almost as brittle as PS. The stress-strain curve of PS/PVAc/PS124TP115 blends appeared especially different from that of the blends containing the other copolymers. As a result elongation at break of PS/PVAc/PS124TP115 increased considerably compared to the other counterparts.

Fig. 4-3 demonstrates that the domain size of the PVAc phase in PS/PVAc/PS124TP115 blends decreased due to the addition of PS124TP115.

The film 0.05±0.02 mm thick of the different copolymers were inserted between PS sheet and PVAc sheet, and then hot pressed at 140°C under 3.1 atm. The PS sheet and the PVAc sheet were then peeled apart and the strength was measured. The results are summarized in Table 4-4. In the absence of the copolymers, the peel test exhibited stable crack growth and gave reproducible results. The reproducibility of the test became poor when the copolymers were inserted between the two sheets. However it is apparent from Table 4-4 that the adhesive strength of PS124TP115 was superior to that of the other copolymers.

Optical micrographs of the surface of the PVAc sheet and that of the PS sheet after the peel test are shown in Fig. 4-3. Linear grooves were formed perpendicular to the direction of the load displacement, corresponding to the stick-slip curve of the peel test results.

When the film of PS145TP110, PS144TP96 or PS162TP89 was inserted most of the copolymer adhered to the PS sheet surface rather than to the PVAc sheet surface. In contrast when PS sheet and PVAc sheet with PS124TP115 in between, were peeled apart, PS124TP115 appeared to adhere not only to the PS sheet surface but also to the PVAc sheet surface confirming better adhesive characteristics of PS124TP115 compared to the other copolymers (Fig. 4-4).

4-4. Reference


Fig 4.1. Tan δ of PVAc-g-PS measured by Rheovibron\textsuperscript{14}
Fig. 4.2. Optical microscopy of copolymer (X 1000)\(^{11}\)
Fig 4-3. Fracture surfaces of the solution blended PS/PVAc/PS124TP115

(a) 70/30/0  
(b) 70/28/2  
(c) 70/26/4  
(d) 70/20/10
Fig 4-4. Micrographs of the surface of the PVAc film and that of the PS film after the peel test (X 100)\textsuperscript{14}

5. Synthesis of PVAc-\textit{g}-PS and Application to Preparation of Porous
Membranes

5-1. Introduction

Living radical polymerization mediated by TEMPO was initiated by George et al.\(^1\)\(^-\)\(^4\) to synthesize PS with narrow PD. Subsequently many researches have been devoted to extend spectrum of polymerizable monomers, to increase polymerization rate and to produce star shaped polymers\(^5\), hyperbranched polymers\(^6\) and random\(^7\) or block copolymers\(^8\)\(^9\).

In this study copolymerization of VAc and styrene in sequence with TEMPO/BPO was carried out. This was interested in the copolymerization, because the copolymer produced would have better defined structure compared to that obtained by the conventional graft copolymerization. As PVAc is immiscible with PS, the copolymer would have a phase-separated morphology, whose domain size depends not only on the copolymer composition but also on the branching architecture of the copolymer.

VAc has been polymerized via a radical mechanism. Many chain breaking reactions take place during the VAc polymerization due to the highly active growing radicals\(^10\).

Aside from the termination reaction, the chain transfer reactions such as the chain transfer to monomer and the chain transfer to polymer inevitably attend the VAc polymerization. The acetoxy methyl groups in PVAc have been reported to be principal sites for the chain transfer to polymer reaction. Therefore PVAc moiety could be separated from PS moiety if the two polymer sections were linked via the acetoxy methyl groups because the branches ramifying from the chain transferred acetoxy methyl groups could be alcoholyzed. Porous membranes with a controlled pore size could be prepared by adjusting the copolymer structure and by removing one of the two polymer fractions.
5-2. Experimental

Materials

VAc (Aldrich) and styrene (Junsei) were purified by two times of vacuum distillation and TEMPO (Aldrich) was used as received. BPO (Acros organics) was purified by precipitation from chloroform into methanol, followed by recrystallization with methanol at 0°C.

Instrumentation

MW and MWD were measured by GPC (Waters 410, RI detector, THF eluent, 1.0 ml/min, 30°C, column (porosity: 10μm, Stragel® HR 1, HR 2, HR 4, Linear)). Narrow molar mass PS standards (Showadenko SL-105) were used for the universal calibration.

Graft copolymer was characterized by 1H-NMR spectra recorded at room temperature on a Bruker AC-250 FT-NMR spectrometer. 10 mg of the copolymer was dissolved in 0.5 ml of CDCl3 (20 wt/vol %) and was subjected to the 1H-NMR measurements.

PVAc-TEMPO Macroinitiator

VAc was bulk-polymerized with different amount of BPO at 60°C and terminated with excess quantity of TEMPO. The product was precipitated into n-hexane and was soxhlet extracted with boiling n-hexane for 2 days to remove the unbound TEMPO, and finally dried in vacuo to attain constant weight.

PVAc-g-PS

PVAc-TEMPO macroinitiator were soluble in styrene and bulk polymerization of styrene in the presence of
the macroinitiator at 120°C was easily carried out. The product was precipitated in methanol and dried *in vacuo* followed by soxhlet-extraction with boiling methanol and boiling cyclohexane in sequence each for 2 days to remove unreacted PVAc-TEMPO macroinitiators and PS homopolymers formed during the copolymerization.

**Polar membranes**

Copolymer films were made by hot pressing at 140°C for 4 min under 4.8 atm, and quickly immersed into ice water. The film thus formed was free from any distortion problems. The film was immersed in 100 ml of 0.5 M NaOH methanol solution, for 48 hrs, washed with distilled water, and dried under vacuum followed by soxhlet-extraction with water for 2 days to remove the unbound PVOH. The film was fractured while immersed in liquid nitrogen. A SEM (Hitachi S-4200) was used to observe the fractured surface morphology.

**5-3. Results and Discussion**

**Preparation of PVAc-TEMPO macroinitiators**

Kinetics of radical chain polymerization in general is expressed as Eq (1)

\[ \frac{2(1 - \sqrt{1 - \varepsilon x}) - \sqrt{1 - \varepsilon}}{1 - \sqrt{1 - \varepsilon}} \ln \frac{\sqrt{1 - \varepsilon x} - \sqrt{1 - \varepsilon}}{1 - \sqrt{1 - \varepsilon}} - \ln \frac{\sqrt{1 - \varepsilon x} + \sqrt{1 - \varepsilon}}{1 + \sqrt{1 - \varepsilon}} \]

\[ = \frac{2 k_p f_k}{k_d} \left(1 - \exp\left(-k_d \frac{1}{2}\right)\right) \]  

where propagation reaction rate constant \((k_p)\), termination reaction rate catalyst \((k_t)\), initiator efficiency \((f)\), initiator decomposition rate constant \((k_d)\) are assumed to be constant. \(\varepsilon\) is introduced here to take into consideration the density increase of the reaction medium.

The value of \(\varepsilon\) is about 0.2 for VAc polymerization and \(k_d\) is \(8.38 \times 10^6\) s\(^{-1}\) for BPO at 60°C\(^{10}\).
With these values, Eq (1) relates the conversion in Table 5-1 to polymerization time as shown in Fig. 5-1, indicating that the kinetics of VAc polymerization can not be expressed as simply as in Eq (1), because the values of the constants in Eq (1) change greatly with the conversion.

According to Table 5-1, the conversion of TP241 was especially much higher than that predicted by Eq (1). This is because BPO of high concentration was used and the conversion reached as high as 60% for the preparation of TP241 and the polymerization rate was accelerated as a consequence of the gel or the Trommsdorff effect.

Actually TP241 contained 12.5 wt% of methanol insoluble fraction, while TP210, TP200 and TP158 were dissolved completely in methanol.

Theoretical value of the $PD\left(M_w/M_c\right)$ is 2.0 for polymers when the chain transfer and the disproportionation termination are the principal dominating chain breaking reactions.

Table 5-1 illustrates that the polydispersity of sol fraction in TP241 was as broad as 3.12, while the other PVAc-TEMPO macroinitiators had polydispersity in the range between 1.64 and 1.84.

The gelation takes place due to the chain transfer to polymer reactions, and therefore PVAc-TEMPO macroinitiators could have different number of TEMPO molecules in their chain depending on the ratio of the radical transfer rate to the radical elimination rate.

Fig. 5-3 (a) demonstrates 1H-NMR spectra of PVAc-TEMPO. The tetramethyl protons of TEMPO exhibit their peak at 0.8–0.9 ppm. Number of TEMPO molecules per VAc unit, $q'$, can be calculated using Eq (2).

\[
\frac{12\theta'}{6 + 5\theta' + 12\theta'} = \frac{\text{Area of peak at 0.8–0.9 ppm}}{\text{Total Peak Area}}
\]

(2)

$M_c$ is expressed in terms of $\theta'$ and weight average degree of polymerization ($DP$) in Eq (3).
\[ M_w = 86(DP - \frac{\theta'}{1 + \theta'}DP) + 241 \frac{\theta'}{1 + \theta'}DP \]  

(3)

Where the \( \theta' \cdot DP/(1 + \theta') \) term corresponds to number of TEMPO molecules per macroinitiator molecule (\( \theta' \)).

In radical chain polymerization system, growing polymer radicals coexist with dead polymer molecules, and the concentration of the former is generally much lower than that of the latter. Therefore the radical transfer takes place mostly onto the dead polymer radical molecules and it is hardly probable that a growing polymer would have more than 2 radicals at the same time.

However, Table 5-1 shows that the values of \( \theta' \) are much greater than those expected. \( \theta' \) was 2.7 mole/mole of macroinitiator even when the conversion was as low as 0.01 which was far below the gel point (TP136).

\( \theta' \) increased as the conversion went up. \( \theta' \) of TP241 was lower compared to the other macroinitiators because radicals on the growing polymer molecules (at a conversion as high as 60%) were terminated by the crosslinking or by the other termination reactions.

**Preparation of PVAc-g-PS**

Radical chain transfer to PVAc occurs mainly on site (C) rather than on site (B)\(^{11} \).

When TEMPO molecules are bonded to (C), they would hydrolyse easily. TP115, whose \(^1\)H-NMR
spectrum is shown in Fig. 5-4 (a), was hydrolyzed in KOH methanol solution for 24 hrs. $^1$H-NMR spectrum of the resulting product is demonstrated in Fig. 5-4 (b). The peak at 0.8 ppm in Fig. 5-4 (a) disappeared from Fig. 5-4 (b) saying that TEMPO molecules bonded to the acetoxy methyl groups were removed during the alcoholysis procedure.

Styrene was bulk polymerized with the PVAc-TEMPO macroinitiators, and the results are shown in Table 5-2. As stated above, one macroinitiator molecules had several TEMPO-bonded dormant sites, the resulting copolymer should be PVAc-g-PS with PVAc backbone chain carrying several PS branches.

Products from the copolymerization were soxhlet extracted with boiling methanol to separate PVAc homopolymer. The amount of the soxhlet extracted fraction was 1.0~2.3\% (Table 5-2 (a)) indicating that almost all the PVAc molecules participated in the copolymerization with styrene.

These results confirm the previous conclusion in that few PVAc molecules were devoid of active radicals on them at least near the conversion where the gel effect came into effect.

The residual fraction after the methanol soxhlet extraction was subjected to cyclohexane soxhlet extraction to remove PS homopolymer by-product. However the amount of VAc units contained in the cyclohexane soxhlet extracted fraction could in no way be negligible (Table 5-2 (b)). Table 5-2 (c) summarizes average $M_W$ of PVAc-g-PS after the two-step soxhlet extraction measured by GPC. In the last column of Table 5-2 (c), $M_w$ estimated using the data of $M_w$ of PVAc-TEMPO and the composition of PVAc-g-PS from the $^1$H-NMR spectra.

$M_n$ and $M_w$ of the copolymer measured by GPC increased linearly with the conversion as demonstrated in Fig. 5-5. However $M_w$ from the GPC measurements was much lower than that estimated from the copolymer composition.

This was ascribed to the fact that the hydrodynamic volume of PVAc-g-PS in the GPC measurement did not increase linearly with the real $M_W$ due to the branched structure of the copolymers.
Contrary to expectations, the content of styrene units was higher in PVAc-g-PS made from PVAc-TEMPO macroinitiator with smaller value of \( \theta \), which seemed to be due to the fact that the copolymer molecules rich in styrene units were removed during the cyclohexane soxhlet extraction.

Fig. 5-6 illustrates that bulk polymerization of styrene using the PVAc-TEMPO macroinitiator can be represented by the 1st order reaction rate constant.

Fig. 5-7 exhibits that the apparent reaction rate constant is a linear function of TEMPO concentration in the macroinitiator saying that all the TEMPO dormant sites participated in the styrene bulk polymerization with equal reactivity.

**Preparation of porous membranes**

The PVAc is converted into poly(vinyl alcohol) (PVA) by the hydrolysis of the copolymer with KOH methanol solution and the PVAc moiety is to be cleaved away from the PS part, because PS branches in PVAc-g-PS are bonded mainly to the acetoxy methyl groups of PVAc. Soxhlet extraction of the resulting copolymer sheet with water below the glass transition temperature of PS would dissolve out the PVA moiety leaving pores behind while the PS matrix remains intact.

Fig. 5-8 shows a fractured surface of PS285TP210 sheet (VAc unit content: 18.8 mole %) after the methanolysis (Fig 5-8 (a)) and after the water soxhlet extraction (Fig. 5-8 (b)). Pores of 2–5\( \mu m \) were created in the soxhlet extracted PS285TP210 sheet. The same experiment was carried out using PS349TP158 (VAc unit content: 13.3 mol %), and the resulting sheet had pores of 1–2 \( \mu m \), indicating that the size of the pores were largely determined by the copolymer composition.

PVAc-g-PS had a phase separated morphology, and the domain size of each phase should be much smaller than that of each phase in a simple PVAc/PS blend.

Pore size of polymer membranes made from polymer blends can be controlled thermodynamically by the
compatibility between the polymer components. More compatible polymer blend system yields membranes with smaller pore size. However, in this case, solvent becomes quite limited to remove selectively one of the polymer components.

This study suggests a possibility for preparation of hydrophobic PS membrane or hydrophilic PVA membrane with controllable pore size by adjusting MW, composition or degree of branching from PVAc-g-PS copolymer.

5-4. Reference


Fig 5-1. Results of vinyl acetate bulk polymerization
Fig 5-2. Block copolymerization of TEMPO terminated PVAc

Copolymerization of TEMPO terminated PVAc
Fig 5-3. $^1$H-NMR spectra of (a) TP210 and (b) PS23TP210
Fig 5-4. $^1$H-NMR spectra of (a) TP210 and (b) after methanolysis
Fig 5-5. Molecular weight as a function of conversion for bulk polymerization of styrene using the macroinitiator TP241. (polymerization temperature 120°C) ($\sigma$ : Mn, $\tau$ : Mw)
Fig 5-6. Semilogarithmic plot of $M_0/M_t$ as a function of polymerization time for bulk polymerization of styrene using TP241 (polymerization temperature 120°C).
Fig 5-7. Effect of Macroinitiator concentration on the rate of styrene bulk polymerization
Modification of Poly(ethylene-co-vinyl alcohol) (EVOH) by Grafting of Polycaprolactone.

1. Grafting of polycaprolactone onto poly(ethylene-co-vinyl alcohol) and application to polyethylene based bioerodible blends.

1-1. Introduction

Collecting refuses in non-degradable bags and burying them in reclamation sites make the ground foundation of the reclamation sites unstable and give rise to the water clogging phenomena causing rain water to overflow leading to contamination of the surrounding river or soil. Due to the excessive price of the biodegradable materials developed so far, compounding of the biodegradable materials with synthetic non-degradable plastics has drawn great interests to bring a solution to the above environmental problems. According to the percolation theory, more than 33 vol% of biodegradable materials should be compounded...
to have microbes eat holes through the compounded materials. However, mechanical properties of the compound usually decrease precipitously as the content of the biodegradable component increases beyond a certain level. Therefore, an appropriate compatibilizer is required to prepare a compound containing biodegradable components above the percolation level without a significant loss in its mechanical properties.

In this study, ring open polymerization of ε-caprolactone was carried out using EVOH as a macroinitiator which was synthesized by saponification of EVA. The saponification process of EVA was analyzed by using 1H-NMR spectroscopy and DSC. EVOH-g-PCL was employed as a compatibilizer for PE/biodegradable MB blends, and its effects were investigated on improvement of mechanical properties of the blends.

1-2. Experimental

Materials
ε-caprolactone (Aldrich) and stannous 2-ethyl-hexanoate (Sigma) were used as received. LDPE (MI=5, $M_c$ 482,000) and biodegradable MB, PCL/starch/MAH (30/60/10)) were donated by Hanwha and LG Co. respectively. Corn starch was received by Samyang Co. Other chemical compounds were of reagent grade and were used as received.

Instrumentation

$M_W$ and $M_M$ were measured using GPC (Waters model 150C, TCB eluent, 1.0 ml/min, 135°C, column (porosity: 10 μm, Stragel® HT6E, HT5, HT3)) employing PS (Showadenko SL-105) as a standard.

Graft copolymers were characterized by 1H-NMR spectra recorded at 110°C on a Bruker AC-250 FT-
NMR spectrometer. 10 mg of the copolymer was dissolved in 0.5 ml of 1,2-dichlorobenzene-d$_4$ (20 wt/vol%) and was subjected to the $^1$H-NMR measurements.

The thermal properties of the polymers were determined by DSC (Perkin Elmer DSC 7). Thermal history of the products were removed by scanning to 200°C with the heating rate of 20°C/min (1$^\text{st}$ scan). After cooling down the sample at the rate of -5°C min to room temperature, it was reheated at 20°C/min to 200°C and the 2$^\text{nd}$ scan DSC thermograms were obtained.

**Preparation of EVOH**

EVA pellets were grounded into powder (ca. 250μm). Ground EVA (6g) was saponified in 200 ml of 0.5M KOH in ethanol solution. The heterogeneous solution was refluxed with stirring for the predetermined time, precipitated by excess distilled water, filtrated, washed with distilled water, and dried under vacuum.

**Synthesis of EVOH-g-PCL**

The saponified EVOH was dissolved in TCB and then were added $\varepsilon$-caprolactone (5 ml) and stannous 2-ethyl-hexanoate (0.2 ml). The polymerization was carried out at 130°C for 24-72 hrs. The product was precipitated into methanol and dried in vacuo followed by the soxhlet-extraction with boiling ethanol for 1 day to remove PCL homopolymer by-product during the graft copolymerization.

**Polymer blending**

The PE/EVOH-g-PCL mixture was first dissolved in TCB at 140°C and kept under N$_2$ blanket to prevent oxidation. After stirring for 30 min, starch was then added to the hot solution and stirred for 10min. The product was precipitated in methanol and dried in vacuo at 60°C.
Blend sheets were made by hot pressing at 200°C for 5 min under 1.55 atm, and quickly immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the film were determined with a tensile test machine (Instron Model No. 4200) at a cross head speed of 50mm/min according to ASTM D 638 at 20°C, RH 65%.

The film was fractured while immersed in liquid nitrogen. SEM (Hitach S-4200) was observed the fractured surface morphology.

1-3. Results and discussion

EVA pellets were ground into powder (ca. 250μm) cryogenically and were saponified in ethanol/KOH solution in a heterogeneous manner.

\[
\begin{align*}
\frac{b + 3b}{4a + 6b} &= \text{peak at } 4.9 \text{ ppm and } 2.1 \text{ ppm} \\
\text{total peak area} &
\end{align*}
\]  

\[
\begin{align*}
\frac{e + 3e}{4a + 3d + 6e} &= \text{peak at } 4.9 \text{ ppm and } 2.1 \text{ ppm} \\
\text{total peak area} &
\end{align*}
\]
The content of the copolymers in Table 1-1 was determined from $^1$H-NMR peaks of methine protons (4.9 ppm) and methyl protons (2.1 ppm) of VAc units (Fig. 1-1) using Eq(1) and (2).

Fig. 1-2 shows the 1st scan DSC thermogram of EVA20 as a function of the saponification time. EVA20 exhibited broad melting peaks at 77.3°C and 105.5°C. The bimodal melting peaks of EVA20 appeared similarly in the 2nd scan DSC thermogram as well.

As the radical copolymerization of ethylene and VAc proceeds quite randomly, the bimodal melting peaks indicates that the reactor for production of the EVA was not a perfectly mixed system. Feeding of the monomers should have been realized in several reaction zones.

It was envisaged that the saponification took place from the surface of EVA20 particles. The shoulder peak of EVA20 in Fig. 1-2 at a short saponification time should be due to the presence of unsaponified or less saponified EVA20 molecules in the particles. The shoulder peak moved and merged into the higher temperature peak with increasing saponification time.

The content of vinyl alcohol (VOH) units in EVOH20 was as low as 6.5 mol% and the length of VOH units in sequence should be too short to crystallize for itself. Nevertheless melting peak of EVOH20 increased and the crystallization peak in the course of cooling at -5°C/min from the melt state appeared at a higher temperature, as the saponificatiom time increased, indicating that a possible intermolecular hydrogen bond between VOH units favored the crystallization of the intervening segments composed of ethylene units.

In the 2nd scan DSC thermogram of EVOH20, the lower temperature shoulder peak disappeared as shown in Fig. 1-3. However when the 2nd scanned sample was annealed at 80°C and reheated from room temperature at 20°C/min, the shoulder peak reappeared and became more intense as the annealing time increased. Therefore it can be said that the disappearance of the shoulder peak in the 2nd scan DSC
thermogram in Fig. 1-3 was not due to the cocrystallization of EVOH20 and unsaponified or less saponified EVA20 but due to the inhibitory effect of EVOH20 on the crystallization of EVA20 molecules.

Fig. 1-4 compares the DSC thermograms of EVA10 and EVOH10 with those of EVA20 and EVOH20. The 1st scan DSC thermogram of EVOH10 did not exhibit a shoulder peak and was almost the same as the 2nd scan one, in contrast to those of EVOH20.

In spite of the fact that the content of VOH units in EVOH10 was as low as 1.7 mol%, the melting temperature of EVOH10 was 8°C higher than that of EVA10. Therefore it can be said again that VOH units increased intermolecular interaction to promote the crystallization of ethylene units segments intervening between VOH units.

Increase of VOH units would raise intermolecular interaction between EVOH molecules, and at the same time it would shorten the segment length of ethylene units in sequence. The former would have a positive effect while the latter would have a negative effect on the crystallization of the ethylene unit segments. This explains the fact that the melting temperature of EVOH10 (Fig. 1-4) was not very different from that of EVOH20 (Fig. 1-3).

Composition of EVOH10 and EVOH20 and their degree of saponification were determined from the respective 1H-NMR spectra using Eq (1), (2) and (3). The results are summarized in Table 1-1.

As was expected the degree of saponification of EVOH20 was higher than that of EVOH10 when both EVA20 and EVA10 were saponized at the same conditions.

The weight average degree of polymerization of EVOH10 and EVOH20 was determined from the respective $M_w$ using Eq(4).

\[ DPw = \frac{M_w \text{ of EVOH}}{28 \times a + 44 \times d + 86 \times e} \]  

\( \epsilon \)-caprolactone was polymerized using EVOH10 and EVOH20 as macroinitiators and the results are shown
in Table 1-2.

Fig. 1-1 (b) demonstrates $^1$H-NMR spectra of EVOH-g-PCL copolymers. The graft copolymerization with EVOH10 produced PCL homopolymer more than EVOH20 did, and the PCL homopolymer was extracted from the respective EVOH-g-PCL by the soxhlet extraction with boiling ethanol.

The peaks at 1.2–2.3 ppm were assigned to the methylene protons in PCL. The methylene protons neighboring to ester linkages in PCL appeared at 4.0–4.2 ppm. The fraction of reacted VOH units after the graft copolymerization was determined from the methine proton peaks of VOH units appearing at 3.6 ppm. The graft copolymerization proceeded homogeneously, because not only EVOH but also EVOH-g-PCL was dissolved in TCB. However the fraction of unreacted of VOH units decreased slowly indicating that all the VOH units were not equally reactive toward the PCL grafting.

The weight average degree of polymerization of PCL branches, $h_w$, in EVOH-g-PCL was calculated using Eq(5).

$$M_w = \{a \times 28 + c \times 86 + f \times 44 + g \times 27 + g \times \{114 \times (h_w - 1) + 131\}\} \times DPw \quad (5)$$

$M_w$ in Eq(5) was measured by GPC, which should be lower than the actual $MW$ due to the decreased hydrodynamic volume of the graft copolymers. Therefore the actual weight average degree of
polymerization of PCL branches should be higher than those listed in Table 1-1.

The weight average degree of polymerization of PCL branches decreased as the graft copolymerization proceeded because of the short branches produced later from the less reactive VOH units. Ester interchange reactions between PCL branches and unreacted VOH units should be another reason for the decrease of the weight average degree of polymerization of PCL branches.

Fig. 1-5 shows the 1st scan and 2nd scan DSC thermogram of EVOH-g-PCL. The lower temperature peak in the 1st scan thermogram should come from melting of PCL domains which moved to a lower temperature region as the grafting time increased. The melting peak of PCL domains in EVOH-g-PCL turned up at 40-50°C, in contrast to the fact that the melting peak of PCL homopolymer appears usually around 60°C. The PCL melting peak disappeared in the 2nd scan thermogram. The higher temperature peak corresponding to melting of EVOH domains in EVOH-g-PCL went down with the grafting time due to the short PCL branches.

Table 1-3 demonstrates that elongation at break and maximum stress of PE/ biodegradable MB compounds were enhanced significantly with the addition of EVOH20-g-PCL03. The morphology of the fractured surface of the compound is shown in Fig. 1-6. It can be seen that the domain size of the biodegradable MB phase decreased when EVOH20-g-PCL03 was added, which explains the positive effect of EVOH20-g-PCL03 on the tensile properties of the compound.

1-4. Reference


Fig 1-1. $^1$H-NMR spectra of EVOH20(a) and EVOH20-g-PCL03(b)
Fig 1-2. The 1st scan DSC thermograms of EVA20 as a function of saponification time.
Fig 1-3. Reappearance of the lower temperature shoulder peak in the 2nd scan DSC thermogram EVOH20 as a function of annealing time at 80°C.
Fig 1-4. Comparison of DSC thermograms of EVA10, and EVOH10(a) with those of EVA20, and EVOH20(b)
Fig 1-5. The 1st scan(……..) and 2nd scan (——) DSC thermogram of EVOH10-g-PCL(a) and EVOH20-g-PCL(b).
Fig 1-6. Scanning electron micrographs of the fractured surface of PE/biodegradable MB/EVOH-g-PCL system.
C. Polymeric Biocides

1. Antimicrobial activity of phenol and benzoic acid derivatives

1-1. Introduction

Even though polymers cannot be directly assimilated by microorganisms, microbes can grow and propagate using bioassimilable contaminants on the surface of the polymers\(^4\). Hence polymers with antimicrobial activity are often required for food packaging, sanitary, or medical applications. Polymeric antimicrobial agents have been prepared by introducing antimicrobial functional groups into the polymer molecules to protect the polymeric materials against harmful microorganisms\(^5,6,9,11\). Many novel antimicrobial agents have been synthesized by chemical means\(^7\) or by microbial fermentation\(^14\) and wait to be compounded or chemically anchored to polymers\(^7,14\).

Antimicrobial effects depended on the molecular hydrophobicity, absorbability, surface activity, electron density, and so on\(^7\). Alqurashi \textit{et al.} found MICs toward enterococcal and streptococcal strains to be 3000-4000 mg/l, 1000 mg/l, 20-200 mg/l respectively for phenol, cresol and chlorocresol\(^5\).

In this study, monomers containing phenol and benzoic acid functional groups were
synthesized in attempt to measure the antimicrobial activity of the monomers and to compare it with that of the respective polymers.

2-2. Experimental

Materials

Hydroquinone (Junsei), acryloyl chloride (Aldrich), allylbromide (Aldrich), $p$-hydroxyphenylacetic acid (Aldrich) were of reagent grade and were used as received.

Synthesis of Allyl $p$-hydroxyphenylacetate ($M1$)

To a solution of $p$-hydroxyphenylacetic acid (1.52g, 0.01 mol) in THF (20 ml) at $5^\circ$C was added dropwise TEA (1.31 g, 0.01 mol). The solution was then treated with allyl bromide (1.21 g, 0.01 mol) and refluxed for 1h. After cooling, the reaction mixture was poured into water (100 ml) and extracted with ethyl acetate (50 ml) three times. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated to give an oil (1.34 g, 49%). $^1$H-NMR (CDCl$_3$) $\delta$ 7.11, 6.75 (ABq, 4H, arom), 6.29 (s, 1H, arom-OH), 6.01-5.20 (m, 3H, vinyl), 4.60 (m, 2H, -OCH$\_2$-), 3.59 (m, 2H, CH$_2$).

Synthesis of $p$-hydroxyphenyl acrylate ($M2$)

To a solution of $p$-hydroquinone (22.0g, 0.20 mol) in THF (200 ml) at $-30^\circ$C was added dropwise TEA (20.2 g, 0.20 mol). Acryloyl chloride was added dropwise over 30 min.
After stirring for 30 min, the reaction mixture was filtered. The filtrate was concentrated in vacuo and the residue was dissolved in ether (200 ml). The etheral solution was washed with brine, dried over Na₂SO₄, and concentrated to give a mixture of M2 and 1,4-diacyloxy benzene. The mixture was purified by chromatograph with 5% ethyl ether in methylene chloride to give M2 as an oil (10.4 g, 64.5%). ¹H-NMR (CDCl₃) δ 6.92, 6.71 (ABq, 4H, arom), 6.65-5.98 (m, 3H, acryl), 5.90 (s, 1H, arom-OH).

**Synthesis of p-2-propenoxy phenol (M3)**

To a solution of p-hydroquinone (5.83g, 0.053 mol) in 1,4-dioxane (20 ml) was added sodium metal (1.5 g, 0.053) in pieces. After stirring for 30 min, the mixture was treated with acetyl bromide (6.4 g, 0.053 mol) and stirred at 80°C for 8 hrs. The reaction mixture was poured into water (100 ml), acidfied with 10 % HCl, and extracted with ethyl acetate (50 ml) three times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatograph with 5% ethyl ether in methylene chloride to give an oil (1.5 g, 25%). ¹H-NMR(CDCl₃) δ 6.89, 6.73 (ABq, 4H, arom), 6.08-5.24 (m, 3H, vinyl), 4.44 (m, 2H, CH₂).

**Synthesis of p-carboxyphenyl acrylate (M4)**

To a solution of 4-hydroxybenzoic acid (1.38g, 0.01 mol) in THF (20 ml) at -20°C was added TEA (2.78 g, 0.02 mol) and then acryloyl chloride (0.905g, 0.01 mol) was added
dropwise over 10 min. After stirring for 30 min, the mixture was poured into water (100 ml) and extracted with ethyl acetate (50 ml) three times. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by recrystallization with chloroform, and n-hexane to give an white solid (1.35 g, 59 %). ¹H-NMR (CDCl₃) δ 9.5 (bs, 1H, arom-COOH) 7.74-6.88 (ABq, 4H arom), 6.40-5.56 (m, 3H, acryl)

**Synthesis of 3-acryloxypropyl o-carboxybenzoate (M5)**

A mixture of 3-hydroxypropyl acrylate (13.0g, 0.10 mol), phthalic anhydride (14.8, 0.10 mol) and p-methoxy phenol (0.02 g) was stirred at 80°C for 14 hrs. After cooling, the reaction mixture was poured into water (100 ml) and extracted with ethyl acetate (50 ml) three times. The organic layer was separated, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatograph with 5% ethyl ether in methylene chloride to give an oil (12.7 g, 45.7%). ¹H-NMR (CDCl₃) δ 7.88-7.55 (m, 4H arom), 6.43-5.82 (m, 3H, acryl), 5.36 (m, 2H, OCH₂), 4.39 (m, 2H, CH₂), 1.37 (m, 2H, CH₂).

**Synthesis of 3-methacryloxypropyl p-hydroxyphenylacetate (M6)**

To a solution of 4-hydroxyphenyl acetic acid (15.1 g, 0.10 mol) in THF (50 ml) was added TEA (2.78 g, 0.02 mol) at -5°C. 3-Bromo-p-propanol (13.9 g, 0.10 mol) was added dropwise and refluxed for 12 hrs. After cooling, the mixture was filtered and the
filtrate was concentrated in vacuo. The residue was dissolved in ethyl acetate (200 ml) and washed with brine, 10% HCl, dried over Na₂SO₄, and concentrated to give an 3-hydroxypropyl p-hydroxyphenyl acetate (14.5 g, 69.5 %). ¹H-NMR  δ 7.01, 6.67 (ABq, 4H, arom), 4.04 (t, 2H, OCH₂), 3.48 (m, 4H, OCH₂), 1.67 (m, 2H, CH₂) 

A mixture of the acetate (6.89 g, 0.80 mol), p-TSA (0.6g), p-methoxy phenol (0.02 g) and chloroform (50 ml) was refluxed for 18 hrs. After cooling the reaction mixture was concentrated in vacuo. The residue was purified by chromatography (10%, ethyl acetate/methylene chloride) to give an oil (11.2g, 50.3%). ¹H-NMR(CDCl₃) δ 7.09, 6.74 (ABq, 4H arom), 6.10 (d, 1H, acryl), 5.56 (d, 1H, acryl), 4.29-4.03 (m, 4H, OCH₂), 3.53 (s, 2H, CH₂CO), 2.17-1.86 (m, 2H, CH₂), 1.92 (s, 3H, CH₃).

Polymerization of monomeric biocides
To a solution of M2 and M3 in THF at -30°C was added TEA dropwise. Acetyl chloride was added dropwise over 30 min. After stirring for 30 min, the reaction mixture was filtered. The filtrate was concentrated in vacuo and the residue was dissolved in ethyl acetate and washed with brine, dried over Na₂SO₄, and concentrated to give M2-acetyl and M3-acetyl. Solution polymerization of M2-acetyl, M3-acetyl and M4 were performed, in the presence of BPO in 1,4-dioxane at 80°C for 15 hrs. The mixture was precipitated by excess of chloroform, filtrated and dried in vacuo. P2-acetyl was dissolved in 20 ml of 0.5M KOH in ethanol solution, and then the mixture was stirred for the predetermined time, precipitated by excess distilled water, filtrated, washed with
distilled water, and dried in vacuo.

**Halo zone Test**

Halo zone tests for the antimicrobial agents against the microorganisms were carried out according to the method described by Bauer et al.\(^3\) under strict adherence to National Committee for Clinical Laboratory Standards (NCCLS)\(^8\). The fungi (*Aspergillus fumigatus* IFO 30870, and *Penicillium pinophilum* ATCC 9644) were incubated on Potato Dextrose Agar (PDA) slant medium at 28°C for 72 hrs. Spore suspension was prepared with 10 ml of sterile distilled water. The final concentration of the spore suspension ranged from 10\(^3\)-10\(^5\) spores/ml. Antimicrobial agents dissolved in dimethyl sulfoxide (DMSO) were spread on a paper disks and exposed to UV for 1h. Agar plates were inoculated using a sterile cotton swab moistened with the spore suspension. The paper disks containing the antimicrobial agents were placed in the middle of the plate. The test plates were incubated at 28 °C for 72 hrs.

The bacteria (*Staphylococcus aureus* ATCC 6538P, and *Pseudomonas aeruginosa* ATCC 15522) were subcultured to nutrient agar and incubated overnight at 37°C. The bacteria (stationary growth phase) were inoculated in 50 ml of nutrient broth medium and cultured for 5 hrs at 37°C. The cells were suspended in the same medium to produce a suspension of 10\(^6\) cfu/ml. Agar plates were streaked with a sterile swab moistened with the bacterial suspension. Antimicrobial agents were dissolved in DMSO
and spread on disks made of a filter paper. The disks were exposed to UV for 1hr and then applied to the surface of the agar plate. All the test plates were incubated overnight at 37°C. The susceptibility of microorganisms to the antimicrobial agents were determined by the size of the inhibitory zone. All the measurements were done in three replicates and the value averaged.

1-3. Results and Discussion

Monomers as shown in Fig. 1-1 were synthesized in order to investigate the antimicrobial activity of polymers containing phenol and benzoic acid derivatives. The antimicrobial activities of the compounds were compared using the halo zone test. Gram-negative bacteria are usually less susceptible to biocides than gram-positive bacteria. The halo zone test results for monomers shown in Table 1-1 indicates that antimicrobial activity of M2, M3 and M4 on \textit{Pseudomonas aeruginosa} was slightly lower than on \textit{Staphylococcus aureus}. The opposite trend was the case for M1.

Phenols are predominantly membrane-active agents. The microbial cell membrane acts as a selective permeability barrier between cytoplasm and the cell’s external environment, and regulates flux of solutes into and out of the cytoplasm. Phenols damage cell membrane and cause release of intracellular constituents. Phenols also cause intracellular coagulation of cytoplasmic constituents leading to the cell death or to inhibition of the cell growth.
Para-substitution of an alkyl chain of up to 6 carbon atoms in length to phenols is reported to increase the antimicrobial activity\textsuperscript{15}. In contrast, the halo zone diameter in Table 1-1 decreased in order of M2 > M4 > M1 ≈ M3 > M5 > M6, and it did not depend systematically on the length of the side chain para-substituted to phenol.

The more hydrophilic nature and more facile diffusivity in the nutrient agar of M2 and M4 compared to M5 and M6 should have contributed at least in part to the generation of the larger inhibition zone.

The mechanism of antimicrobial action of benzoic acid has not been fully understood yet\textsuperscript{15}. Lipophilic acids such as benzoic acid are known to inhibit the active uptake of some amino and acids in \textit{E. coli} and \textit{B. subtilis}\textsuperscript{15}.

M4 showed a larger halo zone diameter than M5 did and the growth inhibitory zone diameter for M4 against \textit{S. aureus} was slightly larger than that against \textit{P. aeruginosa}.

Table 1-2 summarizes the halo zone test results for fungi. The fungal cell wall could not withstand the antimicrobial action of M1, M2, M3 and M4. The order of the halo zone diameter was the same as that for the bacteria, i.e. M2 > M4 > M1 ≈ M3.

M2 and M4 were chosen for polymerization because they showed a larger halo zone diameter than the other monomers when applied on equal weight basis. After polymerization, hydroquinone could be released from P2 (polymers of M2) and \textit{p}-hydroxybenzoic acid from P4 as a result of hydrolysis. In contrast, released of pendant groups from P3 should be much slower than that from P2 or P4, so that the durability of the antimicrobial activity of P3 should be considerably longer than that of P2 and P4. In
this context, M3 was also polymerized for comparison.

Hydroxy groups in M2 and M3 were protected by acetylation to carry out radical bulk polymerization of M2 and M3 at 60°C for 12 hrs because radicals are rapidly scavenged in the presence of phenolic hydroxy groups. A polymer, whose $M_w$ and $PD$ were $8.3\times10^3$ and 1.56 respectively, was obtained, and then was subjected to hydrolysis to strip off the acetyl groups.

In Table 1-3, The halo zone test results for P2, P3 and P4 are collected. It can be seen that polymerization reduced significantly the halo zone diameter of the monomers. However the order of the halo zone diameter for the polymers was the same as that of the monomers. The halo zone diameter was decreased because the polymerization should reduce the diffusivity of the compound significantly. It is also possible that polymerization via the vinyl groups of M2, M3 and M4 could lead to inactivation if the vinyl groups are responsible for the antimicrobial effectiveness. Electrophilic vinyl groups can react with nucleophilic cell entities and thus exert antimicrobial effectiveness.

Antibacterial activity in plastics is dependent on the molecular diffusion of the antimicrobial agents. Hence polymers which exhibit a high glass transition temperature have not been good candidates for compounding with antimicrobial agents compared to polymers with a low glass transition temperature.

Even though the antimicrobial activity of P2, P3 and P4 is much lower than that of the corresponding monomers, these polymers could be coated on glassy polymers.
Concentration of antimicrobial agents on the coated polymeric material surface could be higher than that on the surface of the polymers compounded with low $MW$ antimicrobial agents to show identical or even better antimicrobial activity.

1-4. References


7. T. Maeda, Y. Manabe, M. Yamamoto, M. Yoshida, K. Ojazaki, H. Nagamune,


Table 1-1. Antibacterial activity measured by the halo zone test

(单位：mm)
<table>
<thead>
<tr>
<th>Biocide</th>
<th>Strain</th>
<th>Concentration of biocide (wt% in DMSO)</th>
<th>40</th>
<th>20</th>
<th>10</th>
<th>5</th>
<th>1</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td><em>S.aureus</em></td>
<td>23±1.0 17±0.4 8±0.0 0 0 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>P.aeruginosa</em></td>
<td>23±0.0 23±0.9 16±0.4 13±1.0 0 -</td>
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<td></td>
<td></td>
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<tr>
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</tr>
<tr>
<td></td>
<td><em>P.aeruginosa</em></td>
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<td></td>
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<td>M3</td>
<td><em>S.aureus</em></td>
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<tr>
<td></td>
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<td>18±0.0 17±0.0 15±0.4 12±0.0 - -</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td><em>E.coil</em></td>
<td>12±0.0 10±0.0 10±0.0 - - -</td>
<td></td>
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<td></td>
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<tr>
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<tr>
<td></td>
<td><em>E.coil</em></td>
<td>10±0.0 10±0.0 10±0.0 - - -</td>
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<td></td>
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<td></td>
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</tbody>
</table>

* - not determined; number after ± sign corresponds to the standard deviation

Table 1-2. Antifungal activity of monomers measured by the halo zone test (unit: mm)
<table>
<thead>
<tr>
<th>Biocide</th>
<th>Strain</th>
<th>Concentration of biocide (wt% in DMSO)</th>
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<td></td>
<td></td>
<td>40</td>
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<tr>
<td></td>
<td>A. fumigatus</td>
<td>34±0.9</td>
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<td>P. pinophilum</td>
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<tr>
<td>A. fumigatus</td>
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<td>50±0.5</td>
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<tr>
<td>M2</td>
<td>P. pinophilum</td>
<td>( a_{\text{max}} )</td>
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<tr>
<td>A. fumigatus</td>
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<td>23±0.8</td>
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<tr>
<td>M3</td>
<td>P. pinophilum</td>
<td>41±1.0</td>
</tr>
<tr>
<td>A. fumigatus</td>
<td>39±1.0</td>
<td>35±0.5</td>
</tr>
<tr>
<td>M4</td>
<td>P. pinophilum</td>
<td>61±1.0</td>
</tr>
</tbody>
</table>

\( a_{\text{max}} \): clear zone covered all the agar medium on the petri dish

- not determined; number after ± sign corresponds to the standard deviation

Table 1-3. Antimicrobial activity of the polymers measured by the halo zone test (unit: mm)
<table>
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<tr>
<th>Biocide</th>
<th>Strain</th>
<th>Concentration (wt% in DMSO)</th>
<th>40</th>
<th>20</th>
<th>10</th>
<th>5</th>
<th>1</th>
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</tr>
<tr>
<td>P2</td>
<td><em>S. aureus</em></td>
<td></td>
<td>23±1.0</td>
<td>17±0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td><em>P. aeruginosa</em></td>
<td></td>
<td>21±2.0</td>
<td>16±0.0</td>
<td>12±0.4</td>
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<td><em>A. fumigatus</em></td>
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<td>30±1.0</td>
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<td></td>
<td><em>P. pinophilum</em></td>
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<td>41±0.8</td>
<td>21±0.0</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>P3</td>
<td><em>A. fumigatus</em></td>
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<td>-</td>
<td>10±0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td><em>P. pinophilum</em></td>
<td></td>
<td>-</td>
<td>10±0.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P4</td>
<td><em>S. aureus</em></td>
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<td>13±1.0</td>
<td>12±0.4</td>
<td>11±0.0</td>
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<td>0</td>
</tr>
<tr>
<td></td>
<td><em>P. aeruginosa</em></td>
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<td>16±1.0</td>
<td>12±0.0</td>
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<td><em>A. fumigatus</em></td>
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<tr>
<td></td>
<td><em>P. pinophilum</em></td>
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<td>12±1.0</td>
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</tbody>
</table>

* - not determined; number after ± sign corresponds to the standard deviation

2. Antifungal Effect of Carbendazim Supported on Poly(ethylene-co-
2-1. Introduction

Contamination by microorganisms invites serious problems to polymeric materials for sanitary, biomedical and alimentary applications. One possible way to avoid the microbial contamination is to develop materials possessing antimicrobial activities.

Pentachlorophenol, a well known biocide, has been chemically anchored to polymers by copolymerizing pentachlorophenol methacrylate with MMA by Akagane and Matsuura\(^5\). Pittman copolymerized pentachlorophenyl acrylate with both VAc and ethyl acrylate\(^1\). Pittman's copolymers retarded or prevented growth of *Aspergillus* sp., *Pseudomonas* sp., *Alternaria* sp. or *Aureobasidium pullulans* significantly.

Nonaka and coworkers introduced phenolic hydroxy moiety by treating amine-functionalized resins with *p*-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid and 3,4,5-trihydroxybenzoic acid\(^4\). Antibacterial activities increased in the order of increasing number of hydroxyl groups.

Ikeda and coworkers evaluated the antibacterial activities of trialkyl-vinyl benzyl ammonium chloride monomers and their polymers by the conventional spread plate method and the viable counting method\(^5\). The compounds with dodecyl chain exhibited particularly high activity. They also found that the polymers were more active than the corresponding monomers, due to possibly their favored adsorption onto the bacterial cell
surface and the cytoplasmic membrane with subsequent disruption of its integrity. Polycationic biocides with phosphonium salt were immobilized on polypropylene surface through surface photografting to show high antibacterial activity. The bacterial cells in contact with the immobilized polycationic biocides were observed by SEM to be significantly shrunken and deformed.

Sun and coworkers modified PS by chemically attaching a hydantoin derivatives and a chlorinated triazinedione moiety. These polymeric biocides are water insoluble so that toxicological evaluation would not be required when used for disinfecting potable water. N-halamine polymeric disinfectants were synthesized and tested for efficacy on inactivating bacteria. Polymeric N-halamine has an advantage in that it needs short contact time to kill microorganisms and its biocidal activity can be regenerated once exhausted by simply flowing an aqueous solution of free halogen through it. N-halamine precursor monomers were copolymerized with other monomers in water with the aid of a surfactant to produce latexes, which could be used in numerous coating applications.

Oh and coworkers synthesized 2,4,4′-trichloro-2′-acryloyloxydiphenyl ether, its homopolymer and its copolymer with styrene. The bactericidal activities decreased in the order of monomer > homopolymer > copolymer.

Methyl 2-benzimidazolecarbamate (carbendazim), which has been used since 1960's as various pesticides, has relatively low toxicity (LD$_{50}$=6400mg/kg for rat). Recently it has been discovered that carbendazim inhibits growth of fungi very efficiently.

In this study, CBZ was bonded to EVOH, and its fungicidal effects were investigated.
Release rate of CBZ units was examined during an accelerated hydrolysis test. CBZ was anchored to a bisphenol. A type epoxy precursor (DGEBA) to reduce the hydrolysis of CBZ units. The precursor could be used for various coating applications when crosslinked by curing agents. The cured epoxy resin was subjected to the antifungal test against *p. pinophilum*.

2-2. Experimental

*Materials*

EVA was used as received from Scientific Polymer Products (Sp²). Aluminum isopropoxide (Aldrich) was dried in desiccator under vacuum over 24 hrs. Dimethyl sulfoxide (DMSO; Aldrich) was distilled under nitrogen at reduced pressure. Carbendazim (Aldrich) was recrystallized from toluene. The bisphenol A type epoxy resin YD-128 (epoxide equivalent weight: 184-190g/eq, viscosity: 11,500-13,500cps), i.e. diglycidyl ether of bisphenol A (DGEBA), and the isophoronediamine was obtained from KUKDO CHEMICAL (Korea) and used without further purification. Other chemical compounds were of reagent grade and were used as received.

*Preparation of EVOH*

EVA was dissolved in 200 ml of 0.5M KOH in ethanol solution, and then the mixture was refluxed with stirring for the predetermined time, precipitated by excess distilled
water, filtrated, washed with distilled water, and dried under vacuum.

*Synthesis of EVOH-CBZ*

The mixture of 5g of saponified EVA(EVOH) and 60 ml of DMSO was stirred for 30min at 60°C, and then 2g of carbendazim was added into the above solution. The solution was heated up to 115°C, and then stirred for 150 min in the presence of 0.2g of Al(O-iPr)₃. The resulting solution was precipitated into excess distilled water. The precipitate was filtered, washed with distilled water and ethanol, and dried under vacuum to constant weight. To remove the unreacted carbendazim, the synthesized polymer was stirred in distilled water overnight.

*Characterization of EVOH-CBZ*

EVOH-CBZ was analyzed at 110°C with a Bruker AC-250, 250MHz NMR spectrometer using DMSO-d₆ as a solvent. The thermal characteristics of EVOH-CBZ were examined by a DSC (Perkin Elmer DSC 7). The first DSC thermogram was obtained by scanning to 200°C at the heating of 20°C/min. The sample was maintained at 200°C for 2 min and cooled down to 30°C at the rate of 5°C/min. The second thermogram was carried out by reheating the sample to 200°C at 20°C/min. The dynamic mechanical properties were measured with Rheovibron (DDV-II, Toyo Baldwin Co.). The dimension of the sample was 35×5×0.2 mm³ and the properties were measured in the range between -80 °C and 100 °C.
Antifungal activity test of EVOH-CBZ

Antifungal activity was evaluated by the halo (inhibition) zone test\textsuperscript{18-22}. The fungi used in this study were \textit{A. fumigatus} and \textit{P. pinophilum}. Cultures of \textit{A. fumigatus} (IFO 30870) and \textit{P. pinophilum} were prepared by incubation at 28°C in PDA (Potato dextrose agar) for 72 hrs. By diluting with 10 ml of sterile distilled water, culture containing ca. $10^3$-$10^5$ cells/ml was prepared for each strain and used for the antifungal tests. The sterile Petri dish containing PDA was inoculated by this culture. Fungicide was dissolved in DMSO (0.9 wt%). 20 µl of the solution was placed on paper disc of 10mm diameter. The paper disc sterilized by UV for 1 hr, was placed in the center of inoculated Petri dish. The agar dish was then incubated at 28°C for 72 hrs. The diameter of inhibition zone was measured.

Hydrolysis experiment of EVOH-CBZ

The sample of film type was prepared using hot press. The dimension of the sample was 10×10×0.2mm\textsuperscript{t}. The sample was put in phosphate buffer solution (pH 7.0), maintained at 70°C. CBZ content was measured by \textsuperscript{1}H-NMR spectra recorded at 110°C on a Bruker AC-250 FT-NMR spectrometer.
Synthesis of precursor (DGEBA-CBZ)

The precursor was prepared by reacting of epoxy with carbendazim at 160°C for 30 min after perfectly mixing at 60°C. The absence of the unreacted carbendazim in the synthesized precursor was confirmed by a thin layer chromatography (TLC). Content of CBZ in DGEBA was determined from \(^1\)H-NMR spectra, measured at room temperature with a Bruker AC-250, 250MHz NMR spectrometer using CDCl\(_3\) as solvent.

Crosslinking of DGEBA-CBZ

DGEBA-CBZ (precursor) was dissolved in chloroform and was mixed with IPDA (isophoronediamine). The solution was cast on a glass plate and then cured at 100°C for 3 hrs.

2-3. Results and Discussion\(^\text{26}\)

CBZ supported on EVOH

EVOH was prepared by alcoholysis of EVA containing 43 and 61 mol\% of VAc units in 0.5M KOH ethanol solution. Degree of saponification was controlled by means of the alcoholysis reaction time. The composition of the resulting EVOH was determined from \(^1\)H-NMR spectra as shown in Fig. 2-1, by measuring the intensities of methylene
protons appearing in the range of 0.9-1.8 ppm, those of methine protons in the 4.4-4.8 range and those of methyl protons of the residual acetate groups in the 2.1-2.0 ppm range. The results are summarized in Table 2-1, where aEVOHb indicates EVOH with b mol% of vinyl alcohol units was synthesized from EVA containing a mol% of VAc units.

CBZ was bound to EVOH through the transesterification reaction. CBZ content in EVOH-CBZ complex was determined by \(^1\)H-NMR in Fig. 2-1. Peaks at 6.8 and 7.2 ppm correspond to the protons in the benzimidazole ring. Peak at 10.5 ppm is ascribed to -NH in the carbamate and to that in the benzimidazole ring. Absence of unreacted cabendazim in EVOH-CBZ was confirmed by the fact that peak at 3.7 ppm corresponding to methyl protons of carbendazim disappeared in Fig. 2-1.

Thermal properties measured by DSC are summarized in Table 2-2. Melting behavior was not seen in EVA. \(T_g\) of EVA increased from \(-22.6^\circ\text{C}\) to \(1.1^\circ\text{C}\) as VAc content increased from 43 mol% to 61 mol%. When EVA was saponified, the resulting EVOH became semicrystalline to show melting behavior. Both \(T_m\) and \(T_c\) rose as the degree of saponification was raised. \(T_c\) measured during cooling at \(5^\circ\text{C}/\text{min}\) from melt state increased with vinyl alcohol content, indicating that more highly saponified EVOH crystallized more easily.

It is interesting to note that EVOH from EVA containing 61 mol% of VAc units showed higher \(T_m, T_c\) and \(T_g\) at the comparable level of vinyl alcohol content than EVOH originated from EVA comprising 43 mol% of VAc units. Admitting that VAc are
randomly distributed in EVA, the above results implies that the saponification was not carried out homogeneously. That is to say vinyl alcohol units were unevenly distributed in EVOH so that crystallization took place preferentially where vinyl alcohol units were locally concentrated\textsuperscript{22-24}. $T_m$, which is not very dependent on the degree of saponification of EVOH when made from the identical EVA, supports the above hypothesis. VAc units in 43EVA were more sparsely distributed than those in 61EVA. Hence vinyl alcohol units in 43EVOH was more randomly distributed than those in 61EVOH to show lower melting temperature.

As CBZ units replaced the hydroxyl groups in EVOH-CBZ, $T_m$ and $T_c$ decreased due to the crystallization-repressing action of the bulky CBZ units. $T_g$ increased as a result of the incorporation of CBZ units due to the bulkiness of CBZ units and to the possible interaction between -NH, -OH and carbonyl groups which laid restraint on the segmental motion of the backbone chain.

Carbendazim preserves its antifungal activity when the methyl ester group is replaced by other substituents\textsuperscript{25}. Fig. 2-2 presents the halo zone test results. It can be seen that the inhibition zone around the circular EVOH-CBZ specimens enlarged due to the increasing content of the anchored CBZ.

Fig. 2-3 plots inhibition zone diameter as a function of CBZ concentration. It has been known that inhibition zone diameter increases in proportion to the logarithmic concentration of biocides\textsuperscript{16}. Hence the inhibition zone diameter is expected to increase and level off as the concentration of the biocides increases.
The results in Fig. 2-3 show that the inhibition zone diameter seems to level off above CBZ content of 24 wt%.

Fig. 2-4 shows CBZ content in 61EVOH54CBZ5.9 film (10×10×0.2mm$^3$) after hydrolysis at 70°C, indicating that CBZ units were released from the film due to the hydrolysis.

CBZ content in the film (measured by $^1$H-NMR) decreased sharply in the initial stage of the hydrolysis.

Some of fungal mycelia were observed to grow on the film surface when the film, which was subjected to the hydrolysis for 7 hrs, was placed and incubated amid photato dextrose agar medium inoculated with the fungal spore suspension. This is because the actual content of CBZ on the surface of the film must be lower than that depicted in Fig. 2-4 which was the average content of CBZ in the whole film.

Most of polymeric biocides studied so far have acryloyl or other structures from which biocidal groups could be split off. And service-life of the polymeric biocides depends on the release rate of the biocidal functional groups.

**CBZ supported on epoxy resins**

A mixture of DGEBA and carbendazim (4:1 on weight basis) was heated at 160°C for 30min. $^1$H-NMR spectra of the resulting DGEBA-CBZ is shown in Fig. 2-5. In Fig. 2-5 (b) new peaks appear at 3.7-3.8 and 4.3-4.4ppm due to the incorporation of CBZ units when compared with Fig. 2-5 (a) which corresponds to DGEBA. The peaks at 3.7-
3.8ppm are assigned to methyl protons of CBZ units and the peaks at 4.3-4.4 peaks are methylene protons formed by ring opening of the oxirane groups. Protons in oxirane ring appearing at 2.7, 2.9 and 3.35ppm evidences that some oxirane groups survived the reaction between DGEBA and carbendazim.

FTIR spectra of carbendazim, DGEBA and DGEBA-CBZ are shown in Fig. 2-6. Carbonyl groups of carbamate in CBZ at 1630 cm$^{-1}$ disappeared and instead a new peak at 1760 cm$^{-1}$ appeared in the spectra of DGEBA-CBZ.

The IR-peak shift are thought to be due to change in the chemical structure around the carbonyl linkage of carbamate during the oxirane ring opening reaction, indicating that not only the secondary amine groups in the benzinimidazole ring but also the amide groups of carbamate, which was supposed to be less reactive than the former, participated in the reaction between DGEBA and carbendazim. Zhong and Guo$^{15}$ also observed that peaks for amide carbonyl groups shifted from 1630 cm$^{-1}$ to 1726 cm$^{-1}$ as nylon 6 reacted with DGEBA.

The IR peak at 915 cm$^{-1}$ originating from oxirane groups confirms that some of the oxirane groups in DGEBA remained after the reaction of DGEBA with carbendazim.

Fig. 2-7 exhibits the halo zone test results for DGEBA-CBZ against P. pinophilum. As expected, the inhibition zone diameter increased with increasing CBZ concentration. However when compared with results shown in Fig. 2-3, the antifungal activity of DGEBA-CBZ was less pronounced than that of EVOH-CBZ.

Absence of unreacted CBZ was confirmed by developing DGEBA-CBZ on thin layer
chromatography (TLC) as shown in Fig. 2-8, which also demonstrates that there exists unreacted DGEBA and differently structured DGEBA-CBZ complexes.

The DGEBA-CBZ complex was cured with isophoronediamine (IPDA) and then the residual precursor and IPDA were removed by overnight soxhlet extraction with ethanol. The epoxy resin thus produced was insoluble and cleavage of CBZ units from the epoxy matrix should be much slower than that from EVOH-CBZ. Therefore the antifungal activity could not be tested by the halo zone test for which diffusion of molecules having biocidal effects is absolutely needed. Hence the antifungal activity of the epoxy resin was tested by observing whether fungal mycellia infect and bury the surface of the epoxy resin sheet placed in a nutrient rich media inoculated with fungal spores. Unfortunately the cured DGEBA-CBZ complex sheet did not show any appreciable antifungal activity, saying that release of CBZ units is needed to exhibit antifungal activity. Therefore it can not be said that CBZ supported on polymers will be of much use, because large weight percentages are required for activity and because it could not be used for long-term applications where water exposure would occur.
2-4. Reference


   Korea Patent 94-21450.


Fig 2-1. $^1$H-NMR spectra of 43EVOH42 and 43EVOH42CBZ4.6

A. fumigatus

P. pinophilum

(a) 43EVOH28 (0 wt %)  (b) 61EVOH54 (0 wt %)

CBZ content 0 wt %
Fig 2-2A. Photographs of the halo zone test. The number in the Parentheses is the concentration.

A. fumigatus

P. pinophilum

CBZ content 6.23 wt% (c) 43EVOH28CBZ2.1

CBZ content 13.2 wt% (e) 43EVOH 40CBZ4.3

(g) 43EVOH42CBZ4.6

(h) 43EVOH42CBZ4.6
CBZ content 14.2 wt%  
(i) 61EVOH51CBZ3.8  
(j) 61EVOH51CBZ3.8  

CBZ content 10.4 wt%  
(k) 61EVOH54CBZ5.9  
(l) 61EVOH54CBZ5.9  

CBZ content 15.6 wt%  

Fig 2-2B. Photographs of the halo zone test. The number in the parentheses is the concentration.
Inhibition zone (mm) vs. CBZ content (wt%) for:

(a) *A. fumigatus*

(b) *P. pinophilum*
Fig 2-3. A plot of the inhibition zone as a function of CBZ content.

Fig 2-4. The content of CBZ (mol %) in 61EVOH54CBZ5.9 after hydrolysis at 70°C measured by 1H-NMR.
a) DGEBA

(b) DGEBA-CBZ
Fig 2-5. $^1$H-NMR Spectra of DGEBA and DGEBA-CBZ
Fig 2-6. FTIR Spectra of (a) carbendazim (b) DGEBA and (c) DGEBA-CBZ.
Fig 2-7. A plot of the inhibition zone for *P. pinophilum* as a function of CBZ concentration in DGEBA-CBZ.
Fig 2-8. Thin layer chromatography
(a) cabendazim (b) DGEBA (c) DGEBA-CBZ
Polyethylene (PE)  polypropylene (PP)  1,2,4-trichlorobenzene (TCB)  benzoyl peroxide (BPO)  2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)  PE-TEMPO  PP-TEMPO macroinitiator  PP-BPO/TEMPO  PE-TEMPO  PP-TEMPO styrene bulk PS homopolymer chain transfer. 2. PE-g-PS  PP-g-PS  PS branch  20,000 PS branch PE PP  PE-g-PS  PP-g-PS  PS  Tm  PP-g-PS  PS  Tg  PS homopolymer  Tg  PS  Tg  PE/PS, PP/PS PE/PS compounding morphology  domain size  30~75%  20~40%  PE-g-PS  PP-g-PS  compounding styrene maleic anhydride (MAH) living radical  Styrene styrene/MAH compounding.
Styrene/MAH 1st-order kinetics. styrene/living styrene/MAH, random MAH, styrene rich block. PE-TEMPO/MAH, PE-g-(PS-co-MAH), styrene, PE/PE-g-(PS-co-MAH)/starch PE/starch/ PE-g-(PS-co-MAH), tetrabutyl titanate (TNBT) starch MAH unit. Vinyl acetate (VAc) BPO bulk TEMPO. Radical growing polymer radical dead polymer radical polymer transfer growing polymer radical dead polymer TEMPO termination poly(vinyl acetate) (PVAc) gel point growing PVAc radical active radical PVAc TEMPO bulk chain transfer to polymer acetate methyl PVAc-TEMPO styrene bulk graft PVAc-TEMPO.
TEMPO - dormant site, styrene, methanolysis, PS branch, PVAc backbone, pore size, control, porous membrane.

PVAc-co-PS, PS branch, PVAc backbone, PS/PVAc, poly (methyl methacrylate) (PMMA), poly(3-hydroxybutyrate) (PHB), poly(lactic acid), PVAc-g-PS, PS/PVAc, PE/phase, EVA, EVOH, compounding, master batch (MB), LDPE, blend, EVOH-g-PCL, benzoic acid, vinyl, halo zone, p-hydrophenyl acrylate (M2) > allyl p-hydroxyphenyl acetate (M1) > p-2-propenoxyphenol (M3), saponification, EVOH, 2-
benzimidazole cabamate (carbendazim, CBZ) 

Aspergillus fumigatus 
Penicillium pinophilum 
halo zone 
EVOH-CBZ
CURRICULUM VITAE

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Researcher in Micro Chem, 2001~present
Research Description

1. Grafting of Polystyrene Branches to Polyethylene and Polypropylene
2. Living Radical Copolymerization of styrene/maleic anhydride
3. Synthesis of PE-g-(styrene-co-maleic anhydride) and its Compatibilizing Effects on PE/starch blends
4. Grafting of PCL onto Poly(ethylene-co-vinyl alcohol) and Application to PE Based Bioerodable Blends
5. Antimicrobial activity of phenol benzoic acid Derivatives
6. Antifungal Effect of Carbendazim Supported on EVA and Epoxy resin
7. Synthesis of PVAc-g-PS and Application to Preparation of Porous Membranes
8. Synthesis of PVAc-g-PS and its Compatibilizing Effects on PS/PVAc Blends
9. Determination of \( M_i \) from \( M_n \) and \( M_w \)
10. Thermal and Mechanical properties of Ethylene/\( \alpha \)-olefin Copolymers Produced over (2-MeInd)\(_2\)ZrCl\(_2\)/MAO System
11. Synthesis of Polypropylene using (2-MeInd)\(_2\)ZrCl\(_2\)/MAO System
12. Copolymerization of ethylene/non-conjugated dienes over (2-MeInd)\(_2\)ZrCl\(_2\)/ MAO Catalyst System
13. Copolymerization of PE/\( \alpha \)-olefin over (2-MeInd)\(_2\)ZrCl\(_2\)/MAO and (2-BzInd)\(_2\) ZrCl\(_2\)/MAO System
14. Diffusion Coefficient and Equilibrium Solubility of Water Molecules in Biodegradable Polymers
Publications


Presentation


