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Atom Transfer Radical Polymerization을
이용한 블록 공중합체의 중합 및
양친화성 Oligothiophene의 합성

Syntheses of Block Copolymers
by Atom Transfer Radical Polymerization and
Synthesis and Characterization of
Amphiphilic α,α’-Disubstituted Oligothiophenes

2007 년 2월

仁荷大學校 大學院
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2007 年 2 月

主審__________________

副審__________________

委員__________________
Abstract

Controlled radical polymerization (CRP) technique has attracted recent scientific and industrial attention in the fields of polymer chemistry. The main advantage of this method is the capability of controlling compositions, architectures and functionality of polymeric materials at facile reaction conditions. It can be achieved by rapid propagation and reversible termination or transfer reaction that are much faster than the irreversible termination reaction which enables polymer chains to grow more slowly and continuously with conversion. There are largely three efficient systems in CRP such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT). Especially in ATRP, a radical can be formed reversibly polymeric materials by transfer of a halogen from an alkyl halide to a transition metal complex and molecular weights, polydispersity, compositions and architecture can be easily controlled with conversion. Block copolymers have received much scientific and technological attention due to their ability to self-assemble into a series of periodic ordered microstructures via microphase separation between the constituent block segments. These block copolymers can be used as
thermoplastic elastomers, surfactants, dispersants and thickeners. There are a number of applications by using their phase-separated morphology both in the solid state and in solutions. To synthesize these block copolymers with predetermined molecular weights and low polydispersity, anionic polymerization is usually employed. However, its use is highly limited due to the strict reaction conditions such as extremely low temperature, exclusion of moisture and impurity, and stringent drying. Recently, ATRP has been used in such a manner to build block copolymers of radically polymerizable monomers. In this process, active halogens are incorporated at the chain ends of polymers to form macroinitiators. In the present study, we synthesized a novel diblock copolymer of polyfluorostyrene-$b$-poly(methyl methacrylate) (PPFS-$b$-PMMA) by ATRP technique for potential optical waveguide applications.

$\pi$-Conjugated systems have attracted a great deal of attention, because they have delocalized, conjugated electronic structures in their main chain, which give them unique material characteristics such as photoluminescence (PL), electroluminescence (EL), conductivity and oxidative stability. Most $\pi$-conjugated systems are insoluble, due to the strong, secondary interchain interactions between their highly anisotropic, rigid polymer backbones. Many attempts have been made to enhance their
solubility and performance either by introducing either various substituents/end groups into the polymer backbone or by copolymerizing them with conjugated or non-conjugated copolymers. In this report, we synthesized a novel amphiphilic triblock copolymer C_{15}-3T-EO_{5} containing oligothiophene, which was asymmetrically end-substituted with a hydrophobic alkyl moiety and a hydrophilic oligo(ethylene glycol) by Suzuki and Stille coupling reactions.
국문요약

Controlled radical polymerization (CRP)는 라디칼 중합과 리빙 중합의 단점을 최소화하면서, 두 중합법의 장점들을 결합한 획기적인 합성 방법으로 주목을 받고 있다. CRP는 상대적으로 손쉬운 반응 조건하에서, 다양한 기능성을 가진 단량체를, 원하는 조성과 구조를 가진 고분자로 합성할 수 있기 때문에, 정밀한 제어가 요구되는 분야에서 최근 들어 더욱 폭넓게 사용되고 있다.

CRP는 활성종과 비활성종 간의 평형을 유도 라디칼의 농도를 낮게 유지하여, 비가역적 정지반응을 최소로 일어나게 한다. 가역적인 라디칼 형성의 평형은 각 사슬이 고르게 성장할 기회를 제공한다. CRP는 실현시키는지에 따라, nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT) 등의 3가지 방법으로 크게 분류할 수 있다. 이 중에서, 전이금속을 매개체로 한 할로겐 원소 전달 반응인 ATRP가 가장 보편적으로 많이 쓰이지 고 있다. 블록공중합체는 두 개 이상의 고분자가 끼어 연결된 형태로 합성된 고분자로 자발적인 상분리에 의하여 10 nm에서 100 nm 정도의 크기를 갖는 나노 구조를 형성한다. 블록공중합체는 열가소성수지, 유화제, 분산매, 하강제 등으로 쓰이고 있다. 블록공중합체의 합성에는 좁은 분자량 분포를 갖는 잘 규정된 고분자
를 합성할 수 있는 음아온중합이 많이 사용된다. 기존의 리빙 중합은 사용할 수 있는 단량체의 종류가 제한적이며, 중합 반응시 중간체가 슬기 등의 불순물과 부반응을 쉽게 일으키고, 낮은 온도조건을 요구하는등, 합성 조건상에 어려움이 있다. 무엇보다도, 여러 기능들을 가진 단량체의 경우, 이들의 부반응으로 인하여 중합에 쉽게 적용하지 못하므로, 다양한 기능과 구조의 잘 규정된 고분자를 정밀 합성하는 데에는 한계를 가지고 있다. 현재, ATRP는 라디칼 중합이 가능한 단량체를 이용하여 불록공중합체를 합성하는데 이용되고 있다. 활성 화학저 원소가 붙어있는 macroinitiator를 이용하여 불록공중합체를 합성한다. 본 연구는 광도파로에 사용될 새로운 이중, 삼중 공중합체인 polyfluorostyrene-

$b$-poly(methyl methacrylate) (PPFS-$b$-PMMA), poly(methyl methacrylate)$-b$-polyfluorostyrene-$b$-poly(methylmethacrylate) (PMMS-$b$-PPFS-$b$-PMMA)를 ATRP로 합성하였다.

$\pi$-공액형 시스템은 전자가 비편재화, 높은 전기전도도를 가지고 있다. 이러한 전기적 특징에 의해 photoluminescence (PL), electroluminescence (EL), conductivity, oxidative stability 현상이 나타난다. 그러나 대부분의 $\pi$-공액형 시스템은 rigid한 주체 사이의 강한 인력에 의하여 용매에 녹지 않는 특징을 보인다. 용해도와 성능을 항상 시키기 위하여 주체의 끝 부분을 치환체로 치환하거나,
다른 고분자와 공중합체를 만드는 많은 연구가 진행되고 있다. 본 연구는 친수성의 oligo(ethylene glycol)체인과 소수성의 alkyl 체인을 Suzuki, Stille coupling 반응을 이용하여 oligothiophene의 양 말단에 합성하여 C_{15}-3T-EO5을 만든 후 구조적 특징 및 여러 성질들을 측정하였다.
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Chapter 1

Introduction
1.1 Atom Transfer Radical Polymerization

The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination.\textsuperscript{1,2} Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers.\textsuperscript{3} Despite its tremendous industrial utility, CRP has not been realized until recently, largely due to the inevitable, near diffusion-controlled bimolecular radical coupling and disproportionation reactions.

The past few years have witnessed the rapid growth in the development and understanding of new CRP methods.\textsuperscript{4,5} All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in
reversible addition fragmentation chain transfer processes (RAFT),
alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable
free radical polymerization (SFRP), and potentially even organometallic
species. Free radicals may be generated by the spontaneous thermal
process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via the
degenerative exchange process with dormant species (DT, RAFT).

All of the CRP methods, shown in Figure 1, include activation and
deactivation steps (with rate constants $k_{\text{act}}$ and $k_{\text{deact}}$). Generated free
radicals propagate and terminate (with rate constants $k_p$ and $k_t$), as in a
conventional free-radical polymerization. Thus, although termination

![Figure 1. General Scheme of CRP Methods](image_url)
occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems.

\[ \text{M}_t^{n-}\text{Y} / \text{Ligand} \rightarrow \text{R}^- + \text{X-M}_t^{n+1-}\text{Y} / \text{Ligand} \]

\[ \text{k}_\text{p} \quad \text{monomer} \rightarrow \text{k}_t \quad \text{termination} \]

**Figure 1.2. Transition-Metal-Catalyzed ATRP**

A general mechanism for ATRP shown in Figure 2. The radicals, or the active species, are generated through a reversible redox process catalyzed by a transition metal complex (\(\text{M}_t^{n-}\text{Y} / \text{Ligand}\), where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, R-X. This process occurs with a rate constant of activation, \(k_{\text{act}}\), and deactivation \(k_{\text{deact}}\). Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation \(k_p\). Termination reactions (\(k_t\)) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no
more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, $X-M_r^{n+1}$, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

ATRP also has roots in the transition metal catalyzed telomerization reactions. These reactions, however, do not proceed with efficient exchange, which results in a nonlinear evolution of the molecular weights with conversions and polymers with high polydispersities. ATRP also has connections to the transition metal initiated redox processes as well as inhibition with transition metal compounds. These two techniques allow for either an activation or deactivation process, however, without efficient reversibility. ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the
molecular weights increased linearly with conversion and the polydispersities were typical of a living process. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers. Earlier attempts with heterogeneous catalyst and inefficient initiators were less successful.

1.2. Block Copolymer systems

The fabrication of systems having characteristic dimensions smaller than 100 nm requires the ability to obtain, control, manipulate, and modify structures at the nanometer length scale, a step beyond microtechnology. It is well established that microstructured materials may be industrially prepared, e.g., by photolithography, but as the demand for smaller and smaller feature sizes always impose to lower the current state of-the-art limits, further steps towards miniaturization have been raised in the last decade, focusing on different and more suitable strategies, which are based on both "top-down" and "bottom-up" approaches. Many methods for the fabrication of nanomaterials have been proposed, mainly to meet the demand of the microelectronic industries, ranging from milling techniques to
non-traditional photolithographic and chemical methods, with a strong prevalence of methods based on template synthesis. However, their main weakness still remain in the difficult and poor control of the final morphology of the produced nanostructures. In such a sense polymers represent ideal nanoscale tools, not only due to their intrinsic dimensions, ease of synthesis and processing, strict control of architecture and chemical functionality, but also because of their peculiar mesophase separation both in bulk and in solution, particularly in the case of block copolymers (BCs).

BCs may be considered as two or more chemically homogeneous polymer fragments, i.e., homopolymer chains, joined together by covalent bonds to form more complex macromolecules such as linear di-, tri-, or multiblock copolymers, and nonlinear architectures such as multiarm, starblock, or graft copolymers. In the frequent case of immiscibility among the constituent polymers, the competing thermodynamic effects give rise to different kind of self-assembled morphologies, depending both in structural and dimensional terms on composition, segmental interaction, and molecular weights, and having periodicity suitable for application in nanotechnology. The existence of some morphologies can be theoretically predicted within the self-consistent field theory, on the basis of the volume fraction of the components, the number of segments in the
copolymers, and the Flory-Huggins interaction parameter, as is the case for the spherical, cylindrical, gyroid, and lamellar phases, which have been observed in the simplest amorphous diblock copolymers. Particularly in the case of more complex systems, differences from the theoretical predictions can, however, be expected, mainly because of chain fluctuations and conformational block asymmetries. Also for this reason, more recent efforts have focused on ordered structures obtained from BCs having both rigid and flexible segments\textsuperscript{24} and also from triblock and even tetrablock copolymers, with the observation of a series of novel and unconventional morphologies such as zig-zag, core-shell double gyroid, spheres or rods between lamellae, helices around cylinders, and hexagonal double or triple

\textbf{Figure 1.3.} Block copolymer phase diagram
coaxial cylinder structures. A few of these morphologies, the ones most frequently used for nanofabrication, are illustrated schematically in Figure 1.3.

The potential technological application of such variety of mesostructures, and particularly of those formed in the case of thin films, can be easily appreciated by non-specialists alike and has been widely recognized, e.g., since the first successful attempts to use self-assembly strategy for the preparation of membranes with tunable nanochannels\textsuperscript{25} and the early block copolymer-based nanolithography,\textsuperscript{26} but only partially explored.

A phase diagram constructed from experiments on a series of polystyrene-b-polyisoprene(PS-PI) diblocks in Figure 1.4 and this will be used as a guide for the various microstructures.\textsuperscript{27}

![Figure 1.4. Block copolymer phase diagram](image-url)
1.3. Supramolecular Assemblies of $\pi$-Conjugated systems

With the introduction of $\pi$-conjugated systems in electronic devices and the dream to arrive at molecular electronics based on these systems, the detailed understanding of the supramolecular interactions between the individual $\pi$-conjugated molecules has become one of the most challenging scientific research areas. As a result, nanoscience and nanotechnology are logically merged and academic and industrial endeavors are moving hand in hand. In an unprecedented way, the synthesis of new molecules is guided by the results of device physicists, while devices show improved performance due to progress in the synthesis of new materials. However, the different hierarchies of organization going from molecules to devices have been addressed to a much lesser extent, while it is generally accepted as being the most critical issue. For electronic devices made out of $\pi$-conjugated systems the interchain electronic coupling will determine the device performance. Not only is a perfect fit between the $\pi$-conjugated elements required, but also the anisotropy of the electronic coupling is equally important for a macroscopic performance of these mainly two-dimensional (semi-)conductors. It is an enormous challenge to obtain monodomain ordered structures in the micrometer regime. Only in that way control over all length scales in organic electronic devices is achieved.
In general, the average size of crystalline-like domains is within the range of a few hundreds of nanometers. Knowledge of this scope and limitations of the ordering of $\pi$-conjugated systems at the different length scales has brought the area of supramolecular electronics\textsuperscript{28} to the fore: electronic devices based on individual supramolecular objects in the 5-100 nm regime. This is an area between devices based on thin films of organic materials and molecular electronics based on single molecules.

$\pi$-Conjugated (semiconducting) polymers are by far the most promising functional polymers in view of applications in less expensive and flexible electronic devices. Prototype field-effect transistors (FET)s,\textsuperscript{29} light-emitting diodes (LED)s,\textsuperscript{30,31} photovoltaic cells,\textsuperscript{32} and related devices have already been fabricated, and Philips introduced the first commercial LED

![Chemical structures of several conjugated polymers](image)

**Figure. 1.5.** Chemical structures of several conjugated polymers

based on polymer technology in 2002. Nowadays a plethora of conjugated
polymers exists having a base structure of alternating single and double/triple bonds of which some parent structures are shown in Figure 1.5.33

The performance of organic devices is mainly determined by the chemical structure, purity, and supramolecular organization or morphology of the π-conjugated material. This dependence is not unique for semiconducting materials but also valid for functional polymers in general. However, the importance of control of structure at every structural hierarchy is by far the most delicate for semiconducting polymers. Going from isolated chains to an intermolecular hierarchy, charge transfer between chains is required for conduction in a “microcrystalline” or mesoscopic phase. To arrive at controlled microcrystallinity, it is necessary to have (latent) solubilizing groups, and nowadays a number of ways to control solubility are known. Whereas side chains are useful at the mesoscopic level of microcrystallization, they are sometimes detrimental for the macroscopic ordering. It is evident that materials research in the area of semiconducting polymers is only useful when macromolecular engineering by organic synthesis is combined with investigations to control molecular architecture at all levels of hierarchy(Figure 1.6).
Figure 1.6. Schematic representation on how the properties of optoelectronic devices
1.4. Reference


Chapter 2

Synthesis of a Fluorine-Containing Copolymers of PMMA-\(b\)-PPFS and PMMA-\(b\)-PPFS-\(b\)-PMMA by Atom Transfer Radical Polymerization
2.1 Introduction

Controlled radical polymerization (CRP) technique has attracted recent scientific and industrial attention in the fields of polymer chemistry. The main advantage of this method is the capability of controlling compositions, architectures and functionality of polymeric materials at facile reaction conditions. It can be achieved by rapid propagation and reversible termination or transfer reaction that are much faster than the irreversible termination reaction which enables polymer chains to grow more slowly and continuously with conversion. There are largely three efficient systems in CRP such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT). Especially in ATRP, a radical can be formed reversibly polymeric materials by transfer of a halogen from an alkyl halide to a transition metal complex and molecular weights, polydispersity, compositions and architecture can be easily controlled with conversion.

Block copolymers have received much scientific and technological attention due to their ability to self-assemble into a series of periodic ordered microstructures via microphase separation between the constituent block segments. These block copolymers can be used as thermoplastic elastomers, surfactants, dispersants and thickeners. There are a number of
applications by using their phase-separated morphology both in the solid state and in solutions. To synthesize these block copolymers with predetermined molecular weights and low polydispersity, anionic polymerization is usually employed. However, its use is highly limited due to the strict reaction conditions such as extremely low temperature, exclusion of moisture and impurity, and stringent drying.

Recently, ATRP has been used in such a manner to build block copolymers of radically polymerizable monomers. In this process, active halogens are incorporated at the chain ends of polymers to form macroinitiators.

In the present study, we synthesized a novel block copolymers of polyfluorostyrene-\textit{b}-poly(methyl methacrylate) (PPFS-\textit{b}-PMMA) and poly(methyl methacrylate)-\textit{b}-polyfluorostyrene-\textit{b}-poly(methyl methacrylate) (PPFS-\textit{b}-PMMA-\textit{b}-PPFS) by ATRP technique for potential optical waveguide applications. Evidence of block copolymerization is provided by GPC, \textsuperscript{1}H-NMR, thermal analysis, TEM and small angle X-ray scattering (SAXS).
2.2. Experimental

2.2.1. Chemicals.

Pentafluorostyrene (PFS, Aldrich), methyl methacrylate (MMA, Aldrich) were purchased and passed through a basic alumina column for the removal of the inhibitors, and then they were distilled over CaH$_2$ in vacuo prior to use. Copper bromide (CuBr, Aldrich) was purified by washing with acetic acid and ethanol, ethyl ether subsequently and then dried in vacuo. 2,2′-dipyridyl, α,α′-dibromo-p-xylene, fluorobenzene were purchased from Aldrich and used without further purification.

2.2.2. Characterization.

$^1$H NMR spectra and $^{13}$C NMR spectra were recorded on a VARIAN UNITY INOVA 400 spectrometer at 400 MHz and were referenced to TMS. The thermal transition temperatures were measured by using a Thermal Analysis DSC 2920 under nitrogen atmosphere at a heating rate of 10 °C/min. Molecular weights and molecular weight distributions were determined using a GPC equipped with a Waters Associates 410 RI detector, 510 HPLC pump, and $i$-Styrage columns with pore sizes of 102, 500, 103, and 104 Å. The eluant was THF, and the molecular weights were calibrated with polystyrene standards.
Transmission electron microscopy (TEM, Philips CM-200) was used to measure the self-assembled structure. The XRD measurements were conducted on Beamline 4C1 at the Pohang Accelerator laboratory, Pohang, Korea. The X-ray beam was generated from synchrotron radiation using Co Kα radiation (λ = 1.608 Å) and the storage ring was operated at energy level of 2 GeV. The XRD apparatus employs a point focusing optics with a Si double crystal monochromator followed by Au coated flat mirror. The sample-to-detector distance was 2000 mm and the data were collected in a range in momentum transfer of 0.003 ≤ Q (nm⁻¹) ≤ 1.421, \( Q = (4\pi/\lambda)\sin\theta \). The intensity of the beam was monitored by ionization chamber for the minor decrease of primary beam intensity during measurement. The scattering data profiles were corrected for background and detector efficiency.

2.2.3. Syntheses.

2.2.3.1. Synthesis of PPFS diblock Macroinitiator-Method 1

CuBr (0.014 g, 0.1 mmol), PFS(6.8 g, 35 mmol), PMDETA(0.017 g, 0.1 mmol) and fluorobenzene (5 mL) were added to a dry round-bottom flask with a stir bar. The flask was evacuated and back-filled with N₂ during 30 min. The mixture was stirred at room temperature for
approximately 30 min before the initiator was injected. After heating to 75 °C, the PEBr (0.02 g, 0.1 mmol) initiator was then added slowly using a syringe. The polymer samples obtained were isolated by precipitation with methanol for 17 hrs of reaction time. Samples for GPC measurement were purified via passing them through a column of alumina. The macroinitiators were characterized with ¹H NMR.

2.2.3.2. Synthesis of PPFS Triblock Macroinitiator

Quantities were as follows: CuBr (0.029 g, 0.2 mmol), PFS(5.44 ml, 40 mmol), 2,2’-dipyridyl (0.062 g, 0.4 mmol), fluorobenzene(5.44 mL) and α,α’-dibromo-p-xylene (0.053 g, 0.2 mmol) initiator. The experimental procedure was as described for the preparation of diblock Macroinitiator (Method 1).

2.2.3.3. Preparation of PPFS-b-PMMA-Method2

The PPFS-b-PMMA diblock copolymer was synthesized by ATRP in the bulk state. The synthetic procedure was similar to that of preparation of PPFS macroinitiator which was described earlier. PPFS-Br (0.33 g, 9.7×10⁻⁵ mol) as an initiator was added to a round-bottom flask, equipped with a magnetic stir bar. CuBr (0.015g, 9.7×10⁻⁵ mol), PMDETA (0.02 g, 9.7×10⁻⁵ mol),
mol) and MMA (3.9 g, 39 mmol) were added in the solution. Then the mixture was purged with N₂ and stirred for additional 3 hr.

2.2.3.4. Preparation of PMMA-\textit{b}-PPFS-\textit{b}-PMMA

Quantities were as follows: Br-PPFS-Br (1.65 g, 0.05 mmol) as an initiator was added to a round-bottom flask, equipped with a magnetic stir bar. CuBr (0.0072 g, 0.05 mmol), 2,2’-dipyridyl (0.031 g, 0.2 mmol) and MMA (4 g, 0.04 mol). The experimental procedure was as described for the preparation of diblock copolymer (Method 2).
2.3. Result and Discussion

Figure 2.1 shows the schematic representation of the synthesis of PPFS-\textit{b}-PMMA diblock copolymer which consists of two steps such as the synthesizes of PPFS-Br macroinitiator and PPFS-\textit{b}-PMMA diblock copolymer. Figure 2.2 shows the schematic representation of the synthesis of PMMA-\textit{b}-PPFS-\textit{b}-PMMA diblock copolymer. The synthesis of the PPFS-Br and Br-PPFS-Br macroinitiators were carried out by ATRP in bulk state. In this reaction, the relative mole ratio of monomer/initiator/CuBr/ligand was 200(800)/1/1/4 and the reaction temperature was 110 °C. PPFS protons were confirmed between 1.7 and 3.0 by $^1$H NMR(Fig. 2.3). The molecular weight and polydispersity of PPFS-Br and Br-PPFS-Br were measured by GPC and summarized in Table 1. The synthesis of di and tri block copolymers were carried out at 60 °C in bulk state. In this reaction, the relative mole ratio of monomer/initiator/CuBr/ligand was 800/1/1/2(4). The molecular weight and polydispersity of block copolymers were also shown in Table 1. A slight increase of polydispersity may be due to short period of reaction time. However, after approximate 1 hrs, the viscosity of the solution was highly increased and stirring the reaction solution became rather difficult. The typical DSC of the resulting block copolymers are shown in Figure 2.4.
We observed two glass transition temperatures at 105 °C and 123 °C for PMMA and PPFS block segments.

Figure 2.5 shows the TEM data of di and tri block copolymers, annealed at 180 °C. Due to the chemical dissimilarity between the PMMA and PPFS blocks, both blocks tend to segregate each other to form a microphase-separated morphology in a nanometer level. In these data, we observed a disordered lamellar morphology with a thickness of 35 nm and 37 nm, confirming the microphase separation behavior of block copolymers. Figure 2.6 shows the temperature-resolved SAXS data of di and tri block copolymers measured during heating from room temperature to 230 °C. In this data, we found a transition from the disordered phase to a microphase-separated phase in the temperature range above 130 °C, indicating the existence of a lower critical disorder-to-order transition (LDOT). The observed X-ray peaks were in the ratio 1:2:3, indicating that it forms a micro-phase lamellar morphology with a lamellar thickness of 35nm and 37 nm.

The surface morphology of block copolymers are shown in Figure 2.7. The sample was prepared by spin-coating on a silicon wafer. Applied in a THF solution, the polar PMMA blocks are strongly adsorbed and form a wetting layer on the Si surface. Due to the unfavorable interaction with Si
surface, the PPFS blocks are likely to dewet to yield isolated nanoclusters onto the PMMA blocks. Unlike thick block copolymer films, both blocks form part of surface, thus resulting in a chemically heterogeneous surface structure of less polar PPFS domains surrounded by the highly polar PMMA absorbate layer. In Fig. 2.7, the protruding PPFS clusters are displayed as brighter areas. We attribute it to dense brush layer of ordered copolymer due to the strong attraction between PMMA chains and the native silicon oxide layer on the substrate.\textsuperscript{10}
Figure 2.1. Schematic description of the synthesis of PPFS-b-PMMA
diblock copolymer
Figure 2.2. Schematic description of the synthesis of PMMA-b-PPFS-b-PMMA Triblock Copolymer
Figure 2.3. $^1$H NMR data of macroinitiator and block copolymers
### Table 1. Material Characteristics of PPFS-Br macroinitiator and blockcopolymers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initiator</th>
<th>Monomer</th>
<th>[I]:[M]:[Cu^+] :[ligand]</th>
<th>Mn (g/mol)</th>
<th>Time (hr)</th>
<th>PDI</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>PhEBr</td>
<td>PF5</td>
<td>1:1:2:200:100</td>
<td>14800</td>
<td>30</td>
<td>1.12</td>
<td>38</td>
</tr>
<tr>
<td>P1-1</td>
<td>PPFS-Br</td>
<td>MMA</td>
<td>1:1:2:800:100</td>
<td>61100</td>
<td>2</td>
<td>1.23</td>
<td>58</td>
</tr>
<tr>
<td>P2</td>
<td>PhEBr</td>
<td>PF5</td>
<td>1:1:4:200:100</td>
<td>33000</td>
<td>48</td>
<td>1.13</td>
<td>85</td>
</tr>
<tr>
<td>P2-1</td>
<td>PPFS-Br</td>
<td>MMA</td>
<td>1:1:4:800:100</td>
<td>89000</td>
<td>2</td>
<td>1.33</td>
<td>70</td>
</tr>
<tr>
<td>P3</td>
<td>dibromo-xylene</td>
<td>PF5</td>
<td>1:1:2:200:100</td>
<td>26600</td>
<td>30</td>
<td>1.16</td>
<td>69</td>
</tr>
<tr>
<td>P3-1</td>
<td>Br-PPFS-Br</td>
<td>MMA</td>
<td>1:1:2:800:100</td>
<td>44000</td>
<td>2</td>
<td>1.27</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 2.4. DSC data measured during the second heating
Figure 2.5. TEM image (a) di and (b) tri block copolymers, annealed at 180 °C
Figure 2.6. SAXS patterns (a) di and (b) tri block copolymers
Figure 2.7. The 2-dimensional and 3-dimensional AFM images of (a) di and (b) tri block copolymers, prepared after annealing for 24 hrs at 130 °C of the spin-coated sample on a Si wafer.
2.4. Conclusions

Our study successfully demonstrated the syntheses of fluorinated block copolymers by using ATRP technique. The as-received sample displayed a disordered phase at room temperature, but it formed a nanophase-separated morphology at high temperature, revealing the presence of the lower critical disorder-to-order transition during heating. The SAXS data confirmed a disordered lamellar morphology with a thickness of 35 nm above 130°C. The surface morphology measured from AFM showed that the PPFS blocks are likely to dewet to yield isolated nanoclusters onto the PMMA blocks.
2.5. Reference


8. J. Peng, Y. Xuan, H. Wang, B. Li and Y. Han, Polymer 2005, 46, 5767
Chapter 3

Synthesis and Characterization of

Amphiphilic $\alpha,\alpha'$-Disubstituted Oligothiophenes
3.1. Introduction

Nanoscopic and mesoscopic order in π-conjugated systems is a topic of utmost importance, because it determines the performance of the materials when used as components in organic electro-optical devices such as solar cells,¹ light-emitting diodes (LEDs),² and field-effect transistors (FETs).³,⁴ Well-defined π-conjugated oligomers play an important role in this field, because their precise chemical structure and conjugation length gives rise to well-defined functional properties and facilitates control over their supramolecular organization.⁵ Until recently research in this field has been focused mainly on methodologies for the synthesis and characterization of π-conjugated oligomers with long axis dimensions up to 10 nm.⁶-⁸ Another major issue, which attracts increasing attention, is the control of the spatial orientation and packing of oligomers through the design of molecular and supramolecular architectures. The control of molecular assembly to give well-defined structures on the nanoscale can be carried out via different complementary approaches: (i) Self-assembly can take place in solution; the details of the aggregation behavior are governed by parameters such as the substitution on the conjugated backbone, the nature of the solvent, or the temperature. (ii) Because conjugated oligomers can be sublimed, it is also possible to follow their assembly as they form
thin deposits on surfaces from individual molecules in the vapor phase; in that case, interactions with a solvent are absent and the driving forces controlling the aggregation are the intermolecular interactions between the conjugated species and the substrate surface. (iii) Another possibility is to generate thin deposits from conjugated compounds molecularly dispersed in a solution; aggregation takes place during the deposition and then depends on the interplay among the conjugated molecules, the solvent, and the substrate surface.

Oligomers and polymers based on α, α’-linked thiophenes are at the forefront of organic semiconductor materials with potential for applications in FETs and related structures. To achieve easy processability of these materials, one common route is to substitute the thiophene backbone, either on the β-positions of the rings or on the two terminal α-positions. The corresponding substituted systems, generally bearing alkyl chains, are soluble, allowing the use of processing techniques such as spin-coating and solution casting for device fabrication. For β-substituted polythiophenes, the search for soluble materials led to the concomitant development of strategies for the synthesis of regioregular polymers. The degree of regioregularity has been shown to influence crystallinity, conjugation, conformational order, and charge carrier properties. Similarly, the problem
of solubility in oligothiophenes was overcome by the introduction of alkyl groups at the $\beta$-position or the terminal $\alpha$-positions.\textsuperscript{12} For sexithiophenes, it was demonstrated that the substitution pattern considerably influences the molecular packing and thereby the orientation in the crystal. In particular, $\beta$-substitution leads to a distortion of the molecular conformation and to a larger intermolecular separation in the aggregated state, while $\alpha$, $\alpha'$-disubstituted sexithiophenes resemble the unmodified system in terms of close packing and degree of order.\textsuperscript{13} Recently, other derivatives, such as branched\textsuperscript{14} and star-shaped\textsuperscript{15} oligothiophenes, have been synthesized and used for the fabrication of electronic devices.

In fact, the development of substituted, soluble $\pi$-conjugated materials allows not only a control of their organization in the solid state but also the possibility of determining the degree of order in solution. This has generated a great deal of interest in the supramolecular organization of such systems in organic solvents.\textsuperscript{16} For example, studies of the organization in solution of chirally $\beta$-substituted polythiophenes provided profound insights into the solid-state organization of solution cast films. The formation of supramolecular interactions via hydrogen-bonding arrays in combination with $\pi-\pi$ stacking has also been used to self-assemble oligothiophenes into one-dimensional arrays on surfaces, generating a
material with remarkable high charge carrier mobility.

In this report, we synthesized a novel amphiphilic triblock copolymer C_{15}-3T-EO_{5} containing oligothiophene, which was asymmetrically end-substituted with a hydrophobic alkyl moiety and a hydrophilic oligo(ethylene glycol) by Suzuki and Stille coupling reactions. $^1$H NMR, GC-MS, AFM and DSC were used to confirm the molecular structures of these molecules.
3.2. Experimental

3.2.1. Chemicals.

Methylene chloride (CH\textsubscript{2}Cl\textsubscript{2}) was used after distillation under calcium hydride. 5-bromo-2-thiophenecarboxylic acid (97%), N-bromosuccinimide (99%), N,N-diisopropylcarbodiimide (99%), butyllithium (1.6M solution in hexanes), tertakis(trihenylphosphine)palladium(0), toluene anhydrous (99.8%), N,N-dimethylformamide anhydrous (99.8%), 1-dodecanol (98%) were purchased from Aldrich Chemical Co. and used as received. Tributyltin Chloride and tetraethylene glycol monomethyl ether was purchased from TCI and also used as received. Thiophene-2-boronic acid was purchased from COMBI-BLOCKS Inc. and also used as received. 4-Dimethylamino-pyridinium 4-toluenesulfonate (DPTS) was prepared by following a literature procedure.\textsuperscript{17}

3.2.2. Characterization.

\textsuperscript{1}H NMR spectra and \textsuperscript{13}C NMR spectra were recorded on a VARIAN UNITYINOVA 400 spectrometer at 400 MHz and were referenced to TMS. The thermal transition temperatures were measured by using a Thermal Analysis DSC 2920 under nitrogen atmosphere at a heating rate of 10 °C/min. The PL emission spectra were obtained with a RF-5301PC.
spectrofluorophotometer (Shimadzu, Japan). X-ray analysis was carried out in a Philips PW1847 X-ray diffractometer, operated at 40 kV and 100 mA, using reflection geometry and Cu Kα radiation (wavelength λ = 0.15418 nm). The data were measured within the range of scattering angle, 2θ of 20 - 80°. The as-prepared powders of the specimens were used without further treatment.

3.2.3. Syntheses.

3.2.3.1. 2-TEG-5-bromothiophene-2-carboxylate.(1) 5-bromo-2-thiophenecarboxylic acid (2 g, 9.6 mmol), tetraethylene glycol monomethyl ether (2 g, 9.6 mmol), DPTS (2.85 g) and DIPC (2.25 ml) were stirred in 50ml CH₂Cl₂ at r.t. overnight. The reaction mixture was diluted with CH₂Cl₂ and washed with water. The organic layer was separated, dried over MgSO₄, and solvent removed by rotary evaporation. The product was subjected to a column chromatography using MeOH/CH₂Cl₂ (19:1) as the eluant to afford the product (Yield 6.8 g, 84%).

3.2.3.2. 2-dodecyl 5-bromothiophene-2-carboxylate.(2) Synthesis was as described for compound 1 using 5-bromo-2-thiophenecarboxylic acid (3
g, 14.5 mmol), 1-dodecanol (2.7 g, 14.5 mmol), DPTS (4.27 g, 14.5 mmol) and DIPC (2.25 ml, 14.5 mmol). The product was subjected to a column chromatography using CH₂Cl₂ as the eluant to afford the product (Yield 4.9 g, 86%).

3.2.3.3. 2-dodecyl-5′-bromo-[2,2′]bithiophene-2-carboxylate.(3)

reaction(1) An aqueous solution (2 M, 40 ml) of sodium carbonate was added to toluene solution (50 ml) of mixture of 2 (4.32 g, 11.5 mmol), tertaki-s(triarylphosphine)palladium (0.266 g, 0.23 mmol), and thiophene-2-boronic acid (1.77 g, 13.8 mmol). The reaction mixture was then stirred 80 ℃ for 36 h under nitrogen. After cooling, the reaction mixture was diluted with CH₂Cl₂ and washed with water. The organic layer was separated, dried over MgSO₄, and solvent removed by rotary evaporation. The crude product was subjected to a column chromatography using Haxane/CH₂Cl₂ (9:1) as the eluant to afford the product (Yield 3.8 g, 62%).

reaction(2) In the absence of light, a solution of 0.62 g (4.5 mmol) N-bromosuccinimide (NBS) in 20 ml of anhydrous DMF was added dropwise at 0 ℃ to a solution of 1.1 g (3.0 mmol) of product(1) in 10 ml of anhydrous DMF within 30 min. The reaction mixture was stirred for 4 h
at room temperature. It was then poured on to ice and extracted twice with CH₂Cl₂ and water. The organic layer was separated, dried over MgSO₄, and solvent removed by rotary evaporation. The crude product was subjected to a column chromatography using Haxane/CH₂Cl₂ (1:1) as the eluant to afford the product (Yield 0.8 g).

3.2.3.4. 2-dodecyl-5’-tributyltin-[2,2’]bithiophene-2-carboxylate.(4)

0.5 g of 1 (1.1 mmol) was placed in a flame dried flask cooled under N₂ in anhydrous THF. 0.7 ml of a 1.60 M solution of nBuLi (1.1 mmol) was added via syringe at -78°C. The mixture was stirred for 30 min at -78°C. 0.36 ml of tributyltin chloride (1.2 mmol) was added via syringe at -78°C. The reaction was allowed to warm slowly to room temperature overnight. The THF was removed by rotary evaporation and the products were redissolved in CHCl₃. The organic layer was washed with water to remove lithium salts, separated, dried over MgSO₄ and the solvent was removed by rotary evaporation. Product was used crude in the next reaction.

3.2.3.5. C₁₅-3T-EO₅ 1 (0.71 g, 1.8 mmol) was added to 4 (1.2 g, 1.8 mmol) and tertakis(triarylphosphine)palladium(0.1 g, 0.09 mmol). Anhydrous DMF(20 ml) was added. The reaction mixture was then
stirred 100 °C for 24 h under nitrogen. Reaction mixture was diluted with CH₂Cl₂ and washed water. The organic phase was then dried with MgSO₄ and solvent removed by rotary evaporation. The crude product was subjected to a column chromatography using MeOH/CH₂Cl₂ (1:9) as the eluant to afford the product (Yield 0.85 g). ¹H NMR (600 MHz, CDCl₃) δ: 7.71(dd, J=4.0 Hz, J=9.0 Hz, 2H), 7.21(s, 2H), 7.16(d, J=4.0 Hz, 2H), 4.45(t, J=4.7 Hz, 2H), 4.29(t, J=6.95Hz and 6.59Hz, 2H), 3.81(m, 2H), 3.66(m, 12H), 3.36(s, 3H), 1.74(m, 2H), 1.25(m, 18H), 0.87(t, J=6.95 and 6.59, 3H) MS (GC-MS) calculated for C₃₅H₅₀O₈S₃ 694, found 695.4
3.3. Result and Discussion

The synthesis of the amphiphilic α,α′-disubstituted oligothiophene was described in detail in the experimental section. The α,α′-disubstituted oligothiophene were synthesized by Suzuki coupling and Stille coupling reaction (Figure 3.1). Bromination conditions were adapted from the literature. To synthesize asymmetrically end-substituted oligothiophene, the coupling reaction of TEG-thiophene  and Dodecyl-thiophene  as the last step. The chemical structures of the compounds of ,  and  were confirmed by 1H NMR, as shown in Figure 3.2.

Figures 3.3 showed the DSC data of the C15-3T-EO5 which was measured the second heating scans of the as-prepared sample in the temperature range between 10 ℃ and 100 ℃. Melting Temperature and Crystalline Temperature is 60 ℃ and 48 ℃, respectively.

Figure 3.4 shows a series of PL spectra of aqueous solutions of C15-3T-EO5 at various concentrations. Due to the dissimilarity between the components, C15-3T-EO5 can be self-assembled into a micelle in selective solvents. At low concentrations, we found double peak intensities of λPL ≈ 446 and 467 nm with almost the same peak intensity, but the peak intensity started to decrease upon increasing the concentration, indicating the formation of the micellar aggregate of C15-3T-EO5. The data also
showed that the major PL peak was also red-shifted upon increasing the concentration of the solution, possibly due to the confinement of the C$_{15}$-3T-EO$_{5}$ molecule within the micelle structure, which limits intermolecular energy transfer between the C$_{15}$-3T-EO$_{5}$ molecules.

The surface morphology of the micellar aggregates of molecules C$_{15}$-3T-EO$_{5}$ was monitored by AFM measurements. Figure 3.5 shows the AFM images of the micellar aggregates of C$_{15}$-3T-EO$_{5}$, prepared by spin-coating of C$_{15}$-3T-EO$_{5}$ on mica. The solution concentration was approximately 0.01 % in weight. In this image, we found a number of monodisperse particular aggregates on mica, and their diameters were approximately 7 nm.
Figure 3.1. Schematic description of the synthesis of C_{15}-3T-EO_5
Figure 3.2. NMR of compound 2, 5 and C_{15}-3T-EO_{5}
Figure 3.3. DSC data measured during the second heating
Figure 3.4. PL spectra for aqueous solution of C_{15}-3T-EO_{5}
Figure 3.5. AFM image of C_{15}-3T-EO\textsubscript{5} on mica
3.4. Conclusions

We successfully synthesized a well-defined, amphiphilic triblock oligothiophene with a hydrophobic dodecyl moiety and a hydrophilic tetraoxyethylene unit. The compound was characterized by $^1$H NMR, GC-MS, AFM and its absorption and emission data was also measured. Due to the dissimilarity between the components, this compound was self-assembled into various supramolecular nanostructures in selective solvents. These highly-ordered nanostructures of this compound were also induced on mica surface, which offers a potential to be used in OTFT applications.
3.5. Reference


