

**Fabrication of Well-Defined Architectures of
Ultrahigh-Molecular-Weight Polymers by
Living Radical Polymerization**

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Contents

Chapter 1	General Introduction	1
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Part 1

Concentrated Polymer Brushes with Large Thickness – Synthesis and Tribological Properties

Chapter 2	Synthesis of Concentration Polymer Brushes with Extraordinarily Large Thickness by High-Pressure Atom Transfer Radica Polymerization	23
Chapter 3	Synthesis of Concentration Polymer Brushes with Large Thickness by Atom Transfer Radica Polymerization in Ionic Liquid Solvent Medium	37
Chapter 4	Lubrication Mechanism of Concentration Polymer Brushes with Large Thickness: in Microscopic Scale	51
Chapter 5	Lubrication Mechanism of Concentration Polymer Brushes with Large Thickness: in Macroscopic Scale	59

Part 2

Ultrahigh Molecular Weight Block Copolymers – Synthesis and Application to Gels

Chapter 6	Controlled Synthesis of Ultrahigh-Molecular-Weight Block Copolymer by High-Pressure Atom Transfer Radical Polymerization	71
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Chapter 7	Controlled Synthesis of Ultrahigh-Molecular-Weight ABA Triblock Copolymer and Fabrication of Ionic Gel	83
Summary		107
List of Publications		111
Acknowledgements		113

Chapter 1

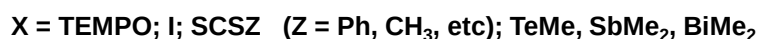
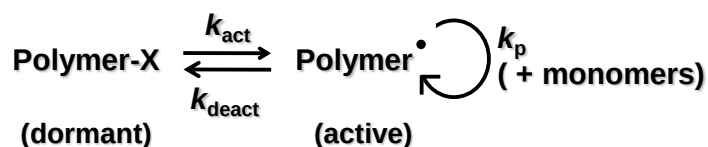
General Introduction

1-1. Living Radical Polymerization (LRP)

Living radical polymerization (LRP), also known as controlled radical polymerization, is one of the most commonly used methods to synthesize well-defined polymers. Compared with other techniques such as anion polymerization, cation polymerization, and coordination polymerization, which require severe reaction conditions (e.g., high-purity reagents, strictly moisture-free conditions, and limited application of monomers), LRP offers a simpler method to synthesize a variety of polymer, including those with functional groups and complex structures.¹ The mechanism of LRP is known to involve reversible activation of the dormant species P-X to polymer radicals P[•], where P-X and P[•] represent the polymer with a protective group capping and the polymer radical, respectively (Figure 1-1). The reaction allows the formation of reproducible radicals, which progress the propagation, termination, and chain transfer reactions during their lifetime before deactivation. In order to obtain a living/controlled polymerization, a suitable design of P-X and the applied catalyst (used to activate P-X) is necessary.

Over many years, the development of LRP has produced many possible methods. In the 1980s, Otsu et al. reported initiator-transfer agent-termination (iniferter) polymerization using a chemical compound (commonly a dithiocarbamate) that acted as initiator, transfer agent, and terminator, and successfully

Reversible activation (general scheme)



Scheme 1-1. Reversible activation process of LRP

exhibited living behavior for radical polymerization despite a relative high polydispersity ($M_w/M_n \sim 2$).² In the 1990s, nitroxide-mediated polymerization (NMP) using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a protective group,³ atom transfer radical polymerization (ATRP) applying initiators with halogen end groups (e.g. -Cl and -Br) and transition metal compounds (e.g. Ru, Cu, etc.),⁴ and reversible addition-fragmentation chain transfer (RAFT) using dithioester compounds as chain transfer agents⁵ were typical discoveries, and are still popular at present. In the 2000s, organotellurium-mediated radical polymerization (TERP) discovered by Yamago et al.,⁶ reversible chain transfer catalyzed polymerization (RTCP), and reversible complexation mediated polymerization (RCMP) by Goto⁷ gained attention as a new class of LRPs with good controllability. The development of LRP has opened up new routes for synthesizing functional polymers with diverse conformations.

1-2. Design of Polymer Architecture

LRP shares the characteristics of conventional free radical polymerization (FRP) in terms of the diversity of monomers and tolerance of various functional groups. One difference, however, is that the living behavior of LRP provides the important advantage of designable polymer structures. Factors affecting polymer structure design can be divided into two points: composition and topology (Figure 1-1). In terms of composition, homopolymers, block copolymers, graft copolymers, and copolymers with monomers in a

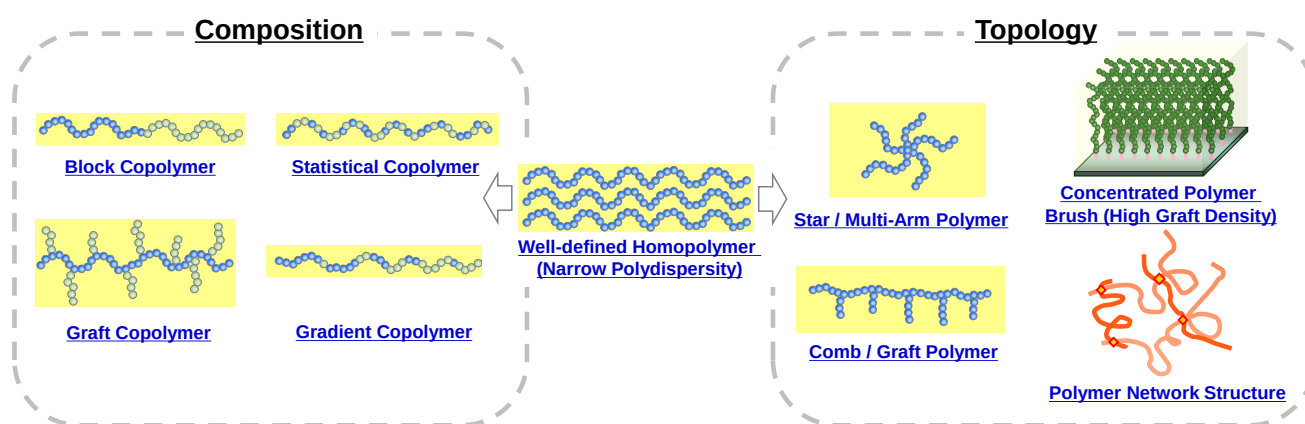


Figure 1-1. Illustration of designable polymer structures achievable by LRP

random, periodic, or gradient arrangement can be synthesized with LRP techniques.⁸ In terms of topology, not only linear polymers, but also branched polymers containing star, comb, brush, branched, and network structures can be prepared by a similar method.⁹ Furthermore, the possibility of using LRP to functionalize such polymers further broadens their applications.¹⁰ Although some structures of polymers, such as block copolymers, can also be synthesized by other techniques (e.g. anion polymerization and cation polymerization)¹¹, the selection of monomers is limited, or requires combination with other reactions (e.g. coupling and click reactions).¹²

With the recent development of LRP, polymers with higher-order architectures such as densely grafted polymer brushes¹³ and network¹⁴ structures (gels) have attracted much attention for tribological and electronic chemistry applications. In this thesis, the synthesis of polymers with two conformations (brush and block segments) was investigated, and will be described in detail in the following sections.

1-2-1. Polymer Brushes

Polymer brushes consisting of polymer chains tethered to a solid surface at one end have attracted increasing attention for their important roles in many areas of science and technology, e.g., colloid stabilization, adhesion, rheology, and tribology.¹⁵ Traditionally, synthesis of the brush conformation has been carried out to introduce polymer chains onto surfaces using physical (physisorption) and chemical (covalent bonding) methodologies, known as the “grafting to” methods.¹⁶ Physisorption involves the absorption of a block copolymer using a segment that sticks to the substrate surface. The covalent bonding (chemical) methodology involves preformed polymers with reactive sites.¹⁷ Owing to the steric effect of grafted polymer chains, the brushes prepared by the “grafting to” method exhibit a relatively low density of grafted chains, resulting in the interpenetration of confronted brushes, thus affecting their tribological properties.¹³ Klein et al. presented a theoretical derivation on the friction of brushes and explained that limited interpenetration of brush layers facilitated effective lubrication.¹⁸ The theoretical expression predicts that the smaller the screening length at the anchoring surface (i.e., increased brush density), the greater the effective lubrication.

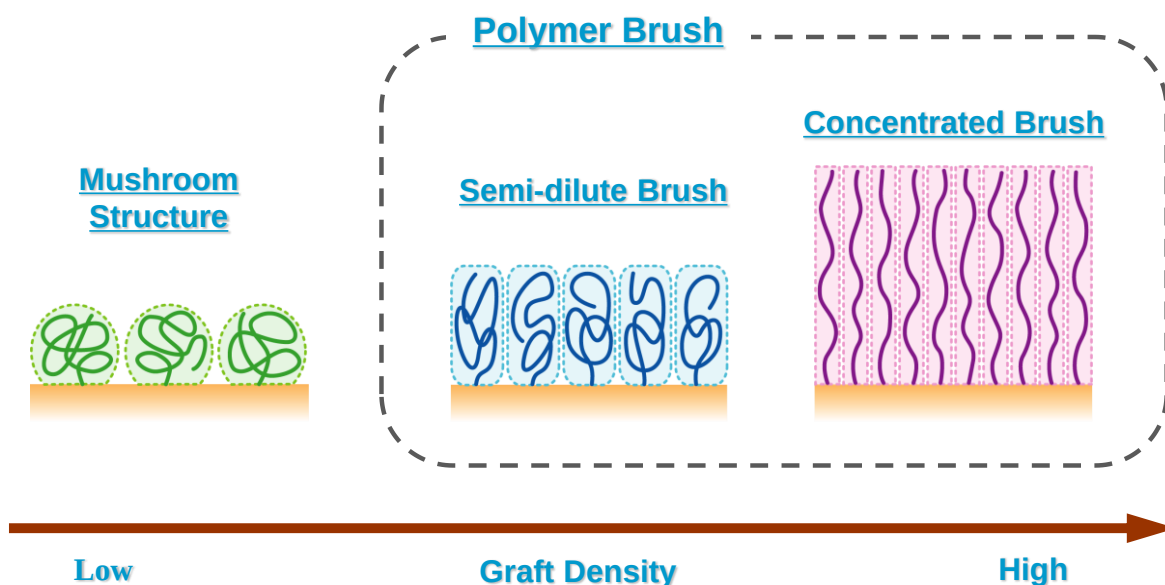


Figure 1-2. Schematic illustration of tethered polymer chains

More recently, the “grafting from” method (also called surface-initiated polymerization), which was first investigated by Prucker and R  he,¹⁹ has allowed the synthesis of densely grafted polymers on various solid surfaces. This technique involves a two-step process: immobilization of surface initiators and polymerization from the immobilized initiating sites. The development of surface initiators has allowed the grafting from method to be used in various polymerization methods, including free radical, living radical, ionic, and ring-opening metathesis.²⁰⁻²⁷ The author’s group firstly succeeded in synthesizing poly(methyl methacrylate) (PMMA) brushes with exceptionally high graft density by applying ATRP to surface-initiated polymerization.^{22a} The success launched a wide range of research initiatives into densely grafted polymer brushes. At present, a variety of LRP methods including NMP, ATRP, RAFT, TERP, and RTCP have already been applied to this technique.²¹⁻²⁵

A series of investigations revealed that conformation of polymer brushes in a good solvent changed dramatically at the boundary of $\sigma^*=0.1$ (where σ^* is the dimensionless graft density).^{13a} This boundary can be used to categorize polymer brushes into two types: semi-diluted polymer brushes (SDPBs) and concentrated polymer brushes (CPBs) (Figure 1-2). In recent studies by the author’s group, it was found that CPBs exhibited several properties quite different from the SDPBs when in a good solvent, e.g. highly

stretched structure, strong repulsion force, super lubrication, and size-exclusion property.^{13b,28} These features specific to the CPB were reasonably attributed to the entropic interaction between extremely high osmotic pressure (to extend the grafted chains and thus impart the repulsion property) and highly stretched chain conformation (to attain a stable state and hence produce low friction, as described in the following section). These features were termed the “concentrated-brush effect”.

1-2-1-1. Particular Reference to Lubrication

As densely grafted polymer chains, CPBs are thought to exhibit greater lubrication than the low density SDPBs, as mentioned above. The lubrication properties of CPBs were previously investigated in the author’s group by microtribological analysis using colloid-probe atomic force microscope (AFM) measurements, which showed an extremely low frictional coefficient of the order of 10^{-4} for confronted CPBs (Figure 1-3). Different frictional properties were observed by this measurement. At a low applied normal force, a frictional coefficient of the order of 10^{-4} was measured in both SDPB and CPB systems. With increasing normal force, CPBs exhibited a normal force-independent super lubrication, whereas a steeply increased frictional

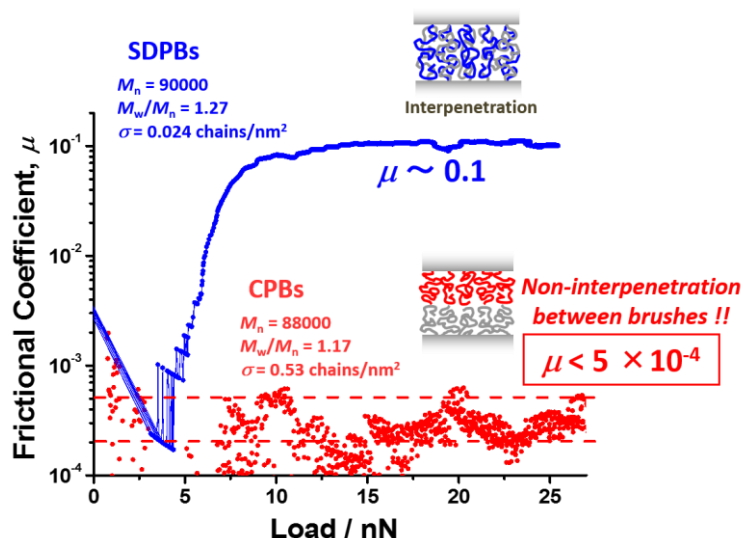
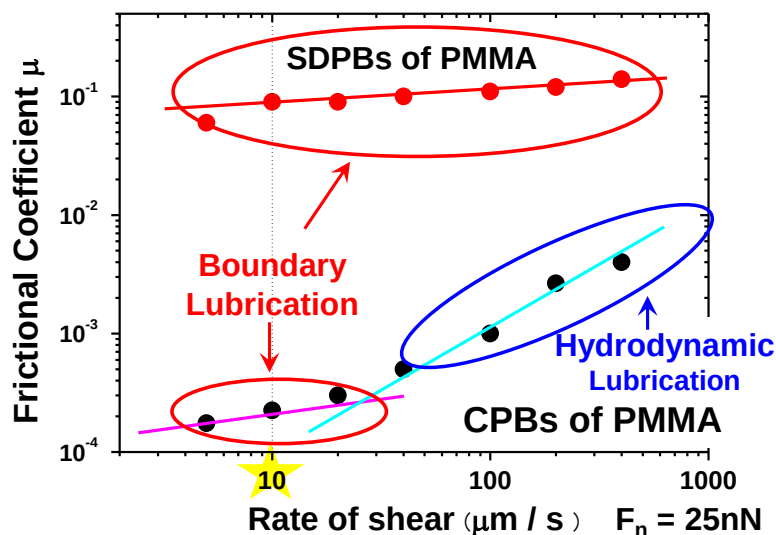


Figure 1-3. Normal force dependence on the frictional coefficient of semi-dilute and concentrated PMMA brushes. This data was referenced from ref.13a.



Boundary Lubrication	Hydrodynamic Lubrication
- Extremely low friction ($\mu \sim 10^{-4}$). - Low shear velocity dependence. - Friction force dominated by the interaction between graft chains.	- High shear velocity dependence. - Friction force dominated by the viscosity resistance and thickness.
	$\Rightarrow F_s \propto \frac{\eta v^\alpha}{d}$

Figure 1-4. Shear velocity dependence on the frictional coefficients SDPBs and CPBs of PMMA. This data was referenced from ref.29a.

coefficient approaching 10^{-1} was measured for SDPBs. The transition for SDPBs was ascribed to interpenetration between grafted chains at a high normal force. The non-interpenetration behavior for CPBs at high normal force was attributed to the high thickness in the dry state, which was greater than the length of a polymer random coil (the most stable state for polymers). Therefore, under increased force, the structures resulted in contracted conformation, rather than interpenetration, in order to attain a relatively stable state.

Recently in the author's group, a detailed lubrication mechanism of CPBs was studied by AFM measurement.^{13b,29} When shearing the confronted CPBs under compression, two distinct regimes were observed by plotting the measured frictional coefficient against the shear velocity, v . The two regimes, boundary lubrication (characterized by low shear velocity dependence and extremely low frictional coefficient) and hydrodynamic lubrication (characterized by high shear velocity dependence) are illustrated in Figure 1-4, which is also known as a Stribeck curve. In hydrodynamic lubrication studies, changing the viscosity and quality of the solvents indicated that the friction in this regime was deeply affected by the

degree of swelling of brushes and viscosity of their lubricating layers. Alternately, from studies of the boundary lubrication by changing the species and graft density of polymer brushes, it was understood that the friction in this regime was dominated by the interaction (interpenetration) between the confronted brushes. These microtribological studies successfully demonstrated the potential of CPBs as lubricating materials. Their macrotribological properties are also relevant for practical applications. However, the achievement of such low friction on a macroscopic scale has remained challenging. Takahara et al. reported a friction measurement for CPBs of PMMA by a sliding-type tribometer. In their study, a frictional coefficient of the order of 10^{-2} was measured, which was much higher than the value observed by AFM analysis.³⁰ A similar result measured by a rheometer was also obtained by the author's group. The increased friction was attributed to the small thickness, which cannot bear such a highly localized contact pressure and thus resulted in some abrasion when a confronted surface with μm -order roughness was applied, or particles of similar size were mixed in.³¹ Very recently, as a solution to the abrasion problem and to achieve low friction on a macroscopic scale, Sato et al. reported molecularly smooth sheets as facing materials successfully showing a low friction coefficient ($\mu \sim 10^{-3}$).

1-2-2. Block Copolymers

Block copolymers (BCPs) have been widely used in many applications for adjustable hybrid physical properties by connecting various monomers into a single polymer chain. For example, blending BCPs into rubbers, a typical method to improve the mechanical properties of rubbers, has been widely applied for the tires in the automobile industry.³² As a conventional method, living anion polymerization has been popularly applied for the synthesis of BCPs, which was firstly discovered by Szwarc et al.³³ Success of this discovery not only contributed to the development of synthetic polymer chemistry, but also introduced precisely designable molecular architectures. Recently, as introduced above, a breakthrough in the development of LRP allowed various types of polymer segments and complex architecture for the design of BCPs.

BCPs are known to form a variety of microphase-separated structures in bulk as well as in a selective

solvent owing to the repulsive interaction between the segments. When in bulk, the morphology depends on the volume fraction of the composition and the interaction, leading to periodically ordered structures. For diblock copolymers, lamellae, gyroids, cylinders, and cubic structures can be formed, along with even more complex structures for multiblock polymers.³⁴ The microphase-separated behavior in the bulk condition is extensive for thermoelastomers.³⁵ When in a selective solvent, a micellar structure will be formed by BCPs, in which the solvent-insoluble segments aggregate as the core part with the solvent-soluble segments swelling as the shell part. In the case of BCPs with multiblocks, such as ABA block copolymers, they are reputed to form physically cross-linked structures. When at a significantly high concentration, the crosslink/bridge structure is conducted by the B segment polymers exhibiting gel behavior. In the last two decades, preparation of the physically cross-linked gels with many kinds of selective solvents (e.g. oils, heptane, xylene, water, etc.) has been conducted, and the morphology structure and physical properties of the gels (e.g. thermal stability, rheology) were widely investigated.³⁶ Recently a new-found selective solvent, ionic liquids, has been developed for fabricating ionic gels which share the characteristics of ionic liquids, including non-flammability, non-volatility, thermal stability, chemical stability, and high ionic conductivity. These ionic gels have been widely applied as the electrolytes for electrical devices such as lithium ion batteries, electric double layer capacitors, and solar cells.³⁷

1-3. Controlled Synthesis of High-molecular-weight Polymers

The key factor for controlling the molecular weight in living polymerization techniques is the elimination of side-reactions. In the example of living anionic polymerization, polymerization control requires strict reaction conditions such a moisture-free environment and high-purity reagents; when such conditions are achieved, this technique enables an ideal increase of molecular weight in the polymerization process. In contrast, the control of LRP is established by the existence of a reversible activation process for the radical polymerization, which is always accompanied by the radical termination. Since radical termination produces dead chains in the polymerization process, the time available to produce well-defined

polymers is limited and hence the range of producible molecular weights is limited. Polymethacrylates, for example, are limited to a maximum molecular weight of the order of 10^5 . In order to access high molecular weights through LRP techniques, special conditions (e.g., a high polymerization rate) are required.

The kinetics of LRP have been studied in detail by Goto and Fukuda.³⁸ In the case of free radical polymerization, the concentration of polymer radicals $[P^*]$ in the stationary state can be written by the following equation:

$$[P^*] = \left(\frac{R_i}{k_t}\right)^{1/2} \quad (\text{stationary state}) \quad (1-1)$$

where R_i and k_t represent the initiation rate and termination rate constants, respectively. Along with equation (1-1), the conversion index $\ln([M]_0/[M])$ is first-order with respect to t :

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p \left(\frac{R_i}{k_t}\right)^{1/2} t \quad (\text{stationary state}) \quad (1-2)$$

where $[M]$, k_p and t are the concentration of monomer, propagation rate constant, and polymerization time, respectively. From this equation, we can understand that k_p and k_t play important roles in the control of the polymerization rate for free radical polymerization. As described above, the mechanism of LRP involves the radical polymerization along with a reversible activation process. Hence, changes in k_p and k_t should be reflected in the LRP process. In the case of ATRP using copper catalysts, the first-order equation can be given as:

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p K_{ATRP} [I]_0 \left(\frac{[Cu(I)]_0}{[Cu(II)]_0}\right) t \quad (1-3)$$

where K_{ATRP} represents the equilibrium constant in ATRP, $[I]_0$, $[Cu(I)]_0$ and $[Cu(II)]_0$ are the initial concentrations of initiator, monovalent copper catalyst, and divalent copper catalyst, respectively.

High pressure is considered one method of improvement which brings a remarkable increase in polymerization rate in conventional free radical polymerization, which occurs as a result of the increased propagation reaction rate constant k_p and the decreased termination reaction rate constant k_t .³⁹ Using this, polymers with molecular weights of the order of 10^6 have been successfully synthesized by applying LRP techniques, e.g. RAFT, ATRP, and activators generated by electron transfer (AGET) ATRP, under a high

pressure.⁴⁰ Aligned with this concept (increased k_p/k_t ratio), the use of ionic liquids as solvent media for free radical polymerization has been reported to accelerate the polymerization rate and increase the molecular weight in comparison with common organic solvents.⁴¹ Haddleton et al. measured the propagation and termination rate constants for MMA by pulsed-laser polymerization size-exclusion chromatography. By this method, k_p for MMA in 50 vol% 1-butyl-3-methylimidazolium, [bmim][PF₆], was increased by 2.5 times, and k_t decreased by about one order magnitude compared with bulk MMA.⁴² The effects of ionic liquid solvents have also been demonstrated in LRP systems by enhanced polymerization rates and increased molecular weights.⁴³

1-4. Background and Purpose of This Thesis

The development of LRP has enabled the production of polymers using various functional monomers with a variety of designed structures. However, the existence of the radical termination reaction limits the range of molecular weights that can be produced. Broadening the range is not only meaningful for the development of polymer science, but important to improve their properties in certain applications. As an example, CPBs demonstrated super lubrication properties on a microscopic scale, and were expected to be suitable lubricating materials for practical applications such as artificial joints, pumps, compressors, and so on. However, the thickness of CPBs prepared by conventional LRP methods was limited to 100 nm due to the radical termination described in **Section 1-3**. Such a small thickness might result in abrasive wear for the brush layer, leading to increased friction on the macroscopic scale. Suppression of the friction resulting from abrasion has been an important issue for practical applications, as it is expected to improve energy efficiency and the lifetimes of mechanical systems. In addition to the CPBs, increased molecular weight BCPs are also of interest for their potential in various applications. For example, increasing the molecular weight of BCPs to around the order of 10^6 will probably enhance the domain size of the formed microphase-separated structures to sub- μm order, giving a tunable bandgap in the visible region and potential applications in photonic materials. For other applications, such as fillers in composite materials and gels, increased

molecular weights are also expected to improve their mechanical properties. For gels in particular, their viscoelastic behavior is deeply affected by molecular weight. The ability to synthesize a wide range of molecular weights is advantageous for rheological studies.

Considering the current knowledge, the author chose the first goal in this thesis to be the synthesis of CPBs with a large thickness by two methods, which were never previously achieved by normal LRP techniques. Additionally, the author will discuss the propagation of grafted chains when accompanied by an enhanced polymerization rate. The achievement of the first goal will lend a significant improvement to the abrasion problems. The elimination of abrasion will provide benefits when studying the macrotribological properties of the polymers, which is essential for practical applications. The lubrication properties of prepared CPBs will be discussed in both microscopic and macroscopic terms.

For the second subject of this thesis, the author aims to synthesize BCPs with ultrahigh molecular weights of both a diblock type and an ABA tri-block type. The polymerization process and catalyst systems will be discussed in detail along with a definite molecular weight characterization. Using the polymerization techniques, ABA triblock copolymers with different molecular weights will be produced and combined with a selective ionic liquid solvent for the preparation of ionic gels. The influence of molecular weight on their gelation behavior and physical properties will be discussed, along with structural analysis using SAXS measurement.

1-5. Outline of This Thesis

The thesis developed the synthesis of high molecular weight polymers involving two kinds of materials: CPBs and BCPs, which naturally divided the content into two parts. For **Part 1**, synthesis of CPBs and their tribological properties will be described in **Chapter 2** to **Chapter 5**; for **Part 2**, synthesis of BCPs and the application to ionic gels will be introduced in **Chapter 6** and **Chapter 7**. The individual chapters are as follows.

Part 1: Concentrated polymer brushes with large thickness – synthesis and tribological properties

In **Chapter 2**, surface-initiated ATRP (SI-ATRP) is performed under a high pressure of 500 MPa to prepare CPBs of PMMA (Figure 1-5). Polymerization under high pressure will contribute to a dramatically high polymerization rate, which will help increase the molecular weights and thickness of prepared PMMA brushes. The author discusses the kinetics of ATRP and the graft density dependence on the concentration of divalent copper Cu(II) catalysts under high pressure conditions. The studies demonstrate the feasibility of high pressure synthesis of CPBs. Under such extreme high pressure conditions, the propagation behaviors for free polymers and graft polymers are also discussed, accounting for the difference in their molecular weights. The author performs a cut-off process to isolate the brush layers from the substrates as a film state to completely collect the graft polymers, which are then characterized by GPC analysis.

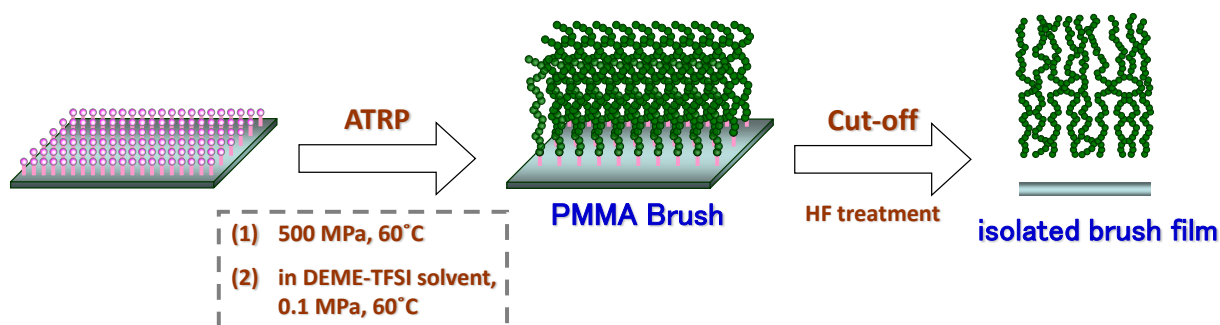


Figure 1-5. Schematic representation of the synthesis of CPBs of PMMA. (1) Under high pressure; (2) in DEME-TFSI solvent.

In **Chapter 3**, an ionic liquid solvent, N,N-diethyl-N-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI) is applied in the SI-ATRP of MMA at ambient pressure (Figure 1-5). Similar to the high pressure effect, ionic liquids can also increase the polymerization rate and thus the thickness of CPBs. Reaction rate constants k_p and k_t for the polymerization in the presence of DEME-TFSI are determined by pulsed-laser polymerization with size-exclusion chromatography analysis. These results demonstrate the ionic liquid effect. The kinetics of ATRP and the propagation behavior of grafted chains are discussed in relation to the effect of Cu(II) catalysts, in order to understand the mechanism of SI-ATRP in an ionic liquid solvent medium. The author also attempts a combination of ionic liquid and high pressure effects in these

systems for a further enhanced polymerization rate and thus thickness.

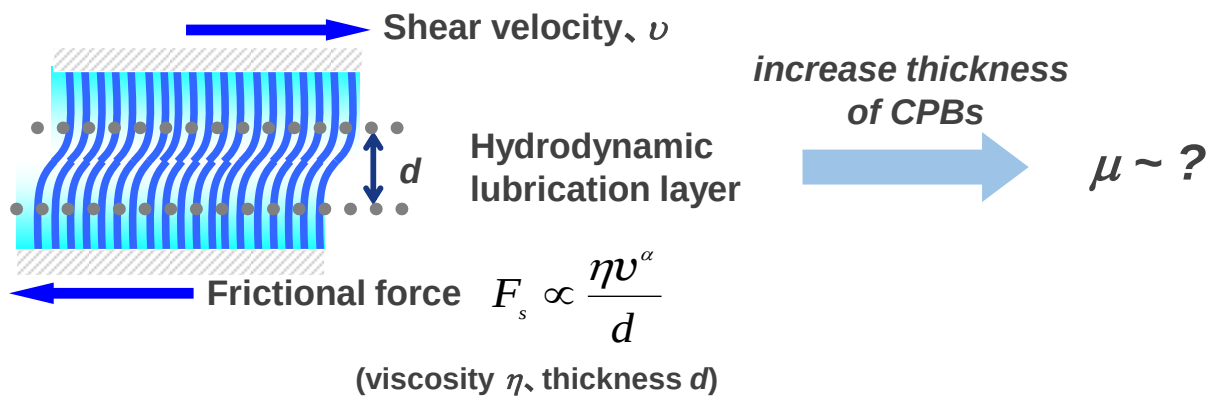


Figure 1-6. Schematic representation of the frictional properties in the hydrodynamic lubrication regime of CPBs of PMMA in toluene.

In **Chapter 4**, the author measures the frictional force and hence frictional coefficient μ on a microscopic scale between CPBs of PMMA by a colloid-probe AFM method. With increasing thickness of CPBs, the degree of swelling and lubrication mechanism containing boundary lubrication and hydrodynamic lubrication are discussed. A prominent issue in this study is the hydrodynamic lubrication friction, which is considered to be affected by the thickness of hydrodynamic lubrication layer. The change in the thickness of CPBs helps to clarify the mechanism of hydrodynamic lubrication and the hydrodynamic lubrication layer.

In **Chapter 5**, the frictional properties in a macroscopic scale between CPBs of PMMA in DEME-TFSI are measured by a ball-on-disc type rotatory tribometer. Friction data are collected while changing the normal forces across a wide range of shear rates. When changing the thickness of CPBs, the anti-abrasion property of the CPB surface is expected to be improved when observed on a macroscopic scale. The lubrication properties of CPBs are discussed in terms of the thickness. Also, the influence of confronted brushes is discussed in three conditions: large thickness, small thickness, and the absence of brush layer. These results concern the study of mechanism of macrotribology for CPBs. To mimic practical application usage, friction tests are conducted with long-term rotatory cycles to confirm their durability.

Part 2: Ultrahigh molecular weight block copolymers – synthesis and application to gels

In **Chapter 6**, BCPs containing poly(methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS) and an ABA-type of PS-*b*-PMMA-*b*-PS with ultrahigh molecular weight are synthesized via ATRP. Synthesis of each block is performed under a high pressure condition of 500 MPa. This polymerization was never previously achieved by the general method of HP-ATRP due to the low block efficiency. The polymerization process and catalyst conditions are investigated with respect to the initiation of second block polymerization and polymerization rate.

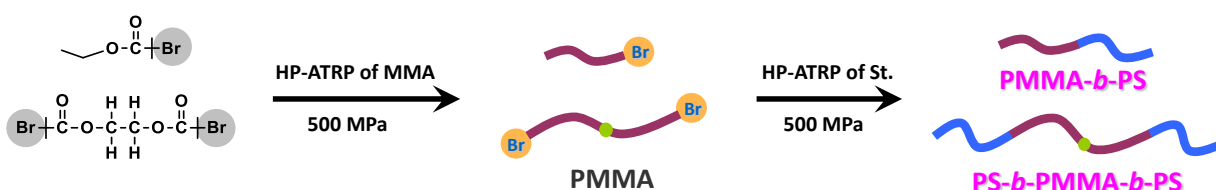


Figure 1-7. Schematic representation of the synthesis of the BCPs of PMMA-*b*-PS and PS-*b*-PMMA-*b*-PS.

In **Chapter 7**, BCPs of PS-*b*-PMMA-*b*-PS are prepared via ATRP in DEME-TFSI. The BCP is processed into a gel formation when solvated into a selective solvent of ionic liquid, which results from the microphase-separation behavior. Molecular weight plays an important role on the viscoelastic behavior of polymers, which significantly affects the rheological properties in a network structure. The rheological properties of formed gels are characterized by a rheometer along with small-angle X-ray scattering (SAXS) measurement to understand their microphase-separation structures in terms of molecular weights.

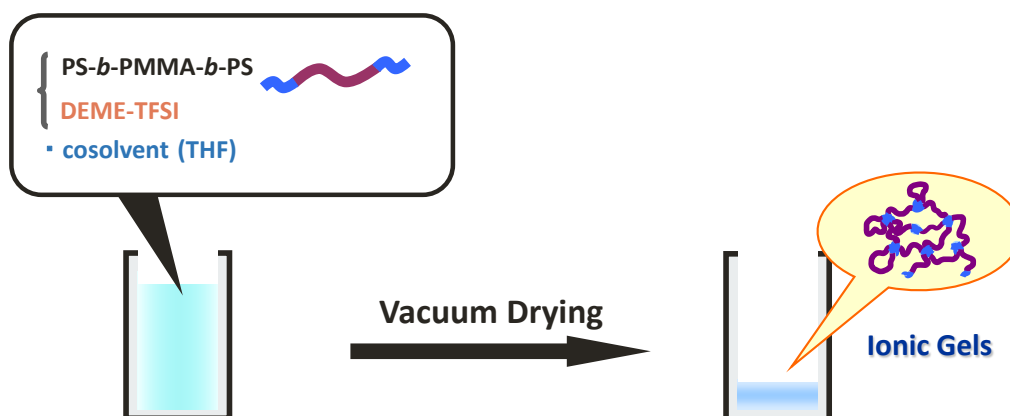


Figure 1-8. Schematic representation of the preparation of ionic gels.

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Part 1

Concentrated Polymer Brushes with Large Thickness – Synthesis and Tribological Properties

Chapter 2

Synthesis of Concentration Polymer Brushes with Extraordinarily Large Thickness by High-Pressure Atom Transfer Radical Polymerization

2-1. Introduction

As a conformation of polymer chains end-tethered to a solid surface, polymer brushes have attracted much attention as a useful method to change various surface properties.¹ In general, synthesis of polymer brushes is categorized into two ways: grafting-to and grafting-from methods. Polymer brushes were previously prepared by free radical polymerization (FRP) combined with the grafting-from method and by end-functionalized polymers or block copolymers with the terminal group or one of the blocks selectively adsorbed on the surface. These method yielded rather low graft densities of typically 0.001-0.05 chains/nm², corresponding to “semi-dilute polymer brush (SDPB)” regime. Recently, with the development of living radical polymerization (LRP) technique, densely grafted well-defined polymers on various kind of materials including inorganic substrates was achieved via surface-initiated LRP (SI-LRP, one method of grafting from).² Graft density of such polymer brushes was more than one order of magnitude higher than those of typical SDPBs, penetrating deep into the regime of “concentrated polymer brush (CPB)”. Mechanistically, the attainment of the high graft density was due to the existence of a reversible activation process.³ This process divided a conventional FRP into numerous activation-deactivation cycles, allowing a high-initiating and well-controlled graft polymerization.

A significant increase in graft density can dramatically change the surface properties of CPBs. Recent studies revealed CPBs show structures and properties quite different from SDPB: most strikingly, CPBs of PMMA swollen in a good solvent exhibited an equilibrium film thickness as large as 80-90 % of the full (contour) length of the graft chains, indicating a highly stretched conformation.⁴ Based on such characteristic, it was found that CPBs exhibit strong repulsion force, extremely low-friction property and size-exclusion property when swollen in a good solvent.⁵ Especially for the low-friction property, an ultralow frictional

coefficient of 10^{-4} order was measured with confronted CPB surfaces in a good solvent by an atomic force microscope (AFM) measurement. Through the investigation in microtribology, the potential of CPBs as a lubricating material has been successfully demonstrated. However, despite the “living-like” mechanism for LRP, radical termination cannot be completely suppressed, which causes the synthesizable molecular weight be limited within $M_n \sim 10^5$ order (thickness ~ 100 nm for CPBs). Such small thickness could result in a limitation of CPBs on practical applications. For example, when applied in a lubricating practical system, small thickness could hardly bear a macroscopic contact, which would lead an abrasive wear and hence give rise to an increased friction.^{5e}

In order to increase molecular weight / thickness before the radicals terminate, high pressure effect is one of the effective solutions. As known, high pressure brings about a remarkable increase in polymerization rate in FRP, as a result of increased propagation rate constant, k_p , and decreased termination rate constant, k_t .⁶ Recently, the feasibility of high pressure ATRP (HP-ATRP) for synthesizing well-defined polymers of extraordinarily high molecular weight ($M_n \sim 10^6$) was demonstrated.⁷ In addition, not only the ATRP, but reversible addition-fragmentation chain transfer (RAFT) polymerizations under high pressure were reported.⁸ In the case of SI-LRP, Matyjaszewski et al. has reported a successful synthesis of silica-PMMA hybrid particles with a number-average molecular weight, M_n of 1600000 and graft density of 0.30 chains/nm² by applying activators generated by electron transfer (AGET) ATRP.⁹ In this work, the author focused on the chain growth behavior at a high pressure condition of 500 MPa. CPBs of PMMA were synthesized on silicon wafers with various feed composition of deactivated catalysts, which allowed an adjustable polymerization rate. With controlling the polymerization rate, a kinetics study of HP-ATRP for both free polymers and graft polymers of PMMA was investigated.

2-2. Experimental

2-2-1. Materials

MMA was obtained from Nacalai Tesque Inc., Japan and purified with distillation. Ethyl 2-

bromoisobutyrate (EBIB) was used as received from Tokyo Chemical Industry Co., Ltd., Japan. (2-Bromoisobutyryloxy) hexyltriethoxysilane (BHE) synthesized as described previously was immobilized on a silicon wafer as an initiator for graft polymerization.^{5a} 4,4'-Dinonyl-2,2'-bipyridine (dN-bipy) was purchased from Aldrich and purified with recrystallization in ethanol twice. Copper bromide (CuBr) and Copper dibromide (CuBr₂) were purchased from Wako Pure Chemicals, Japan, and used as received.

2-2-2. Measurements

Gel permeation chromatographic (GPC) analysis was carried out to determine the M_n , weight-average, M_w and polydispersity, M_w/M_n of the free PMMA with a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. The M_n and PDI were estimated by the calibration prepared by PMMA standards (Polymer Laboratories, $M_p = 1.31 \times 10^3$ - 1.64×10^6) and then complemented by polystyrene standards (Polymer Laboratories, $M_p = 1.93 \times 10^3$ - 1.32×10^7). ¹H (300 MHz) NMR spectra were recorded on JEOL/AL300 spectrometer. The thickness of PMMA brushes were determined by a spectroscopic ellipsometer (M-2000U, J. A. Woolam, Lincoln, NE).

2-2-3. Surface-Initiated ATRP under High Pressure

All sample preparations were carried out in a glove box purge with argon, and all chemicals were deoxygenated before use in a glove box. The reaction mixture (ca. 2 mL) of MMA (9.4 M), EBIB (0.047 mM), Cu(I)Br/L₂ + Cu(Br)₂/L₂ (17 mM), where L compounds are referred as dN-bipy, and a silicon wafer (1 cm × 1 cm, with an immobilized monolayer of BHE) was put into a cryogenic vial purchased from Corning Incorporated. The sample was further packed in a polyethylene-coated aluminum sheet to prevent oxygen contamination and then put into the high-pressure reaction system (HPS-700, Syn Corporation, Kyoto, Japan) with a thermostated at 60°C and pressurized up to 500 MPa. After a prescribed time, the system was depressurized and the samples were taken out for NMR measurement to estimate the monomer conversion and for GPC analysis to determine the molecular weight and the polydispersity. The polymeric substrate was

thoroughly washed by a Soxhlet extractor with toluene to remove physisorbed free polymer.

2-3. Results and discussion

2-3-1. High-Pressure SI-ATRP of MMA

PMMA brushes were synthesized by performing SI-ATRP in the presence of catalysts - Cu(I)Br/L₂ and Cu(II)Br₂/L₂ complexes at 60°C and 500 MPa. Addition of Cu(II) catalyst in small amounts was previously demonstrated for bringing about an excellent control of ATRP along with maintaining such a high polymerization rate even with an extremely low concentration of initiator.^{7a} For the SI-ATRP, BHE was used as the surface-initiator which was immobilized on the silicon wafers. Free initiator (EBIB) was added into the reaction mixture for the purpose of producing free polymers, which were then used as an index to analyze the molecular weights of graft polymers. Figure 2-1 and Figure 2-2 show polymerization results of free polymers (synthesized from EBIB) in plots of conversion index $\ln([M]_0/[M])$ vs. polymerization time t and the M_n and M_w/M_n of products vs. monomer conversion of ATRP at 500 MPa with the feed ratio of Cu(II)Br₂ in a range from 2% to 16%, where the ratio represents $[Cu(II)Br_2/L_2] / [Cu(I)Br/L_2] + [Cu(II)Br_2/L_2]$, respectively. All the plots in Figure 2-1 exhibit good linearity as well as low polydispersity ($M_w/M_n < 1.5$),

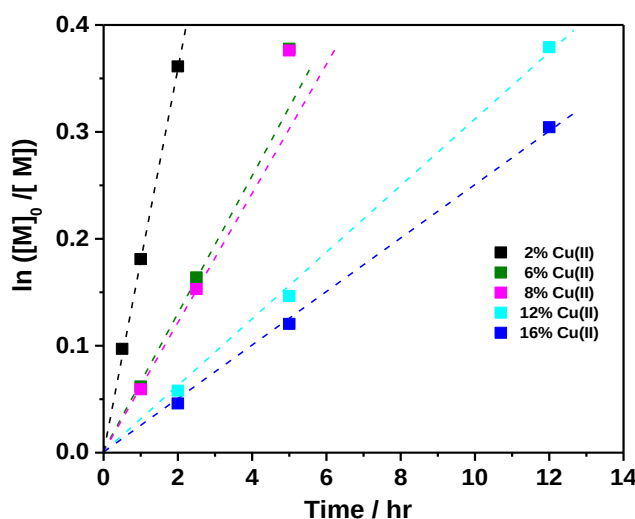


Figure 2-1. Plot of $\ln([M]_0/[M])$ vs. t for the surface-initiated ATRP of MMA at 60 °C and 500 MPa; $[EBIB]_0 = 0.047$ mM, $[Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 17$ mM; $[Cu(II)Br_2/L_2]_0 / [Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 0.02$ (■), 0.06 (■), 0.08 (■), 0.12 (■), 0.16 (■).

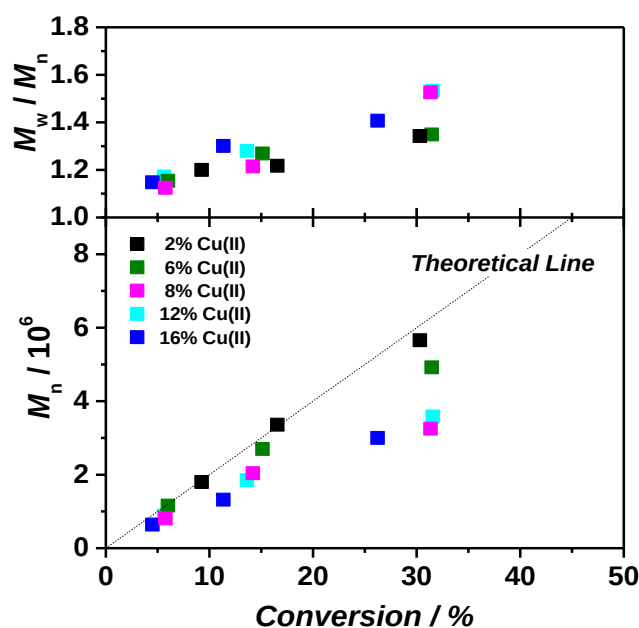


Figure 2-2. Plots of number-average molecular weight, M_n , and polydispersity, M_w/M_n vs. conversion for the surface-initiated ATRP of MMA at 60 °C and 500 MPa; $[EBIB]_0 = 0.047$ mM, $[Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 17$ mM; $[Cu(II)Br_2/L_2]_0 / [Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 0.02$ (■), 0.06 (■), 0.08 (■), 0.12 (■), 0.16 (■).

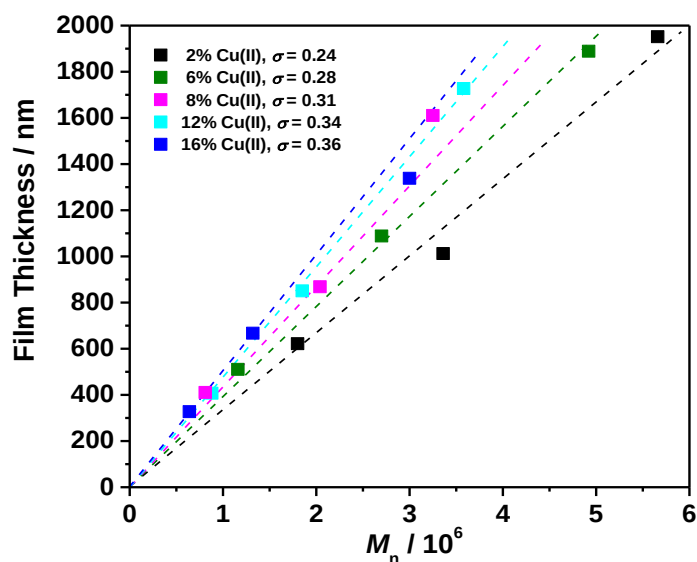


Figure 2-3. Plot of dry film thickness, L_d , vs. number-average molecular weight, M_n for the surface-initiated ATRP of MMA at 60 °C and 500 MPa; $[EBIB]_0 = 0.047$ mM, $[Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 17$ mM; $[Cu(II)Br_2/L_2]_0 / [Cu(I)Br/L_2]_0 + [Cu(II)Br_2/L_2]_0 = 0.02$ (■), 0.06 (■), 0.08 (■), 0.12 (■), 0.16 (■).

revealing a well-controlled polymerization. By the high-pressure condition, polymerization rate was dramatically enhanced and hence led a highly increased molecular weight which was maximally over 5×10^6 . Figure 2-3 shows the data of thickness in dry state L_d for CPBs of PMMA plotted with the M_n of PMMA free polymer. In this figure, all the data were similarly plotted in good linearity, indicating the control of the graft polymerization. Similar with results of free polymers, PMMA brushes were obtained with a large thickness, which has even reached to 2 μm despite of a relative low graft density σ of 0.24 chains/ nm^2 (Figure 2-3,■; σ calculated from the slope of the line)(σ is usually > 0.5 chains/ nm^2 by normal ATRP conditions). The high molecular weights and large thickness of PMMA brushes showed that the high pressure effect of increased k_p and decreased k_t was well-reflected in the SI-ATRP system. With using these data, the kinetics study of the equilibrium constant of ATRP, K_{AT} , and propagation behavior of the grafted chains under high pressure were discussed as in the following.

2-3-2. Equilibrium Constant K_{AT} under High Pressure

In a ATRP system, addition of a deactivator catalyst plays an important role on the polymerization rate control. As shown in Figure 2-1, the slopes of the lines (represent as well as the polymerization rates) varied with the feed ratio of activator and deactivator catalysts ($\text{CuBr}/\text{CuBr}_2$, in this study). As known, polymerization rate in ATRP system obeying the kinetic theory formula can be written as

$$\ln[M]_0/[M] = (k_p K_{AT} [\text{EBIB}]_0 [\text{CuBr}/\text{L}_2]_0 / [\text{CuBr}_2/\text{L}_2]_0) t \quad (2-1)$$

where $(k_p K_{AT} [\text{EBIB}]_0 [\text{CuBr}/\text{L}_2]_0 / [\text{CuBr}_2/\text{L}_2]_0)$ can be seen as the slope of the lines in Figure 2-1. Figure 2-4 shows the plot of the slopes vs. $[\text{CuBr}/\text{L}_2]_0 / [\text{CuBr}_2/\text{L}_2]_0$. This plot exhibited in good linearity, in which the slope of this line can be referred as $k_p K_{AT} [\text{EBIB}]_0$, indicating the well-controlled polymerization rate for this system under 500 MPa. Applying the value of k_p at 500 MPa as $1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $[\text{EBIB}]_0$ as 0.047 mM along with the slope in Fig.5,^{7a} we have the value of $K_{AT} = 1.5 \times 10^{-6}$ at 500 MPa, which is about one order larger than the value of $\text{CuCl}/\text{L}_2 / \text{CuCl}_2/\text{L}_2$ catalyst system ($K_{AT} = 1 \times 10^{-7} - 3 \times 10^{-7}$) reported in the author's group previously. The difference in the values of K_{AT} between these two catalyst systems was ascribed to the difference in the activity of halogen functional groups, which was also well-understood at ambient pressure

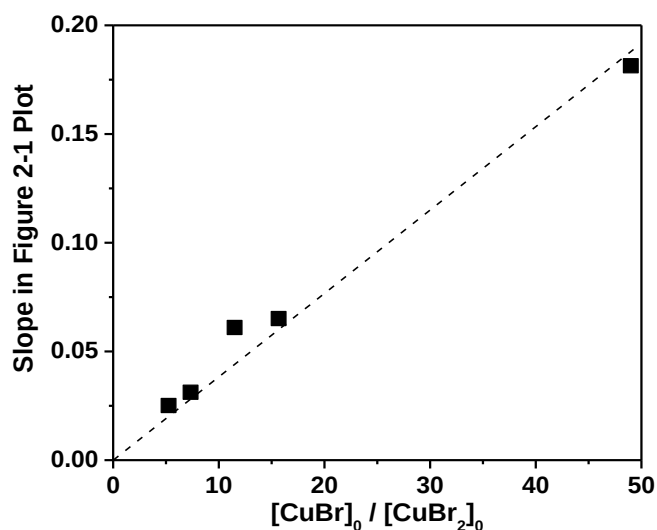


Figure 2-4. Plot of slopes in Figure 2-1 vs. $[\text{CuBr}]/[\text{CuBr}_2]$ for the surface-initiated ATRP of MMA at 60 °C and 500 MPa; $[\text{EBIB}]_0 = 0.047$ mM, $[\text{Cu(I)Br}/\text{L}_2]_0 + [\text{Cu(II)Br}_2/\text{L}_2]_0 = 17$ mM.

condition.^{3d} Furthermore, as a comparison of the pressure effect, value of K_{AT} for EBIB initiator with CuBr/L₂ system at ambient pressure in the presence of acetonitrile at 22 °C was measured as 3×10^{-8} , referenced from ref.11. Despite of a small difference of the catalyst systems between this study and the reference data, the value at 500 MPa is about two order of magnitude greater than at ambient pressure condition, indicating significantly increased activation rate for ATRP when at high pressure. This data shows a good agreement with the result reported by Buback et al..

2-3-3. [Cu(II)] Dependence on Graft Density

As mentioned above, the high-pressure condition brought about the enhanced molecular weights and thickness of CPBs, however it also led a relatively low graft density. For the condition of low $[\text{CuBr}_2/\text{L}_2]$, σ of PMMA brushes was obtained as 0.24 chains/nm². Noted that the dimensionless graft density, σ^* is 0.13 (the definition of σ^* is clearly described in ref. 2c), which is still included in the concentrated regime ($\sigma^* > 0.10$). Interestingly, whereas with increasing the feed ratio of CuBr₂/L₂ from 2% to 16%, slope of the lines in Figure 2-3 which can be signified as the graft density of polymer brushes show that the graft densities increase from 0.24 chains/nm² to 0.36 chains/nm². As plotted the graft density σ against $[\text{Cu(II)Br}_2/\text{L}_2]$, it is

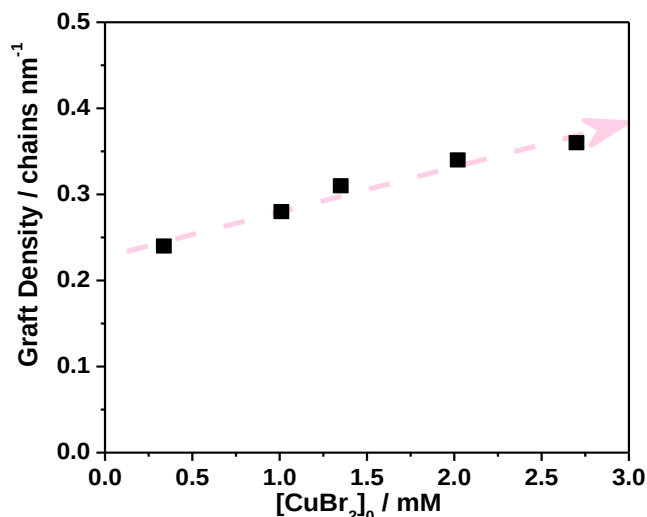


Figure 2-5. Plot of graft density, σ , vs. $[\text{Cu(II)Br}_2/\text{L}_2]_0$ for the surface-initiated ATRP of MMA at 60 °C and 500 MPa; $[\text{EBIB}]_0 = 0.047$ mM, $[\text{Cu(I)Br}/\text{L}_2]_0 + [\text{Cu(II)Br}_2/\text{L}_2]_0 = 17$ mM.

obviously that the concentration of $\text{Cu(II)Br}_2/\text{L}_2$ catalyst deeply influenced the graft density of the products (Figure 2-5).

Adding the Cu(II) catalysts in a ATRP system can supply the deactivation reaction, which limits the propagation of monomers and hence provides a well-controlled polymerization. The amounts of monomer addition to one polymer radical in one activation-deactivation cycle for normal LRP (denoted as N_m), which can be calculated from the pseudo-first-order activation and deactivation rate constant, k_{act} and k_{deact} , was known as only a few amounts ($N_m < 5$) at ambient pressure.^{3c,d} When under a high pressure condition, the N_m should increase along with the increased k_p . It should be noted that even the N_m increased under high pressure, as the reversible activation process repeated within necessary cycles, we could obtain the products with low polydispersity (the reason for a well-controlled HP-ATRP). On the other hand, when in the system of SI-ATRP, N_m is also important for the growing process of graft chains. For example of surface-initiated free radical polymerization, the chain growth typically proceeds within a short lifetime of a radical (similar with normal FRP in bulk solution). During the lifetime, the N_m might even reach to about 1000-10000. However, the σ would exhibit a quite low value (typically in the regime of SDPB) due to the influence of steric

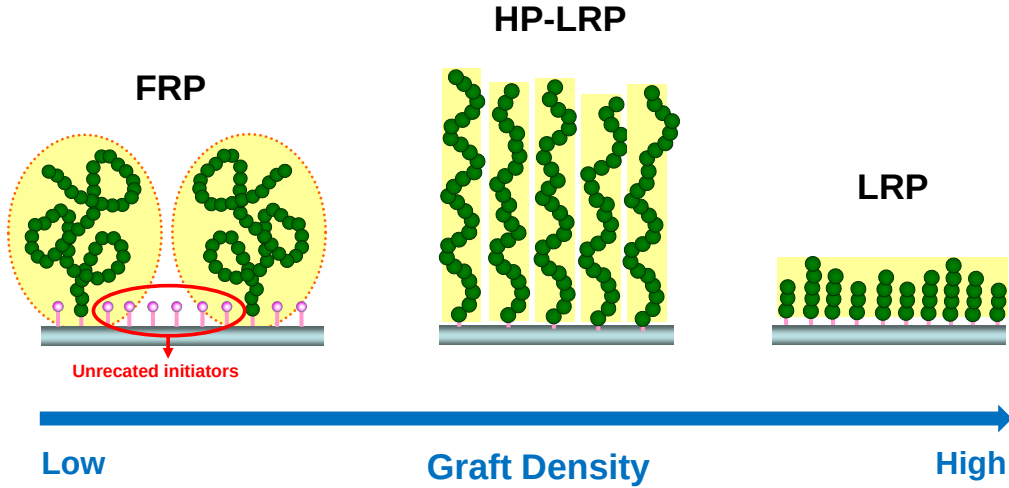


Figure 2-6. Illustration of chain growth in FRP, LRP and HP-LRP processes.

hindrance. In contrast, the low N_m in the case of surface-initiated LRP, allows a slow and equal growth for immobilized initiating groups, resulting in a high σ (Figure 2-6). Based on this concept, when at condition of low $[\text{CuBr}_2/\text{L}_2]$ for HP-ATRP, the decreased σ was attributed to the "too fast polymerization rate" which however led a relatively large N_m .

Here the author made a calculation of the N_m between in the ambient pressure and under high pressure for the catalyst system in this study. The lifetime (τ) of radicals during one LRP cycle can be derived by

$$\tau = (R_{\text{deact}})^{-1} = (k_{\text{deact}}[\text{CuBr}_2/\text{L}_2][\text{P}^*])^{-1} \quad (2-2)$$

Using Equation (2-2), N_m can be estimated by

$$N_m = \tau \times R_p = k_p[\text{M}](k_{\text{deact}}[\text{CuBr}_2/\text{L}_2])^{-1} \quad (2-3)$$

Because of the lack of k_{deact} value for the $[\text{EBIB}/\text{CuBr}/\text{dN-bipy}]$ system, k_{deact} values of $[\text{MBrP}/\text{CuBr}/\text{PMDETA}]$ system ($k_{\text{deact}} = 8.01 \times 10^7 \text{ L mole}^{-1}\text{sec}^{-1}$ at 5000 bar and $4.32 \times 10^7 \text{ L mole}^{-1}\text{sec}^{-1}$ at 1 bar) were applied to calculate the values of N_m .¹⁰ According to Equation (3), the N_m s are given as 0.5 (1 bar, with 2% Cu(II)), 6.6 (5000 bar, with 2% CuBr_2), 0.8 (5000 bar, with 16% CuBr_2) as a crude estimate (as a reference, the N_m in the $[\text{EBIB}/\text{CuBr}/\text{dN-bipy}]$ system with 2% CuBr_2 under 1 bar is 2.8). By this calculation, the N_m under 5000 bar is about 10 times larger than one in 1 bar, for which such difference was considered to lead the decreased σ in this study. And with increasing the CuBr_2 catalyst from 2% to 16%, the

N_m decrease to nearly the same order as in 1 bar, although σ increased only to around 0.36 chains/nm², which was still lower than the synthesizable value when at ambient pressure condition, revealing some other factors to affect the chain growth but hard to discover. In spite of a decreased polymerization rate which was due to the increased feed ratio of CuBr₂/L₂, the rapid activation caused from the increased K_{AT} under high pressure still gave a high polymerization rate for synthesizing a CPB with large thickness.

2-3-4. Molecular Weight Characterization of Grafted Polymers

Molecular weight of free polymers is usually applied as an index for the determination of graft density of CPBs. For synthesis of CPBs at ambient pressure condition, the author's group previously obtained similar molecular weight between free polymers and grafted polymers synthesized on silica particles, in which grafted polymers were cut-off from surface of particles via a hydrofluoric acid (HF) treatment.^{2d} However, there are no evidence to show whether similar result can be obtained at a high pressure condition. Different from the cut-off process for brushes on silica particles, it was usually difficult to collect enough graft polymers from a substrate such as silicon wafer to determine their molecular weights by the traditional method. Here, the author attempted a new method by cutting off the brush layers from a silicon wafer as the form of a film. By this technique, graft polymers can be perfectly collectable, allowing the determination of their molecular weights. Figure 2-7 shows the schematic illustration of the "cut-off" experiment. First, the silicon substrate grafted with PMMA was put on the hydrofluoric acid solution (10%) for one day. In this step, the hydrolysis occurred only on the silica and the BHE layers, which enabled separation of the graft polymer layer from the silicon substrate (graft layer somehow still attached on the substrate due to some remaining interaction). The silicon substrate was then put into the water, and the graft layer was spontaneously peeling off from the silicon substrate by the surface tension of water (as shown in the photo in Figure 2-7). The collected graft polymers were then characterized by GPC analysis for their molecular weights (see Figure 2-8). Compared with the molecular weights of free polymers, this figure indicate the similar molecular weights between graft polymers and free polymers synthesized even at such a high pressure

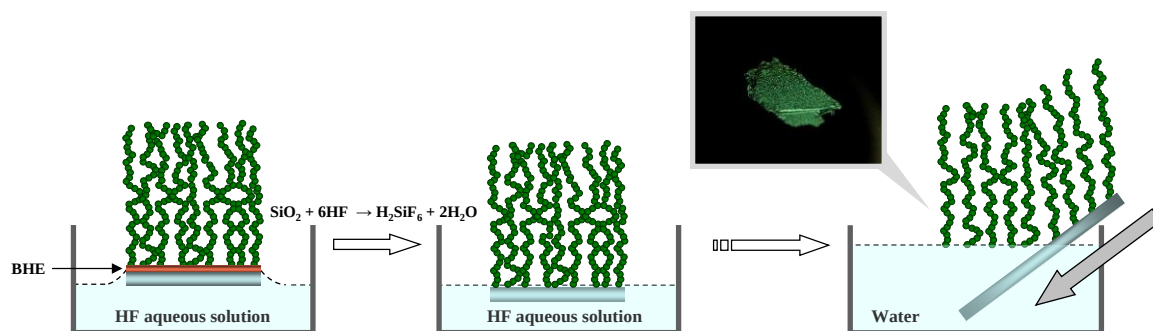


Figure 2-7. Illustration of approach of “cut-off” experiment to separate graft polymers from silicone substrate and photo of graft polymer film taken after separation from silicone substrate

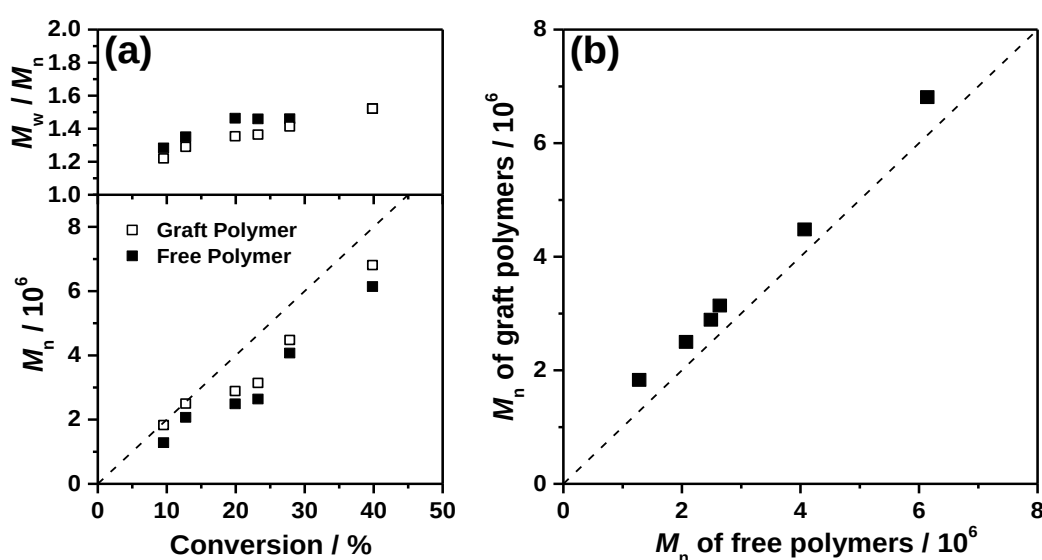


Figure 2-8. Plots of (a) number-average molecular weight, M_n , and polydispersity, M_w/M_n , of the free (■) and graft (□) polymers vs. conversion and (b) M_n of the free polymers vs. graft polymers for the surface-initiated ATRP of MMA at 60 °C and 500 MPa.

condition, which was similar with the result at ambient pressure condition. From this result, the author successfully confirmed the absolute graft densities of PMMA brushes synthesized by HP-ATRP, which exactly penetrated into the CPB regime.

2-4. Conclusions

Synthesis of PMMA brushes by SI-ATRP was investigated under a high pressure of 500 MPa. Through

the high pressure effect, thickness of prepared PMMA brushes in this study maximally reached up to 2 μm despite the low graft density ($\sigma = 0.24$). Polymerization with various feed ratio of $\text{Cu(II)Br}_2/\text{L}_2$ allowed the determination equilibrium constant K_{AT} at 500 MPa as 1.5×10^{-6} , indicating well-controlled polymerization rates in this system. A $[\text{Cu(II)}]$ dependence on the graft density was confirmed with changing the feed ratio of $\text{Cu(II)Br}_2/\text{L}_2$. This was ascribed to the amounts of monomer addition during the activation cycles. The “cut-off” process combined with GPC measurement exhibits a similar result of molecular weights between the graft polymers and free polymers synthesized even at a high pressure condition. Despite of the decreased molecular weight and thus thickness of CPBs resulted from the addition of $\text{Cu(II)Br}_2/\text{L}_2$ catalyst, the optimum polymerization in this study provides an effective method for synthesizing CPBs of PMMA with thickness and graft density of about 1 μm and 0.34 chains/ nm^2 . Such enhanced thickness is considered as be helpful for the tribological study of CPBs and also practical applications.

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Chapter 3

Synthesis of Concentration Polymer Brushes with Large Thickness by Atom Transfer Radical Polymerization in Ionic Liquid Solvent Medium

3-1. Introduction

Abrasion problem has been an important issue for CPBs to such practical applications. Increase the thickness of CPBs is considered as one of the effective methods for improvement. In Chapter 2, the author applied the high pressure effect¹ to SI-ATRP and succeeded in synthesizing CPBs of PMMA with a μm order thickness. Despite the high performance of high-pressure effect for synthesizing CPBs with large thickness, in order to achieve a high-pressure condition (e.g. 500 MPa), a specific reaction equipment is required, which however limits the synthesis process for practical materials. For such reason, a simpler method is necessary for synthesis of CPBs with large thickness.

The key to the success described in Chapter 2 was the increased k_p (rapid polymerization) and decreased k_t (less radical termination) for the polymerization performed under a high-pressure condition. Based on this concept to achieve the increased k_p and decreased k_t at a ambient pressure condition, the author focused on the solvent effect of ionic liquids (ILs). ILs have attracted considerable attention as “green solvents” for their specific properties including non-flammability, non-volatility, thermal stability, chemical stability and high ionic conductivity,² and have been widely applied as the electrolytes to improve the safety and durability for some electrical devices, *e.g.* lithium ion batteries, electric double layer capacitors and solar cells, etc.³ Recently, ILs have also been popularly investigated as the solvent media in polymerization processes including conventional FRP, LRP, anionic polymerization, cationic polymerization.^{2b,4} For FRP, an acceleration on polymerization rate has been demonstrated for ILs rather than common organic solvents. Haddleton et al. has firstly measured the propagation and termination rate constants for MMA by pulsed-laser polymerization size-exclusion chromatography (PLP-SEC) method.⁵ By this method, propagation rate

constant, k_p , for MMA in 50 vol% 1-butyl-3-methylimidazolium, [bmim][PF₆], increased by 2.5 times, and termination rate constant, k_t , decreased about one order of magnitude than bulk MMA. Even though the reason about the ILs solvent effect is still remained debated, it is generally described that the enhancement in propagation reaction is due to the polar effect, and the reduction in termination reaction is due to the viscosity effect. In this work, the author applied an ionic liquid of *N, N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI) as the solvent media to SI-ATRP. The solvent effect of DEME-TFSI was investigated with a pulsed-laser polymerization experiment to determine the values of k_p and k_t for a MMA solution containing DEME-TFSI. The kinetics study for determination of the equilibrium constant K_{AT} and the synthetic condition for SI-ATRP of MMA in the presence of DEME-TFSI were investigated in detail.

3-2. Experimental

3-2-1. Materials

MMA was obtained from Nacalai Tesque Inc., Japan and purified by passing through a column filled with activated basic alumina to remove inhibitor. (2-Bromoisobutyryloxy) hexyltriethoxysilane (BHE) synthesized as described previously was immobilized on a silicon wafer as an initiator for graft polymerization.⁶ Copper chloride (CuCl, 99.9%, Wako Pure Chemical Industries, Ltd., Japan) was washed with glacial acid to remove any soluble oxidized, filtered, washed with ethanol and diethyl ether, and dried. Ethyl 2-bromoisobutyrate (EBIB, >98.0%, Tokyo Chemical Industry Co., Ltd., Japan), copper dichloride (CuCl₂, 98%, Nacalai Tesque), 4,4'-dinonyl-2,2'-bipyridine (dN-bipy, >97%, Wako), anisole (99%, Wako), dimethyl sulfoxide (DMSO, 99.0%, Wako), *N,N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI, Kanto Chemical Co., Inc., Japan) and 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (Irgacure 369, Ciba Geigy) was used as received.

3-2-2. Measurements

GPC analysis was carried out to determine the M_n , M_w and M_w/M_n of the free PMMA with a Shodex

GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). THF was used as an eluent at a flow rate of 0.8 mL/min. The M_n and polydispersity were estimated by the calibration prepared by PMMA standards (Polymer Laboratories, $M_p = 1.31 \times 10^3$ - 1.64×10^6) and then complemented by polystyrene standards (Polymer Laboratories, $M_p = 1.93 \times 10^3$ - 1.32×10^7). ^1H (300 MHz) NMR spectra were recorded on JEOL/AL300 spectrometer. The thickness of PMMA brushes were determined by a spectroscopic ellipsometer (M-2000U, J. A. Woolam, Lincoln, NE).

3-2-3. Surface-Initiated ATRP in Ionic Liquid

All sample preparations were carried out in a glove box purge with argon, and all chemicals were deoxygenated before use in a glove box. ATRP in an ionic liquid solvent medium was carried out as follows. The reaction mixture containing MMA (3.1 M), EBIB (0.3 mM), CuCl/L_2 (5.4 mM), $\text{Cu}(\text{Cl})_2/\text{L}_2$ (0.1 mM), where L compounds are referred as dN-bipy, and DEME-TFSI (75 wt %) was put into a Schlenk tube and then heated in an oil bath with thermostated at 60°C. For comparison of the solvent effect, similar condition of ATRP was also performed in organic solvent (75 wt%): DMSO and anisole. For the synthesis of concentrated polymer brushes with large thickness, SI-ATRP of MMA was typically carried out at 60°C in the reaction mixture of MMA (3.1 M), EBIB (0.3 mM), CuCl/L_2 (5.4 mM), $\text{Cu}(\text{Cl})_2/\text{L}_2$ (0.1 mM) and DEME-TFSI (75 wt %) along with a BHE-immobilized silicon wafer (1 cm²). After a prescribed time, the polymerization solutions were analyzed by NMR to estimate the monomer conversion and by GPC to determine their molecular weights and distributions. The polymeric substrate was thoroughly washed by a Soxhlet extractor with toluene to remove physisorbed free polymer and then proceeded a thickness measurement by ellipsometry analysis.

3-2-4. PLP-SEC experiment

Pulsed-laser experiments were performed by using a YAG laser with a harmonic generator to generate light of wavelength 355 nm typically at a pulse energy of 40 mJ. The temperature was kept constant within 0.5°C. Reaction mixture containing photoinitiator of Irgacure 369 (0.5 mM), MMA (25 wt%) and solvents

(DEME-TFSI, DMSO, and anisole; 75 wt%) were deoxygenated and then exposed to the pulsed laser with a pulsed repetition rate of 10 Hz for a 10 minutes. After polymerization, molecular weight distribution was measured by SEC analysis.

3-3. Results and discussion

3-3-1. ATRP of MMA in DEME-TFSI

Feasibility of DEME-TFSI as the solvent medium in ATRP was investigated by carrying out the ATRP run of MMA in the presence of DEME-TFSI (75 wt%) at 60°C. Figure 3-1 and Figure 3-2 show the monomer conversion index $\ln([M]_0/[M])$ vs. polymerization time t and the M_n and polydispersity of products vs. monomer conversion, respectively. ATRP in DEME-TFSI (Figure 3-1 and Figure 3-2, ■) proceeded in a good linearity as well as a low polydispersity, revealing a well-controlled polymerization in the presence of DEME-TFSI. For comparison of the solvent effect, organic solvents of DMSO and anisole were also applied as solvent media in similar ATRP condition (☆ for DMSO and □ for anisole, in Figure 3-1 and Figure 3-2).

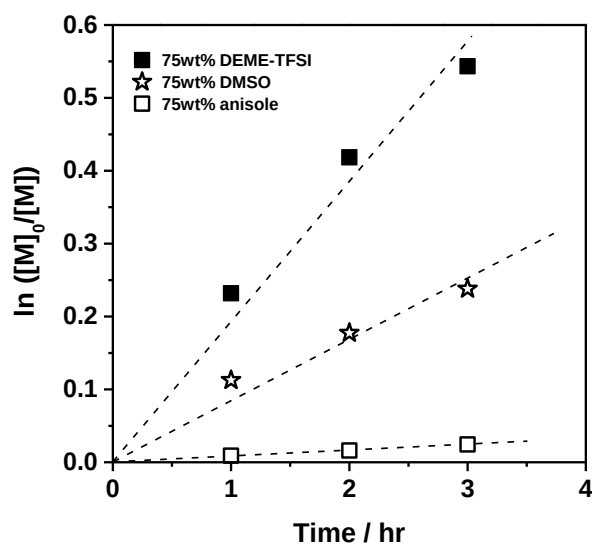


Figure 3-1. Plot of $\ln([M]_0/[M])$ vs. t for the ATRP of MMA at 60 °C; $[EBIB]_0:[MMA]_0:[Cu(I)Cl/L_2]_0:[Cu(II)Cl_2/L_2]_0 = 1:10000:17:0.9$ in 75 wt% DEME-TFSI(■), DMSO(☆) and anisole(□).

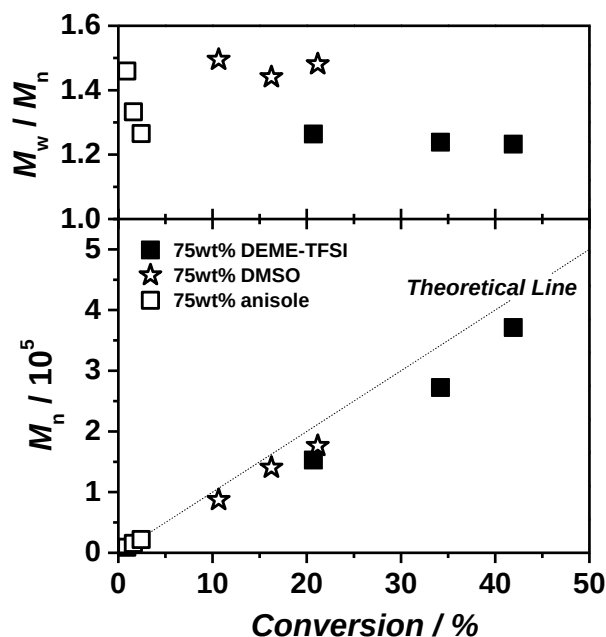


Figure 3-2. Plots of number-average molecular weight, M_n , and polydispersity, M_w/M_n vs. conversion for the ATRP of MMA at 60 °C; $[EBIB]_0:[MMA]_0:[Cu(I)Cl/L_2]_0:[Cu(II)Cl_2/L_2]_0 = 1:10000:17:0.9$ in 75 wt% DEME-TFSI(■), DMSO(☆) and anisole(□).

Polymerizations in the presence of DMSO and anisole were also well-controlled (despite the relatively high M_w/M_n when in DMSO), whereas the polymerization rate varied definitely with the using solvent media. As expected, ATRP in different solvent media exhibited polymerization rate in the order as in DEME-TFSI > in DMSO > in anisole, where polymerization rate in DEME-TFSI was 2.3 and 23.5 times greater than in DMSO and anisole (estimated from the slope of the lines in Figure 3-1), respectively. The rapid polymerization rate of ATRP in DEME-TFSI was suggested to be due to the solvent effect of ILs for giving the increased k_p and decreased k_t similar with other reported ILs (e.g. bmim-PF₆).⁵

3-3-2. Determination of k_p and k_t of MMA in the Presence of DEME-TFSI

For investigation of the solvent effect of DEME-TFSI on ATRP, the rate constants, k_p and k_t of MMA in different solvent media were measured by the PLP-SEC technique.⁷ Experiments of PLP were carried out at 60°C using MMA solution containing 75 wt% solvents (anisole, DMSO, DEME-TFSI). Figure 3-3 shows the typical molecular weight distribution of PMMA obtained in the presence of DEME-TFSI on irradiating

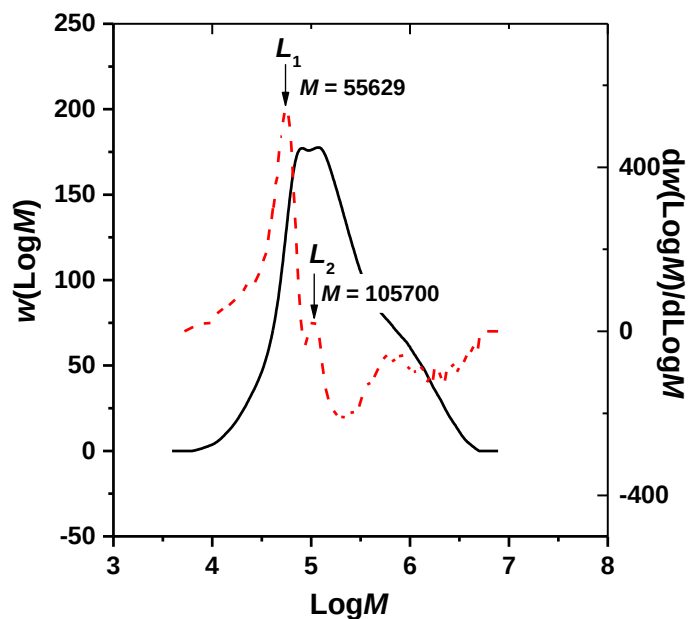


Figure 3-3. MWD $w(\log M)$ vs. $\log M$ (full line) and the first derivative (broken line) for pulsed-laser polymerization of MMA in DEME-TFSI (75wt%) at 60°C for 10 minutes; [Irgacure 369]₀=0.5 mM; pulsed-energy: 40 mJ; dark time t_0 =0.1 second.

Table 3-1 PLP-SEC of MMA in different solvents at 60 °C

	DEME-TFSI	DMSO	Anisole	Bmim-PF6 ^(a) (50 vol%)	Bulk (MMA) ^(a)
L_1	550	406	260	-	-
k_p (L mol ⁻¹ S ⁻¹ , 60 °C)	1.70×10^3	1.53×10^3	1.05×10^3	1.60×10^3	8.6×10^2
k_t (L mol ⁻¹ S ⁻¹ , 60 °C)	2.79×10^7	2.19×10^8	2.45×10^8	3.0×10^7	1.0×10^8
viscosity (mPsa, 20 °C)	120	1.98	1.20	272	0.57

(a) k_p and k_t data of bmim-PF₆ and bulk MMA are referenced from Ref. 4.

10 Hz of 355 nm light at 60°C for 10 min. In pulsed-laser polymerization, it is well-known that when a propagation radical is terminated by the i -th pulse after the initiating pulse, the chain length L_i of the polymer formed is determined by the following equation:

$$L_i = i k_p [M] t_0 \quad (3-1)$$

where $[M]$ is the monomer concentration, t_0 is the dark time between pulses, and i is an integer. With using the chain length from the first derivation peaks in Figure 3-3, the value of k_p can be obtained from Equation (3-1). For the calculation of k_t , the following equation was applied as referenced from ref.4:

$$P_w \nu_p = k_p^2 / k_t [M]^2 (3-\delta) \quad (3-2)$$

where P_w is weight-average degree of polymerization, ν_p is the rate of polymerization, δ is the contribution of disproportionation to overall termination (used as $\delta=0.7$).

Table 3-1 shows the measured k_p and k_t of MMA in different solvent media. By PLP-SEC technique, the values of k_p and k_t of MMA containing 75 wt% DEME-TFSI at 60°C were determined as 1.70×10^3 and 2.79×10^7 , respectively. From this result, the measured values of k_p and k_t show not much difference with other reported ionic liquids, e.g. bmim-PF₆; whereas compared with DMSO, anisole and bulk MMA, it showed an increased k_p and decreased k_t in DEME-TFSI, where the k_p and k_t were about 2 times larger and 3.5 times smaller than values in bulk MMA, respectively.

3-3-3. SI-ATRP of MMA in DEME-TFSI

Applying the solvent effect of ionic liquids to surface-initiated ATRP is expected to give an increased thickness of CPBs. Surface-initiated ATRP in the presence of DEME-TFSI (75 wt%) was performed with using Cu(I)Cl/L₂ and Cu(II)Cl₂/L₂ as the catalyst system at 60°C and ambient pressure. In this polymerization,

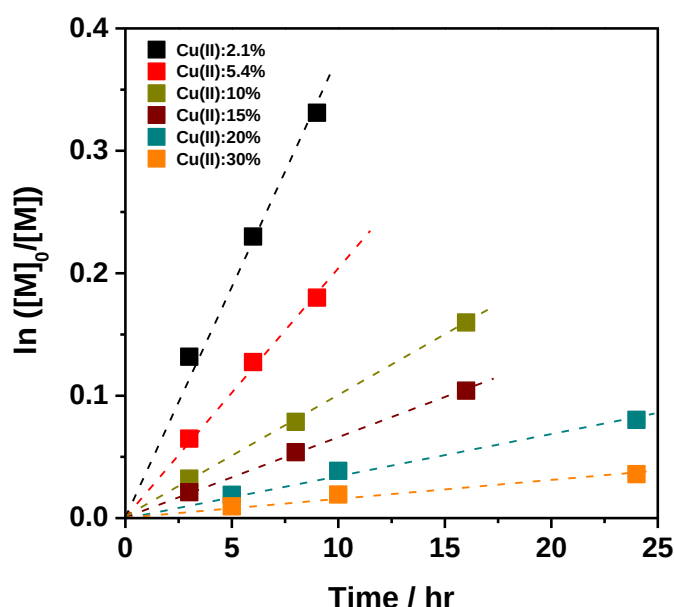


Figure 3-4. Plot of $\ln([M]_0/[M])$ vs. t for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C ; $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 0.12$ mM(■), 0.31 mM(■), 0.59 mM(■), 0.94 mM(■), 1.3 mM(■), 2.3 mM(■).

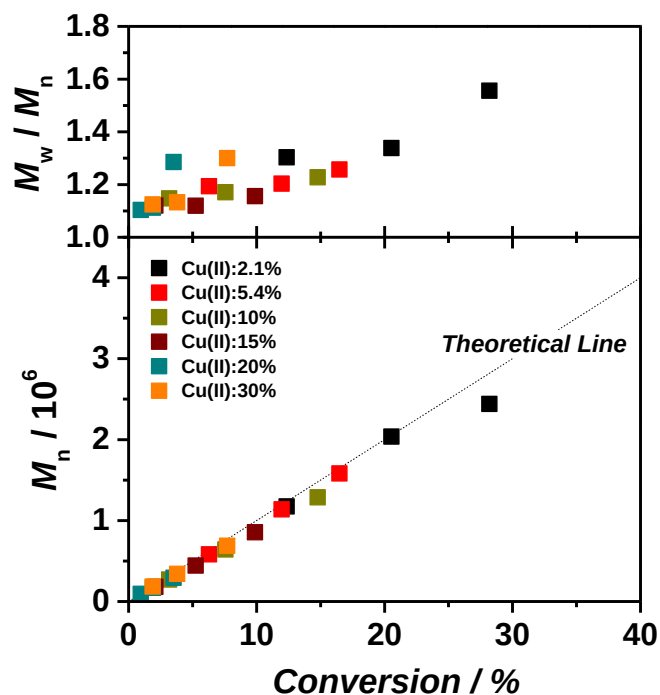


Figure 3-5. Plots of number-average molecular weight, M_n , and polydispersity, M_w/M_n vs. conversion for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C; $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 0.12$ mM(■), 0.31 mM(■), 0.59 mM(■), 0.94 mM(■), 1.3 mM(■), 2.3 mM(■).

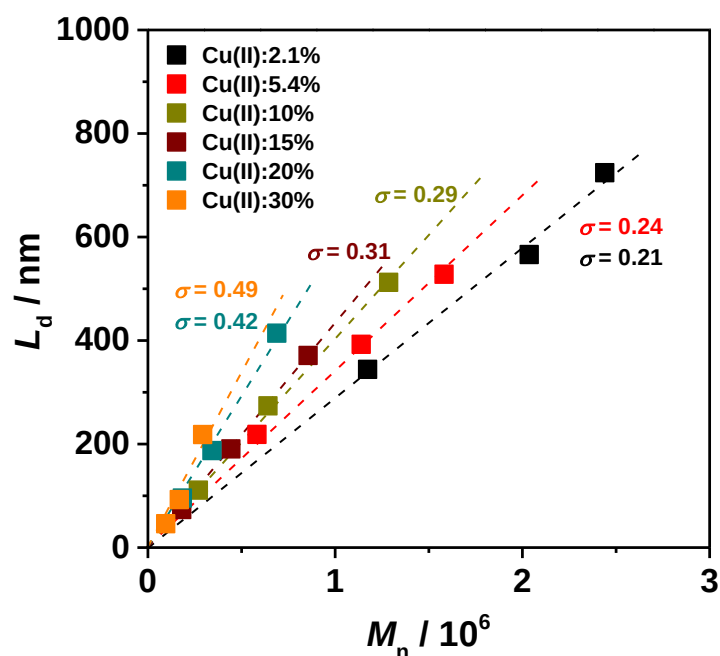


Figure 3-6 Plot of dry film thickness, L_d , vs. number-average molecular weight, M_n for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C; $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 0.12$ mM(■), 0.31 mM(■), 0.59 mM(■), 0.94 mM(■), 1.3 mM(■), 2.3 mM(■).

BHE as the surface initiator which was immobilized on a silicon wafer was added into the polymerization medium along with a free initiator of EBIB (0.025 mM). Addition of EBIB was for producing free polymers, which were then used as an index to characterize the molecular weights of graft polymers. Figures 3-4 and Figure 3-5 show the monomer conversion index $\ln([M]_0/[M])$ vs. polymerization time t and the M_n and M_w/M_n of products vs. monomer conversion performed with different concentration of $\text{Cu(II)Cl}_2/\text{L}_2$ catalyst, respectively. Data of thickness, L_d of PMMA brushes in dry state were plotted with the M_n of free polymers as shown in Figure 3-6. Even in the ambient pressure condition, M_n of PMMA was maximally over 2'000'000 with a polydispersity within ~ 1.3 , and the thickness of synthesized PMMA brushes successfully reached over 500 nm in the condition of $[\text{Cu(II)Cl}_2/\text{L}_2]$ as 0.12 mM (■). Although ILs have less effect of increased k_p and decreased k_t compared with high pressure effect, the solvent effect of ILs still provides an excellent potential for synthesizing high molecular weight polymers as well as CPBs with large thickness.

Similar with the result in Chapter 2, slopes of the lines in Figure 3-5 varied with $[\text{Cu(II)Cl}_2/\text{L}_2]$, revealing the $[\text{Cu(II)Cl}_2/\text{L}_2]$ dependence on the polymerization rate. In this result, the first-order plot can be presented as the following equation:

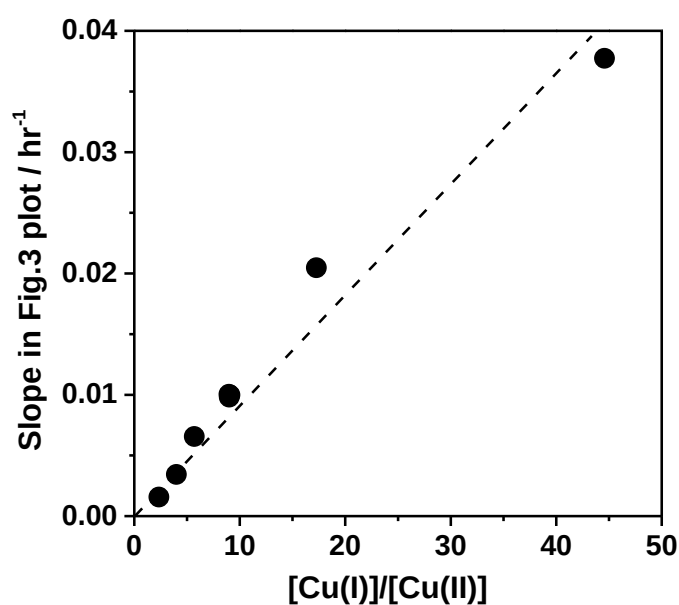


Figure 3-7 Plot of slope values in Figure 3 vs. ratio of $[\text{Cu(I)}]_0/[\text{Cu(II)}]_0$ for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C; $[\text{MMA}]_0 = 3.1 \text{ M}$, $[\text{EBIB}]_0 = 0.031 \text{ mM}$, $[\text{Cu(I)Cl/L}_2]_0 = 5.4 \text{ mM}$.

$$\ln[M]_0/[M]=(k_pK_{AT}[EBIB]_0[CuCl/L_2]_0/[CuCl_2/L_2]_0) t \quad (3-3)$$

where K_{AT} represents the ATRP equilibrium constant, and value of $(k_pK_{AT}[EBIB]_0[CuCl/L_2]_0/[CuCl_2/L_2]_0)$ can be obtained from the slope of the lines. Figure 3-7 shows slopes of the lines in Figure 3-4 vs. $[Cu(I)Cl/L_2]/[Cu(II)Cl_2/L_2]$. This plot exhibited in good linearity, where the slope of the line can be referred as $k_pK_{AT}[EBIB]_0$, indicating the obedience of kinetics theory for this system. With applying the measured k_p (1.70×10^3), the value of K_{AT} was obtained as 4.81×10^{-6} . For comparison, values of K_{AT} in DMSO and anisole was determined as 3.06×10^{-6} and 4.66×10^{-7} , respectively, by applying the measured k_p directly along with the first-order plot. Apparently, ATRP in the presence of DEME-TFSI gave a high activation rate, which was even about 10 times faster than in anisole.

In Chapter 2, graft density was demonstrated to be dependent on the concentration of divalent copper catalyst during synthetic procedure, in which speed of chain growth, especially during one time of the activation cycle, was known to influence the graft density when under a high-pressure condition. In this study, PMMA brushes synthesized in the presence of DEME-TFSI similarly exhibited a varying graft density with

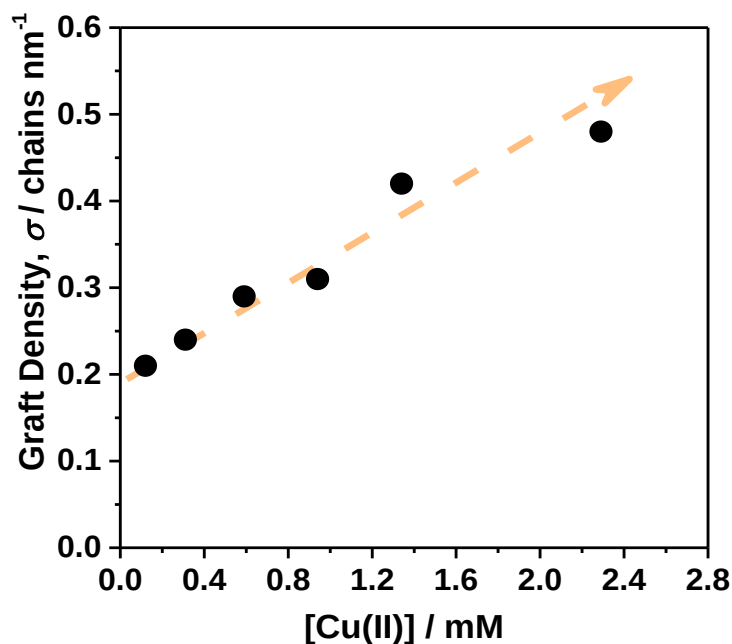


Figure 3-8. Plot of graft density, σ vs. $[Cu(II)]$ for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C

[CuCl₂/L₂] (Figure 3-8). When in a condition of low [CuCl₂/L₂] of 0.12 mM, a low graft density was obtained as $\sigma = 0.21$ chains/nm²; whereas σ was improved as to 0.49 chains/nm² with increasing the [Cu(II)Cl₂/L₂] to 2.3 mM. This data was ascribed to the amounts of monomer addition during the activation cycles, which was similar with the high pressure effect. Nevertheless, the increased [CuCl₂/L₂] resulted in a slow polymerization rate. In the condition of [CuCl₂/L₂] = 1.3 mM, it took 24 hours for the chain growth to achieve a thickness around 400 nm. A condition to improve the polymerization rate and keep the high graft density is desirable. Here, the author performed the polymerization with a combination of a “pressure-up”. SI-ATRP of MMA in the presence of DEME-TFSI (75 wt%) was carried out at 60 °C and 50 MPa. Polymerization results are as shown in Figure 3-9 to Figure 3-11. As expected, polymerization with a small applied pressure exhibited an increased polymerization rate, which was 2 times faster than the result in similar condition performed at ambient pressure. In this condition, synthesizable molecular weight reached over 10⁶ along with an increased thickness to 600 nm. As mentioned above, polymerization under a pressure condition for several hundred

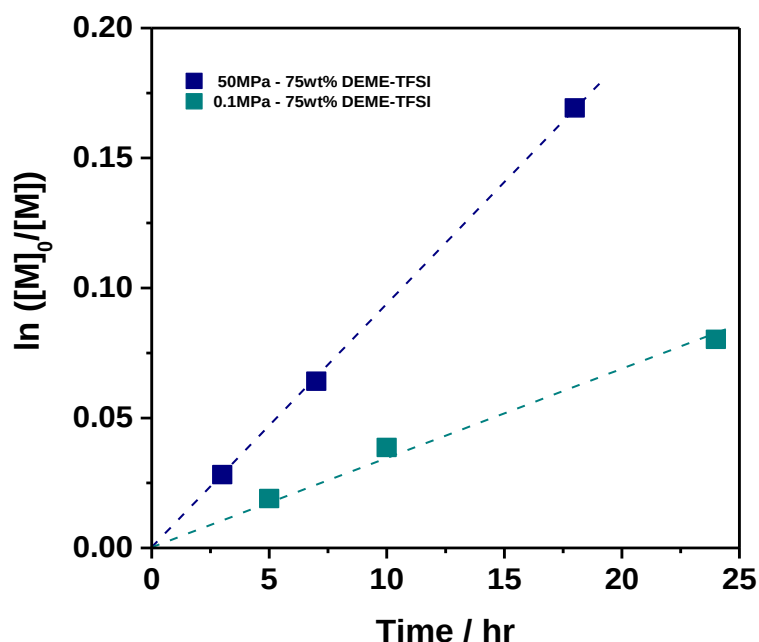


Figure 3-9. Plot of $\ln([M]_0/[M])$ vs. t for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C at 0.1 MPa (■) and 50 MPa (■); $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 1.3$ mM.

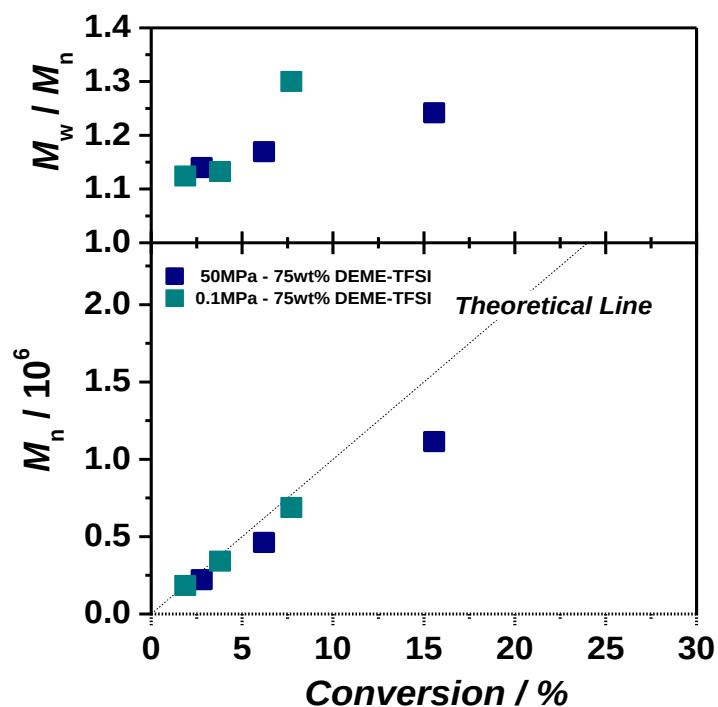


Figure 3-10. Plots of number-average molecular weight, M_n , and polydispersity, M_w/M_n vs. conversion for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C at 0.1 MPa (■) and 50 MPa (■); $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 1.3$ mM.

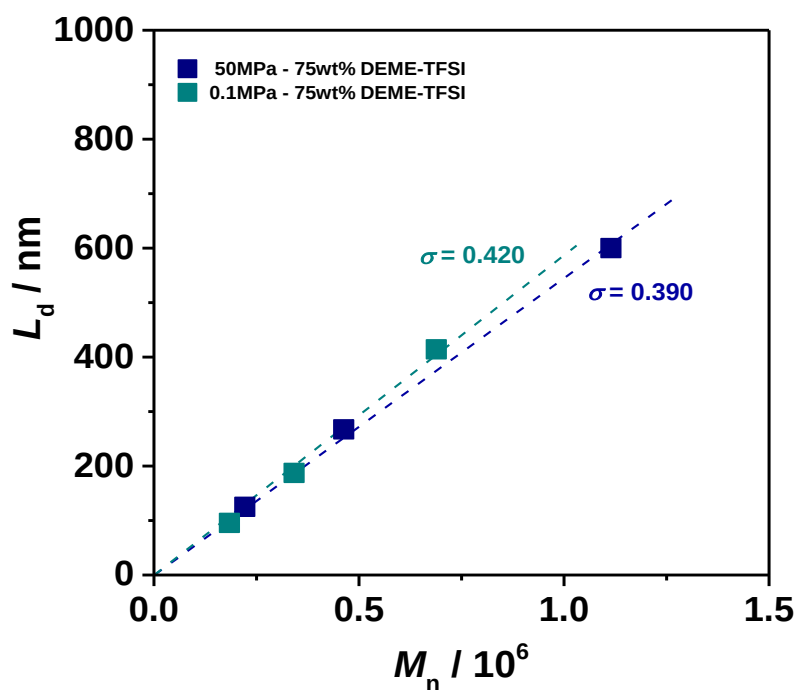


Figure 3-11. Plot of dry film thickness, L_d , vs. number-average molecular weight, M_n for the surface-initiated ATRP of MMA in 75 wt% DEME-TFSI at 60 °C at 0.1 MPa (■) and 50 MPa (■); $[MMA]_0 = 3.1$ M, $[EBIB]_0 = 0.031$ mM, $[Cu(I)Cl/L_2]_0 = 5.4$ mM, $[Cu(II)Cl_2/L_2]_0 = 1.3$ mM.

MPa is limited by the use of specific equipment. Whereas, a small applied pressure (< 100 MPa) can be relatively easy to achieve by some devices such as autoclave and pumps used in liquid chromatography systems, giving the simple method to synthesize CPBs with large thickness.

3-4. Conclusions

Synthesis of PMMA brushes with a large thickness was investigated by applying an ionic liquids of DEME-TFSI as the solvent medium. Feasibility of DEME-TFSI as the polymerization medium for ATRP was confirmed along with a high polymerization rate. By PLP-SEC technique, the values of k_p and k_t of MMA containing 75 wt% DEME-TFSI at 60°C were measured as 1.70×10^3 and 2.79×10^7 , respectively. Applying the solvent effect of ILs to SI-ATRP gave an increased thickness of PMMA brushes up to 700 nm even at the ambient pressure. Similar to the result discovered under high pressure, deactivator catalyst ($\text{Cu(II)Cl}_2/\text{L}_2$) also played an important role on the graft density of the prepared PMMA brushes in this system. A small applied pressure of 50 MPa to the polymerization in the presence of DEME-TFSI, an effectively enhanced polymerization rate with keeping the high graft density when in high $[\text{CuCl}_2]$ condition was discovered.

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Chapter 4

Lubrication Mechanism of Concentration Polymer Brushes with Large Thickness: in Microscopic Scale

4-1 Introduction

In Chapter 2 and Chapter 3, the synthesis of CPBs with large thickness by applying the high-pressure effect¹ and solvent effect² of ionic liquids was discussed. These methods allow a dramatic increase in the thickness of CPBs, especially for under a high pressure of 500 MPa, the thickness even achieved to a μm -order. The success in increasing the thickness of CPBs is expected to improve the abrasion problem for practical applications. In addition, the achievement is also helpful for the structure characterization and study of their lubrication mechanism, which were hardly achieved by a thin CPB. For example, with an increased thickness of a CPB, it allows the measurement of birefringence for the brush layer to determine the orientation property of graft chains by such as prism coupler³ and ellipsometry⁴ analysis. For studies of lubrication mechanism for CPBs, film thickness was considered as a factor to dominate the friction in hydrodynamic lubrication. The microtribology mechanism of CPBs has been previously studied in the author's group for both boundary lubrication and hydrodynamic lubrication. When in boundary lubrication, friction is dominated by the interaction (typically the interpenetration) between the confronted polymer brushes.^{5,6} On the other hand, viscosity resistance is dominant for the friction in hydrodynamic lubrication. The viscosity resistance consists of the viscosity and thickness of the lubricating layer, in which thickness is inversely proportional to the friction.^{7,8} The increase in film thickness of CPBs was expected to bring about an increased thickness of lubricating layer, leading a decreased friction in hydrodynamic lubrication. In this study, the author focused on the effect of thickness on the frictional properties of CPBs. CPBs of PMMA with a thickness of 1 μm and 100 nm (denoted as CPB-thick and CPB-thin, respectively) were applied for a friction measurement by AFM colloid-probe method in a microscopic scale. The friction in both boundary and hydrodynamic lubrications is discussed with the relationship of brush thickness.

4-2. Experimental Section

4-2-1. Materials

Silicon wafer (Ferrotec Corp., Japan, thickness 0.5 mm) was used as substrates for polymer brush surfaces. Silica particle (SiP, HIPRESICA SP, diameter 10 μm) obtained from Ube Nitto Kasei Co., Ltd., was used as probe of AFM for friction measurement. CPBs of PMMA were fabricated on the surfaces of silicon wafer by surface-initiated ATRP at ambient pressure for CPB-thin and high pressure for CPB-thick, as described in Chapter 2 and in ref-6, respectively. As the probe for AFM measurement, CPB of PMMA grafted on SiP was synthesized as referred to ref-6. The characteristics of polymer brushes used in this study were summarized in Table 4-1. Toluene (Wako Pure Chemicals., 99%, spectroscopic grade) was used as solvent

Table 4-1. Characteristics of CPB samples

Sample	substrate	M_n	M_w/M_n	L_d (nm)	graft density σ (chain/nm ²)
CPB-thick	Si wafer	2.19×10^6	1.42	950	0.31
CPB-thin	Si wafer	2.50×10^4	1.08	104	0.30
CPB-Probe	Si particle	3.30×10^4	1.17	-	-

for friction measurement.

4-2-2. AFM Force Measurement

Normal and friction forces were measured by an atomic force microscope (AFM) (Seiko Instruments Inc., Japan, SPI3800 controlled with SPA400 unit) equipped with a rectangular-shaped OMCL-RC800 cantilever (Olympus Optical Co., Ltd., Japan, vertical spring constant, $k_n = 0.1$ N/m, lateral spring constant $k_s = 23$ N/m) for measurement of frictional coefficient, and a V-shaped OMCL-TR800 cantilever (Olympus, $k_n = 0.15$ N/m) for characterization of swelling degree. A brush-modified SiP was attached on the cantilever with two-component epoxy resin adhesive. The detailed procedures has been described in ref-6.

4-3. Results and discussion

Frictional force and hence frictional coefficient μ were determined by AFM measurement in toluene. CPB of PMMA with a thickness of 950 nm ($M_n = 2.2 \times 10^6$, $\sigma = 0.3$ chains/nm²; denoted as CPB-thick in the following) was prepared on a silicon wafer (1 cm $\times$ 1cm). For the CPB of PMMA on the confronted side on a silica particle, since an increased thickness of brush layer will bring about a decreased graft density on the topmost brush surface (due to an increased space of curvature), a CPB of PMMA ($M_n = 4.9 \times 10^4$; denoted as CPB-Probe in the following) grafted silica particle with a radius of 5 μ m was applied as a probe for the AFM measurement.

Figure 4-1 shows the normal force dependence on the μ value of the CPB-thick vs. CPB-probe system at shear velocity $v = 10$ μ m/s. As shown as in Figure 4-1, CPB-thin vs. SDPB(PMMA) exhibited a very low value of μ (<0.001) at a low normal force, and an increased value with the increasing normal force, approaching to $\mu = 0.01$. Compared with SDPB, CPBs showed a compression-independent ultra-low

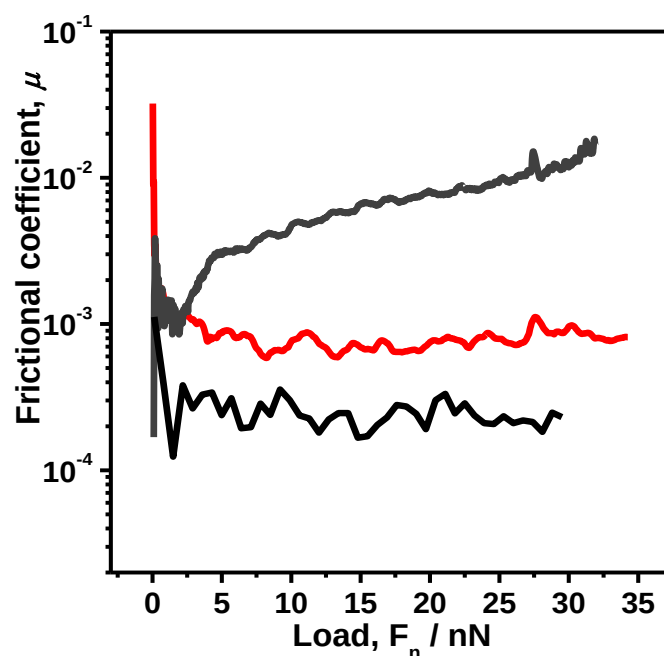


Figure 4-1. Plot of frictional coefficient μ vs. normal force F_n measured at a shear velocity v of 6 μ m/s for CPB-thick vs. CPB-Probe (red line), CPB-thin vs. CPB-thin (black line) and CPB-thin vs. SDPB (grey line) systems in toluene; CPB-thin vs. SDPB system was referenced from ref-6.

frictional property in boundary lubrication regime, in which μ was measured as $\sim 10^{-4}$. However, a small difference in μ value was observed between CPB-thick and CPB-thin. With the increased thickness, an increased value in μ from 3×10^{-4} to 7×10^{-4} . From previous studies, the extremely low-friction property for confronted CPBs in a good solvent was ascribed to a non-interpenetration state between the confronted brushes. However, as reported very recently in the author's group, a small portion of interpenetration still occurred between CPBs chains due to the unevenness of the topmost brush layer, which can be understood as the origin of the μ value as 10^{-4} order.⁸ In other words, the μ value should even decrease when the interpenetration is completely eliminated, which was demonstrated by immiscible CPBs⁸ and charged CPBs⁹ systems, achieving a μ value as 10^{-5} order, in the author's group. For CPB-thick, the increasing of film thickness was considered to accompany with an increase of unevenness on the topmost brush layer, which increased the portion of interpenetration at free ends of graft chains and hence resulted in an increased μ . It should be noted that in spite of the increased portion of interpenetration occurred in the CPB-thick vs. CPB-probe system, an extremely low μ as in 10^{-4} order was still obtained in a wide range of applied normal force, revealing the excellent lubricating property of CPB.

Figure 4-2 shows the ν dependence on μ at $F_n = 20$ nN for the CPB-thick vs. CPB-probe and CPB-thin vs. CPB-thin systems. In the range of ν in this plot, friction was measured in boundary lubrication and hydrodynamic lubrication. This shows the shift of lubrication mechanism of CPBs; friction states in hydrodynamic lubrication at high ν region turn into boundary lubrication state when μ decreases. The μ of CPB-thick shown in Figure 4-1 is in boundary lubrication state, exhibiting the super lubrication property as described above. Generally, for friction in the hydrodynamic lubrication regime, the frictional force F_s can be formulated to the equation of viscosity resistance as,

$$F_s = \nu \eta / d \quad (4-1)$$

where d denotes the thickness of a fluid lubricant layer. For friction of CPBs in the hydrodynamic lubrication regime, the μ was demonstrated to change with the viscosity of applied solvents.⁶ The increase in thickness

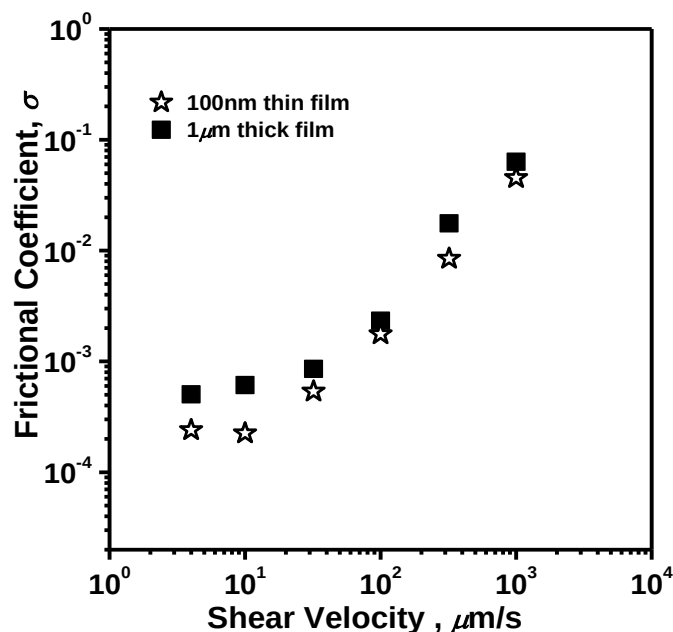


Figure 4-2. Plot of frictional coefficient μ vs. shear velocity u for CPB-thick vs. CPB-Probe (■) and CPB-thin vs. CPB-thin (☆) measured in toluene at $F_n = 20$ nN

of CPBs was considered to bring about an increased thickness of the lubricating layer, leading a decreased μ in hydrodynamic lubrication. However, as shown in Figure 4-2, the μ between these two systems showed no difference in hydrodynamic lubrication. Considering that the swelling degree of CPBs deeply affects the viscosity of brush layers and thus the friction, which was demonstrated by tuning the solvent quality for CPBs in the author's group, the swelling property of CPBs in toluene was investigated in different thickness. Figure 4-3 shows the plots of thickness of CPBs in dry state, L_d vs. thickness in equilibrium state, L_e in toluene and the swelling degree, $L_e/L_{c,w}$, where $L_{c,w}$ is the counter length of graft chains. As shown in Figure 4-3, the swelling degree of CPBs in toluene was confirmed as a constant value independent of the L_d . This indicated a constant viscosity of the brush layer whether the change in the thickness of CPBs. From these results, friction in hydrodynamic lubrication regime is inferred to be independent of the L_d . Hydrodynamic lubrication for CPBs was previously considered as being contacted for confronted CPBs. The data in this study suggests two probability of formation for CPBs in hydrodynamic lubrication. One is the contacting CPBs formation with a constant thickness of lubricating layer; the other one is the separating formation with

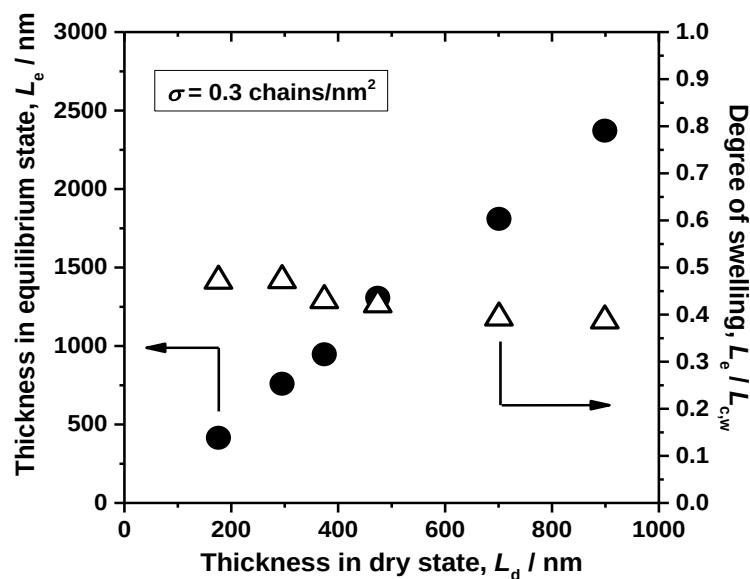


Figure 4-3. Plots of (left axle) thickness in equilibrium/swelling state and (right axle) swelling degree $L_e/L_{c,w}$ vs. thickness in dry state L_d for CPB-thick with a graft density σ of 0.3 chains/nm² measured in toluene by AFM. $L_{c,w}$ represents the counter length of the graft chain.

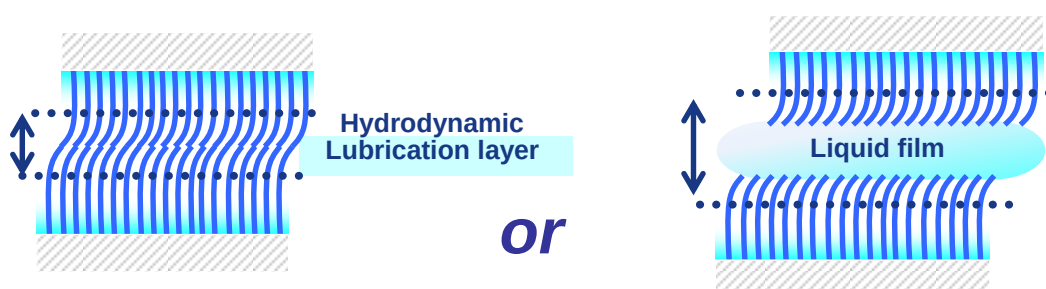


Figure 4-4. Schematic representation of the formation of confronted polymer brushes in hydrodynamic lubrication regime during the microtribological measurements.

the liquid lubricant existing between CPBs (Figure 4-4). As mentioned above, the change in the μ in hydrodynamic lubrication was confirmed with tuning the swelling degree of CPBs, revealing the contact of the CPBs (in the situation of separating surfaces, μ must be swelling degree independent). Another data for the immiscible CPBs system also indicated the contact formation by the varied μ in hydrodynamic lubrication. Summarizing the result in this work along with the previous studies, the author suggests that friction in hydrodynamic lubrication for CPBs measured by the AFM analysis should be established as the contacting

formation, in which μ is dominated by a lubricating layer consisted in a constant thickness. For a confirmation of this speculation, a distance measurement for the confronted substrates is necessary, however remained difficult for the AFM measurement. This might be able to be achieved by a friction measurement in macroscopic scale combined with optical interferometry method. Some discussion about the dynamic lubrication mechanism will be described with friction measurement in macroscopic scale in Chapter 5.

4-4. Conclusions

The AFM microtribologic technique was applied to investigate the frictional properties of CPBs of PMMA with a large thickness of 1 μm in toluene. Lubrication mechanism for frictional coefficient μ was discussed in both boundary lubrication and hydrodynamic. In boundary lubrication, a thick CPB was confirmed to showing the super lubrication characteristic of CPB for an extremely low μ as 10^{-4} order. Although the increased thickness brought about an increased interpenetration between the brushes, there were no influence for a thick CPB to exhibit the super lubrication property. In hydrodynamic lubrication, no difference in μ was observed with the change in thickness of CPBs. The friction in hydrodynamic lubrication for CPBs was suggested to independent of the film thickness due to a constant thickness of lubricating layer formed by contacted CPBs.

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Chapter 5

Lubrication Mechanism of Concentration Polymer Brushes with Large Thickness: in Macroscopic Scale

5.1 Introduction

Studies of CPBs in microtribology have demonstrated the potential of CPBs as a lubricating material for providing a super lubrication when solvating in a good solvent. However, this property of super lubrication was hardly reflected to their macrotribological properties. Takahara et al. have reported the friction measurement for poly(methyl methacrylate)(PMMA) of CPBs by a sliding-type tribometer.² In their study, a frictional coefficient as in 10^{-2} order was measured, which was much higher than the obtainable values in AFM analysis. Similar result was also obtained in our group by a rheometer measurement, which showed some abrasion damage on the surface of CPBs after the test (Figure 5-1). This was ascribed to the small thickness of CPBs, which cannot bear a high localized contact pressure resulted from the applied confronted surface with μm -order roughness some mixed-in particles with similar size order. In order to overcome such drawback, groups of Spencer et al.³ and Takahara et al.⁴ applied charged polymers (polyelectrolytes) to CPBs in an aqueous phase, exhibiting an ultralow frictional coefficient $\mu < 0.001$. Very recently, Sato et al. reported a molecularly smooth sheets as facing materials for ionic liquid type CPB, successfully showing a low frictional property ($\mu \sim 10^{-3}$).⁵

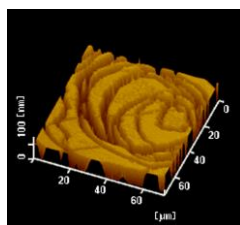


Figure 5-1. AFM image of CPB-thin surface after a friction measurement by rheometer, indicating extensive abrasion wear of brush layer.

In this thesis, the effect of thickness as a factor was investigated for the tribological properties of CPBs. In Chapter 2 and 3, the synthesis of CPBs with large thickness were discussed; and in Chapter 4, microtribological properties of the thick CPBs was described. A dramatic increase in the thickness of CPBs is expected to improve the increased friction problem resulted from occurred abrasive wear when applied in a macroscopic scale system, contributing to energy-saving⁶ and improved lifetime⁷ for practical applications, i.e. automatic vehicles, compressors, artificial joints and pumps, etc. In this work, the author measured the macrotribological properties of CPBs in terms of the thickness. Frictional properties were measured by a rotatory tribometer for CPBs of PMMA in an ionic liquid, *N,N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI), which is a good solvent for PMMA. The property of durability which is important for practical applications was also investigated.

5-2. Experimental Section

5-2-1. Materials

Glass discs (ϕ : 30 mm, thickness: 1 mm, surface flatness: λ , Sigmakoki Co., Ltd., Japan) and glass lens (diameter: 10 mm, curvature radius: 7.79 mm, Sigmakoki) were used as substrates and probes for polymer brush surfaces. CPBs of PMMA were fabricated on the surfaces of discs and lens by surface-initiated ATRP under high pressure as described in Chapter 2, and surface-initiated ATRP at ambient pressure as referred to ref-1b. The characteristics of polymer brushes used in this study were summarized in Table 5-1. *N,N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI, Kanto Chemical Co., Inc., Japan) was used as solvent for friction measurement.

Table 5-1. Characteristics of CPB samples

Sample	substrate	M_n	M_w/M_n	L_d (nm)	graft density σ (chain/nm ²)
CPB-thick	glass disc	1.93×10^6	1.43	950	0.36
	glass lens			-	-
CPB-thin	glass disc	8.85×10^4	1.19	66	0.53
	glass lens			-	-

5-2-2. Friction Measurement

The frictional force and frictional coefficient between CPBs of PMMA were measured in DEME-TFSI) by a ball-on-disc type of rotatory tribometer (UNMT-1, Bruker Corporation, United States). A glass lens of a curvature radius of 7.79 mm was bonded on a metal pin and then set in a holder with spring sensor. For this measurement, a flat glass disc was confronted by the glass lens, achieving a contact between CPBs in macroscopic scales. The friction force and hence frictional coefficient were measured in different loads (normal force) and rotatory velocities.

5-3. Results and discussion

Frictional force and frictional coefficient between CPBs of PMMA were measured in an ionic liquid, DEME-TFSI by a ball-on-disc type of rotary tribometer. The choice for DEME-TFSI as lubricant was due to the high viscosity (67 cP @ 25°C), which allows a wide range of measurement to achieve a Stribeck curve. In this friction test, the glass lens was set on a location with a distance of 6 mm from the rotating center, and the frictional force was determined by the average of the detected value in clockwise and counter clockwise

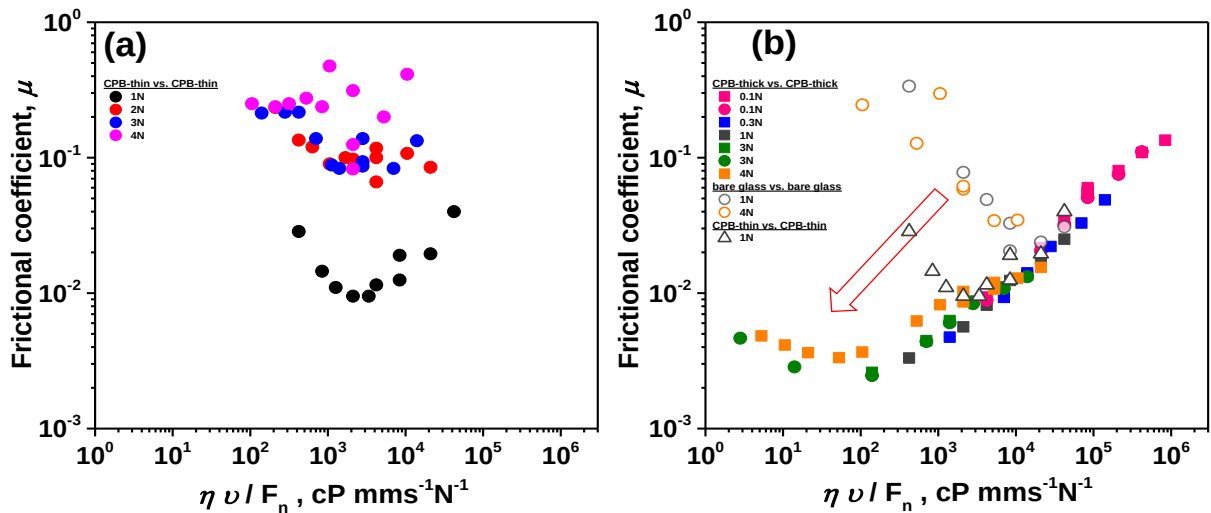


Figure 5-2. Plots of frictional coefficient μ vs. characteristic parameter $\eta \nu / F_N$ for (a) CPB-thin vs. CPB-thin system at $F_N = 1 \sim 4$ N (b) CPB-thick vs. CPB-thick (close symbols), bare-glass vs. bare glass (open circle) and CPB-thin vs. CPB-thin (close triangle) at $F_N = 0.1 \sim 4$ N, measured in DEME-TFSI.

rotation. Figure 5-2a shows the so-called Stribeck plot, i.e., μ vs. $\eta v/F_N$ for the CPB-thin versus CPB-thin system, where η represents the viscosity of solvent, measured in ranges of shear velocity v of 6 ~ 630 mm/s and applied load F_N of 1 ~ 4 N. With an applied F_N of 1N in this case, a Stribeck-plot like curve was obtained; however, the μ in boundary lubrication exhibited a high value as $\sim 10^{-2}$. Moreover, with the increase in F_N , the μ value tended to increase to around 10^{-1} , revealing the damage of the brush layer. A wear track with a depth of several μm was observed by a laser microscope measurement (VK-X200/250, Keyence Corporation, Japan), which means the wear damage reached to glass substrate and the contacting brush layer was almost worn out (Figure 5-3). The obtained μ shows identical to the value reported by Takahara et al.,² indicating the difficult to attain low friction with small thickness in such a macroscopic scale.

Figure 5-2b shows the friction data for the CPB-thick versus CPB-thick system in DEME-TFSI measured in ranges of shear velocity v of 6 ~ 630 mm/s and applied load F_N of 0.1 ~ 4 N. For comparison, the data of bare glass/bare glass (open circle) and CPB-thin/CPB-thin (open triangle) were also plotted into the graph. This data was reasonably categorized into two regimes: boundary lubrication and hydrodynamic lubrication. In the hydrodynamic lubrication, the μ value decreased with decreasing $\eta v/F_N$, approaching a less dependent regime of boundary lubrication, showing very similarly with our AFM data. Compared with the results of bare glass/bare glass and CPB-thin/CPB-thin systems, these two regimes of lubrication were

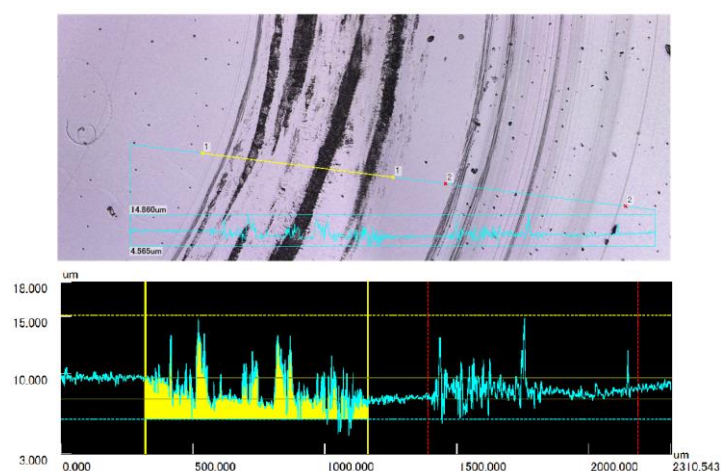


Figure 5-3. (Upper) Optical image of CPB-thin surface after the friction measurement taken by laser microscope, (lower) the profile of wear depth in the upper image.

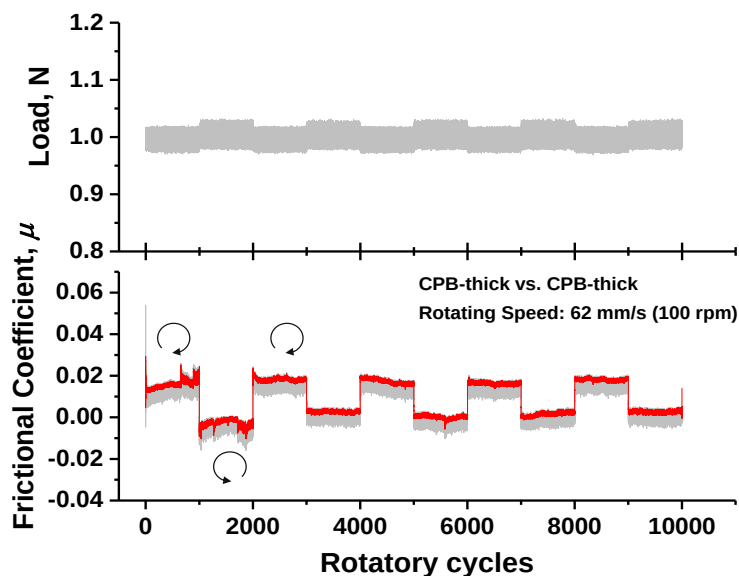


Figure 5-4. Plot of normal force (upper) and frictional coefficient (lower) vs. rotatory cycles for CPB-thick vs. CPB-thick system measured in DEME-TFSI with a rotatory frequency of 100 rpm (speed as 62 mm/s) and a load of 1 N.

observed with little wearing even in macroscopic scale, which also reflected in the decreased value of μ in boundary lubrication as in 10^{-3} order.

Figure 5-4 shows the result of durability test for CPB-thick/CPB-thick system with an applied F_n of 1 N. In this test, the rotatory frequency was 100 rpm (60 mm/s), and the rotatory direction shifted in between clockwise and counter clockwise per 1000 rotatory cycles. As shown in Figure 5-4, the μ value shows a consistent value of approximately 0.01 (noted that the μ value also fitted in the Stribeck curve as shown in Figure 5-2b) even though at least 10000 rotatory cycles, demonstrating excellent durability and the potential for practical application of lubrication. A calculation was carried out to determine the values of contact area and pressure by Hertz model. Here, a glass ball/glass substrate system was applied since the difficult of calculation for the real case (CPBs grafted on glass lens and glass disc). From this calculation result, we can understand that with an applied F_n of 1 N in our measurement, the contact area was in the range of 136 μm , and the contact pressure was 164 MPa. Taking account that the swelling thickness of the CPB-thick was approximately 2 μm (referred to Figure 4-3 in Chapter 4), which was much smaller than the calculated value

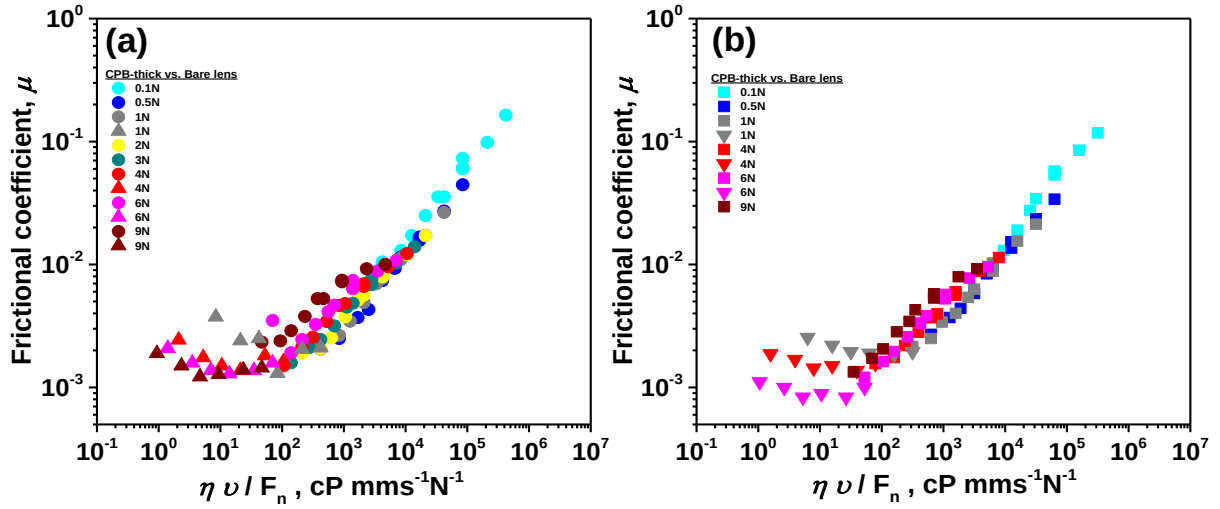


Figure 5-5. Plots of frictional coefficient μ vs. characteristic parameter $\eta\nu/F_n$ for (a) CPB-thick vs. bare lens (b) CPB-thick vs. CPB-thin systems at $F_n=0.1\sim 9$ N, measured in DEME-TFSI.

of contact area, the error for the real value in our case could be less than 10%.

Figure 5-5 shows friction data for the CPB-thick versus bare lens and CPB-thick versus CPB-thin systems in DEME-TFSI measured in ranges of shear velocity ν of $6 \sim 630$ mm/s and applied load F_n of $0.1 \sim 9$ N. Interestingly, from these results, the low μ as 10^{-3} order was similarly obtained in a high normal force up to 9 N from the system which CPB-thick was grafted on only side of substrate (Figure 5-5a). This result was never obtained from the microtribological system due to an occurred adhesion between CPB and silica particle. With changing the facing material to a CPB-thin, friction was observed as almost similar with data in Figure 5-5a, indicating a less influence of facing materials on the friction as long as in the presence of CPB-thick on one side of surface (Figure 5-5b). Furthermore, a friction shift in hydrodynamic lubrication regime at $\nu/F_n = 10^2 \sim 10^4$ was observed with an increasing normal force. The shift in friction was considered to be probably due to the contact of the brushes and the glass lens. When in a high shear velocity, it was non-contact state between the two surfaces; with lowering the shear velocity, the two surfaces became contacted (Figure 5-6). As applied a high normal force, the brush layer would be compressed and lead a high viscosity, resulting in an increased μ . Despite of the hypothesis, the data exhibit the necessity to confirm the mechanism of hydrodynamic lubrication, especially for the region of high shear velocity. A measurement such as SFA

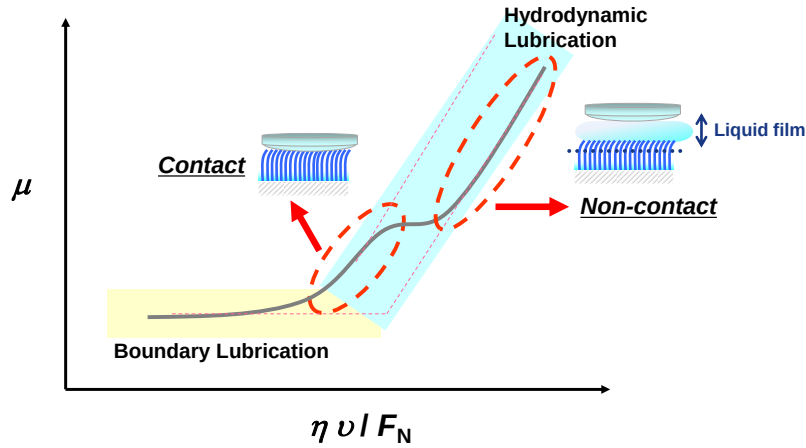


Figure 5-6. Schematic representation of friction shift in hydrodynamic lubrication regime when under a high normal force.

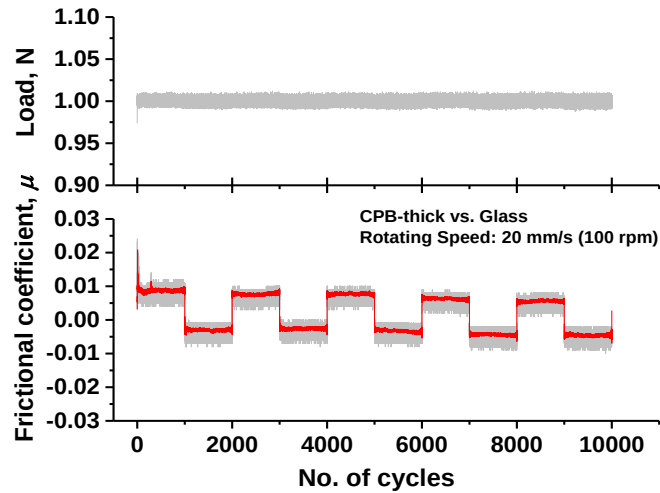


Figure 5-7. Plot of normal force (upper) and frictional coefficient (lower) vs. rotatory cycles for CPB-thick vs. bare lens system measured in DEME-TFSI with a rotatory frequency of 100 rpm (speed as 20 mm/s) and a load of 1 N.

analysis might be an effective method to determine the distance between the two surfaces. Figure 5-7 shows the result of durability test for CPB-thick/bare lens system with an applied F_n of 1 N and rotatory frequency of 100 rpm (20 mm/s). As shown in Figure 5-7, even applying only one side of substrate with CPB-thick prepared, a good durability was demonstrated within at least 10000 rotatory cycles similar with data in Figure 5-4. Although it is hardly to say that no abrasion occurred on the surface of brushes, the results in this study

confirms the excellent lubricating properties containing super low friction and good durability for a thick CPB, which might provide the possibility for CPBs in such practical systems.

5-4. Conclusion

CPBs of PMMA with extraordinarily thickness, i.e., a μm order, were successfully prepared by applying ATRP under high pressure. The friction property for confronted CPB-thicks as well as CPB-thick/glass systems in a macroscopic scale was measured, revealing ultra-low frictional as well as good lubricating properties. In addition, good abrasion resistance and durability was confirmed, especially for the durability test, the friction remained stable value even through 10000 rotatory cycles. From these results, we believe that this study will open up a new route for practical lubricating applications.

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Part 2

Ultrahigh Molecular Weight Block Copolymers – Synthesis and Application to Gels

Chapter 6

Controlled Synthesis of Ultrahigh-Molecular-Weight Block Copolymer by High-Pressure Atom Transfer Radical Polymerization

6.1 Introduction

A block copolymer (BCP) as a multi-conjunctive segment polymer is known to form a variety of microphase-separated structures in bulk as well as in a selective solvent owing to the repulsive interaction between the segments. A so-called “nano morphology” with a domain size of 10-nm order has been widely developed and used as a nano-patterned and nano-porous template, especially in lithographic applications.¹ BCPs with a domain size of sub-micrometer order have also been attracting attention as potential photonic materials with a tunable bandgap in the visible region.² In this case, a well-defined BCP with a high molecular weight (M_n) of around 10^6 is required; in particular, the controlled synthesis of functional BCPs remains a challenge.

BCPs are mainly synthesized by living polymerization techniques. Among them, living anionic polymerization has been widely used as a termination-free polymerization strategy, which allows the formation of polymers with a narrow polydispersity as well as a continuous increase in the molecular weight until the monomer is completely consumed.³ However, this technique requires high-purity reagents and strict moisture-free conditions. In the last decade, LRP has been intensively developed, providing a simpler method to synthesize a variety of well-defined BCPs, including those with functional groups and complex structures (e.g., star polymers, graft polymers).⁴ Among the LRP methods, ATRP is widely used for synthesizing BCPs.⁵ However, as mentioned in previous chapters, the controllable molecular weight of the polymers synthesized by ATRP is limited to a specific range, for example, at most the order of 10^5 for polymethacrylates. This is also the case with other LRP methods because of the intrinsic reaction kinetics, that is, the inevitable radical-radical termination. Recently, the author's succeeded in synthesizing

poly(methyl methacrylate) (PMMA) with a molecular weight of up to 3.6×10^6 (more recently, 6.5×10^6) by performing ATRP at a pressure of 500 MPa.⁶ Matyjaszewski et al. also reported AGET-ATRP at high pressures and the synthesis of PMMA with the molecular weight reaching 1.9×10^6 even at room temperature (AGET stands for activators generated by electron transfer).⁷ As was previously revealed in conventional free radical polymerization (therefore also in LRP), increase in pressure can accelerate radical propagation and suppress radical termination, resulting in fast polymerization with a smaller degree of termination and affording polymers with very high molecular weights. These results motivated the author to synthesize an ultrahigh-molecular-weight BCP. In this work, synthesis of block copolymer poly(methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS) was investigated with ATRP under a high pressure condition of 500 MPa. In order to achieve a fast polymerization with a high block efficiency, the polymerization process and catalyst system were discussed.

6-2. Experimental Section

6-2-1. Materials

MMA and St were obtained from Nacalai Tesque Inc., Japan, and purified by passing through a column filled with activated basic alumina to remove any inhibitor. Copper chloride (CuCl; 99.9%, Wako Pure Chemical Industries, Ltd., Japan) and copper bromide (CuBr; 99.9%, Wako) were washed with glacial acetic acid (99.7%, Wako) to remove any soluble oxidized impurities, filtered, washed with ethanol (99.5%, Wako) and diethyl ether (99.5%, Wako), and dried. Ethylene bis(2-bromoisobutyrate)(2F-BIB) was synthesized as referred to ref-8a. Tris(2-dimethylaminoethyl)amine (Me₆-TREN, 97%) was received from Sigma-Aldrich Co. LLC. and purified with distillation. Ethyl 2-bromoisobutyrate (EBIB; >98.0%, Tokyo Chemical Industry Co., Ltd., Japan), copper dichloride (CuCl₂; 98%, Nacalai Tesque), copper dibromide (CuBr₂; XX%, Wako), 4,4'-dinonyl-2,2'-bipyridine (dN-bipy; >97.0%, Wako) and anisole (99.0%, Wako) were used as received.

6-2-2. Measurement

GPC analysis was carried out to determine the M_n , M_w and polydispersity M_w/M_n of the free PMMA with a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). THF was used as an eluent at a flow rate of 0.8 mL/min. The M_n and M_w/M_n were estimated by the calibration prepared by PMMA standards (Polymer Laboratories, $M_p = 1.31 \times 10^3$ - 1.64×10^6) and then complemented by polystyrene standards (Polymer Laboratories, $M_p = 1.93 \times 10^3$ - 1.32×10^7). ^1H (300 MHz) NMR spectra were recorded on JEOL/AL300 spectrometer.

6-2-3. Polymerization

All sample preparations were carried out in a glove box purged with argon, and all chemicals were deoxygenated in a glove box before use. High-pressure ATRP was carried out as follows. The anisole solution containing typically, MMA (4.8 M), EBIB (0.48 mM), Cu(I)Cl/dN-bipy₂ (32 mM), and Cu(Cl)₂/dN-bipy₂ (0.67 mM) was placed and sealed in a cryogenic vial purchased from Corning Incorporated. The sample vial was further packed in a polyethylene-coated aluminum sheet to prevent oxygen contamination and then placed in the high-pressure reaction system (HPS-700, Syn Corporation, Kyoto, Japan) preheated at the polymerization temperature and pressurized up to 500 MPa. After the prescribed time, the system was depressurized, and the samples were taken out for NMR measurements (AL300, JEOL, Japan) and GPC analysis (GPC-101, Shodex, Japan) to estimate the monomer conversion and the molecular weights, respectively. For the synthesis of low-molecular-weight PMMA, the anisole solution containing MMA (2.5 M), EBIB (8.2 mM), Cu(I)Cl/dN-bipy₂ (31 mM), and Cu(Cl)₂/dN-bipy₂ (1.6 mM) was polymerized at 60°C and 300 MPa for 2h; for synthesis of PMMA with two functional groups, the anisole solution containing MMA (4.8 M), 2F-BIB (0.48 mM), Cu(I)Cl/dN-bipy₂ (30 mM), and Cu(Cl)₂/dN-bipy₂ (3.3 mM) was polymerized at 60°C and 500 MPa for 5h.

The sequential block copolymerization was carried out as follows. After the first polymerization was complete, the vial was transferred to a glove box, and St (3 g), anisole (3 g) and then Me₆-TREN (0.023 g, 0.1mmol) were added to the polymerization solution, stirring until the solution became homogeneous. The

Polymerization was carried out as per the previously described process, at room temperature and 500 MPa, for the prescribed time.

6-3. Results and discussion

In general, the LRP-based routes to BCPs can be grouped into two classes. One is the so-called macro-initiator method, where a homopolymer constituting one of the block segments is synthesized, isolated (purified), and finally used as a macro-initiator for the polymerization of the second monomer. This method is more widely adopted in practice. The other method is sequential polymerization (also known as one-pot synthesis), where the second monomer is added to the reaction medium after the first monomer is almost completely consumed. This method is much simpler, but the disadvantage is that a small amount of residual first monomer often contaminates the second-block segment.

In this study, the macro-initiator method was first applied via high-pressure ATRP (HP-ATRP) to synthesize an ABA-type BCP. The B-block polymer was synthesized by the ATRP of MMA using CuBr/4,4'-dinonyl-2,2'-bipyridine (dN-bipy) as a catalytic system and ethylene bis(2-bromoisobutyrate) (2F-BIB) as a bi-functional initiator. The polymerization was carried out at 60°C and a high pressure of 300 MPa for 1 h. Thus obtained PMMA with $M_n = 1.53 \times 10^5$ and $M_w/M_n = 1.11$ purified by repeated re-precipitation was used for the block copolymerization, i.e., the ATRP of styrene (St), with the same catalytic system at 110°C and ambient pressure. After 24 h of polymerization, the product was recovered by re-precipitation using methanol and then heated cyclohexane (the latter for removing the possible byproduct, the homopolymer of St). Figure 6-1a shows the result of GPC measurements before and after the block copolymerization. Unexpectedly, a very small shift in the GPC curve was observed, suggesting that almost no St monomers were added. This is not the case with the PMMA synthesized by the normal ATRP (at ambient pressure): a high initiation efficiency was achieved under such conditions, yielding a low-polydispersity BCP. The chain-extension test, i.e., the ATRP of MMA using this macro-initiator, was also carried out at 70°C. Figure 6-1b shows the GPC traces with the polymerization time elapsed, indicating little

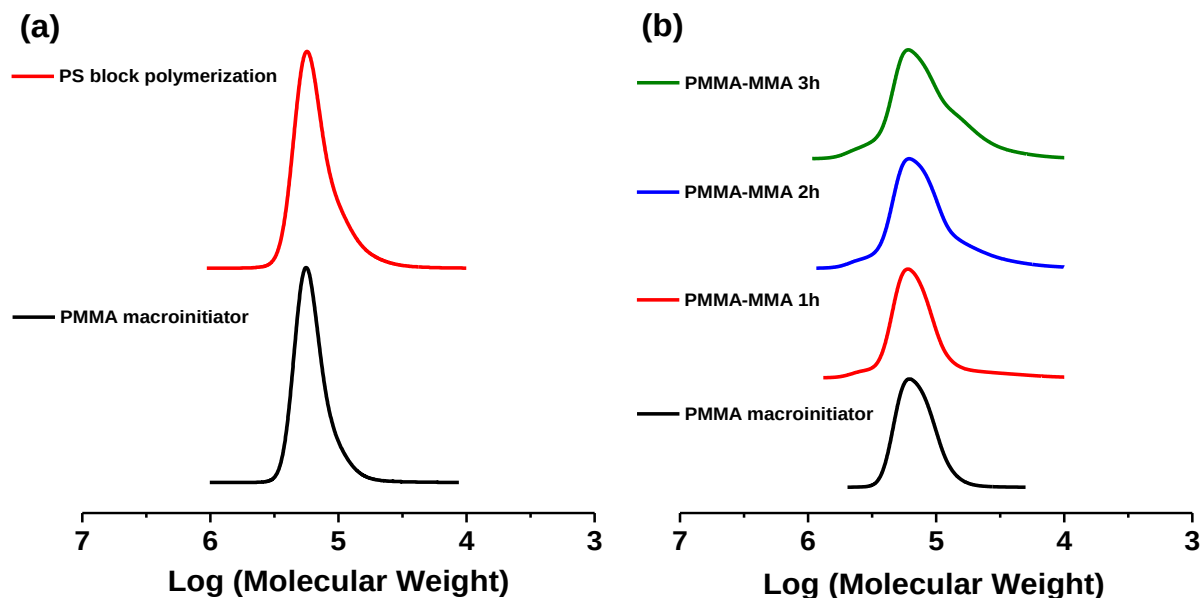


Figure 6-1. GPC traces (RI detection) of PMMA macro-initiators (black line) and the products obtained in the batch procedure by (a) the ATRP of St (block copolymerization) at 110°C and 0.1 MPa; (b) the ATRP of MMA (chain extension) at 60°C and 0.1 MPa. The polymerization time, t , is indicated in the figures, and the feed composition in anisole (50 wt%) is [monomer]:[initiator]:[CuCl/L₂]:[CuCl₂/L₂] = (a) 6000:0.5:60:1, (b) 6000:1:10:0.2.

increase in the molecular weight. The same results were obtained for other PMMA macro-initiators of different molecular weights that were synthesized by HP-ATRP, indicating that during the course of preparation of such macro-initiators, the chain end became inactive and the polymerization could not be re-initiated. The synthesis route consists of the following steps: (1) pressuring and polymerization, (2) de-pressuring, (3) isolation and purification. In the first step, the successful progression of polymerization suggests that the polymer chain end remains active during the high-pressure polymerization process. In order to verify the second step, the HP-ATRP was carried out through alternating pressuring/polymerization and de-pressuring steps. The GPC curve was shifted to the higher-molecular-weight region even in the de-pressuring step during the course of polymerization, indicating that de-pressuring does not damage the chain end (Figure 6-2). This consideration suggests that the chain-end became inactive in the isolation/purification step. However, this possibility was ruled out at least under the ambient conditions, i.e., the PMMA macro-initiator prepared by the normal ATRP at ambient pressure and with the same isolation/purification step

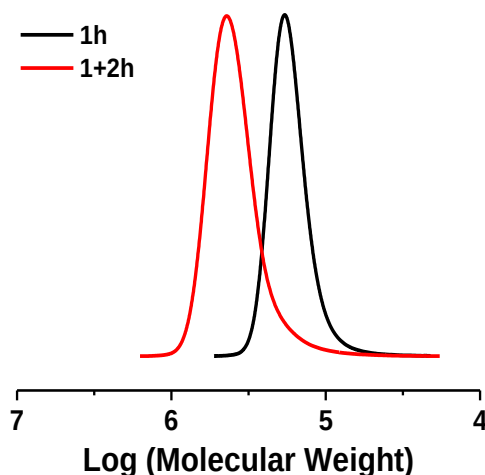


Figure 6-2. GPC traces of the products obtained by the ATRP of MMA at 60°C and 500 MPa for 1 h (black line) and for additional 2 h (red line) through the de-pressuring step. The polymerization time, t , is indicated in the figures, and the feed composition is [MMA]:[EBIB]:[CuBr/L₂]:[CuBr₂/L₂] = 10000:1:8:1 in bulk condition.

effectively initiated the ATRP of the second monomer, giving a BCP. At present, the reason for the inactivation of the macro-initiator prepared by HP-ATRP remains unclear. One plausible reason may be that a small and undetectable amount of the byproduct deactivates the chain-end when the polymerization solution is exposed to air for recovering the product. In order to overcome this issue, we attempted the sequential polymerization without the isolation/purification step for the synthesis of BCPs.

The chain-extension test by the sequential polymerization of MMA (block copolymerization) was carried out to investigate the activity of the produced polymer. The ATRP of MMA with the CuCl/dN-bipy catalytic system and ethyl 2-bromoisobutyrate (EBIB) initiator was performed at 60°C and a high pressure of 300 MPa for 2 h, to afford PMMA with $M_n = 2.93 \times 10^4$, $M_w/M_n = 1.10$ at a monomer conversion higher than 99.8%. To this polymerization solution were added MMA and anisole in an Ar-atmosphere glove box (without exposure to air), and the mixture was heated at 60°C and ambient pressure. As shown in Figure 6-3a, the GPC traces were shifted to the higher molecular-weight region with a monomodal distribution; after 4 h of polymerization, PMMA with $M_n = 5.94 \times 10^4$, $M_w/M_n = 1.11$ was obtained at a monomer conversion of 4%, and the estimated block efficiency was 84 %. This block efficiency was in good agreement with that

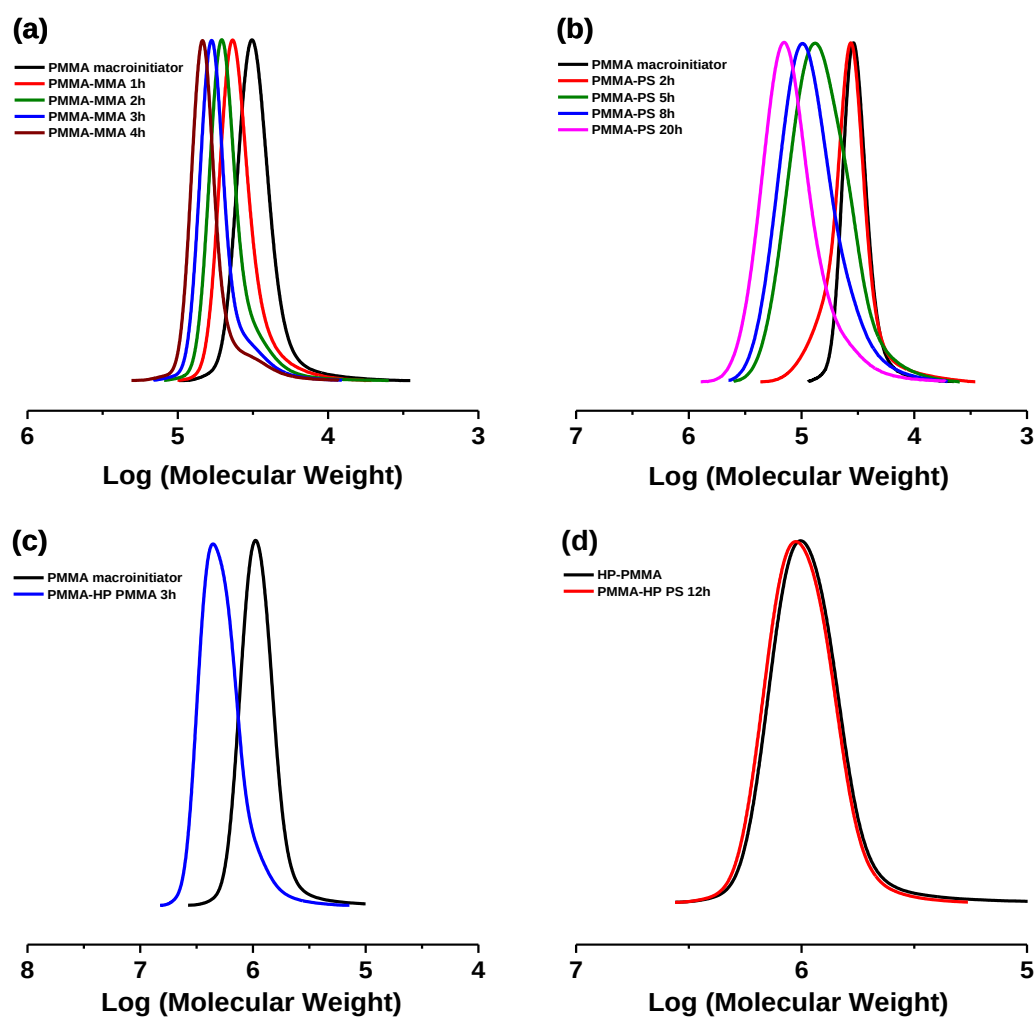


Figure 6-3. GPC traces (RI detection) of PMMA macro-initiators (black line) and the products obtained in the sequential procedure by the ATRP of MMA (chain extension) (a) at 60°C and 0.1 MPa, (c) at 60°C and 500 MPa; and by the ATRP of St (block copolymerization) (b) at 110°C and 0.1 MPa, and (d) at 70°C and 500 MPa. The polymerization time, t , is indicated in the figures, and the feed composition is (a) 1st block product solution (denoted as 1st): 4.7 g, MMA: 5 g, (b) 1st: 4.8 g, St: 5 g, (c) 1st: 1.2 g, MMA: 3 g, anisole: 3 g, (d) 1st: 2.7 g, St: 6 g, anisole: 6 g.

evaluated from the shoulder area corresponding to the macro-initiator in the GPC trace. This result revealed that PMMA synthesized by HP-ATRP exhibited sufficiently high chain-end activity even after MMA was almost completely consumed. Using a similar method, the block copolymerization of St was carried out at 110°C. As shown in Figure 6-3b, the GPC traces were shifted to the higher-molecular-weight region with the

polymerization time elapsed, suggesting the formation of a BCP. The block efficiency for the ATRP of St was determined to be 82%, which was in good agreement with the abovementioned value, confirming the successful block copolymerization through this sequential procedure.

To synthesize a BCP with an ultrahigh molecular weight (M_n over 10^6), both the first and second polymerizations were carried out at high pressure (500 MPa). The ATRP of MMA at 500 MPa for 2 h gave PMMA with $M_n = 8.28 \times 10^5$, $M_w/M_n = 1.17$ and almost full monomer conversion. Using this PMMA as a macroinitiator, chain-extension test with MMA and block copolymerization of St were sequentially carried out at 60°C and 70°C, respectively, at 500 MPa. Figures 6-3c and 6-3d show the GPC traces of the thus-obtained polymers. For the chain-extension test, the GPC trace was shifted to the higher-molecular-weight side, with monomodal distribution, and a block efficiency as high as 82%, similar to the results obtained at ambient pressure (Figure 6-3c). However, for the block copolymerization of St, a very small shift was observed (Figure 6-3d). This was ascribed to the low polymerization rate even at high pressure. For St, the polymerization temperature was set to be relatively low, 70°C, in order to suppress thermal initiation. Thermal initiation causes serious problems resulting in broadening of the molecular-weight distribution, especially when polymerization is carried out with a very low concentration of initiator to obtain a very high molecular weight polymer. In order to improve the polymerization rate at a low temperature, we attempted the exchange of ligands from dN-bipy to tris(2-dimethylaminoethyl)amine ($\text{Me}_6\text{-TREN}$). $\text{Me}_6\text{-TREN}$ is known to be a high-performance ligand for the ATRP catalytic system; this ligand in combination with CuCl(or CuBr) affords a high rate of activation, and hence, a very high polymerization rate is achieved even at room temperature.⁸ Generally, a CuCl (or CuBr)/ $\text{Me}_6\text{-TREN}$ catalyst is insoluble in non-polar solvents and is hence used as a heterogeneous system. Eventually, we found that the ligand exchange procedure allowed us to successfully develop a homogeneous system containing the CuCl/ $\text{Me}_6\text{-TREN}$ catalyst even in anisole, a non-polar solvent. Homogeneity in the reaction system could usually improve the polymerization rate. Figure 6-4 shows the results of the HP-ATRP of St using a homogeneous CuCl/ $\text{Me}_6\text{-TREN}$ catalytic system. The procedure was as follows. Using dN-bipy as a ligand, CuCl and CuCl₂ were dissolved in anisole

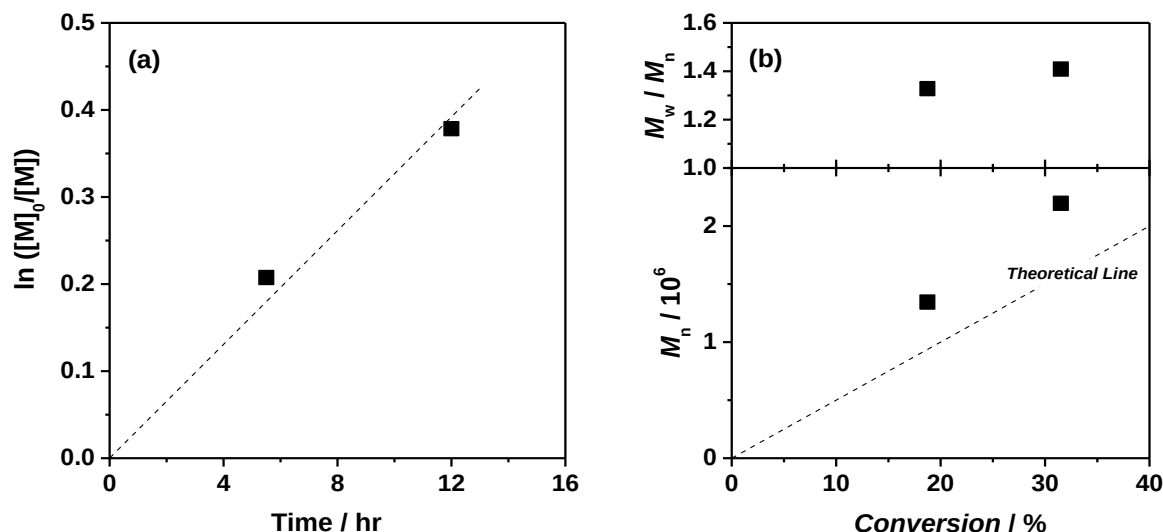


Figure 6-4. Plots of (a) $\ln[M]_0/[M]$ vs. t (b) number-average molecular weight, M_n , and polydispersity, M_w/M_n , vs. conversion for ATRP of St at room temperature ($\sim 27^\circ\text{C}$) and 500 MPa; the feed composition in anisole (50 wt%) is $[\text{St}]:[\text{EBIB}]:[\text{CuCl/L}_2]:[\text{CuCl}_2/\text{L}_2]:[\text{Me}_6\text{-TREN}] = 50000:1:98:2:150$.

containing St as a monomer and EBIB as an initiator; then, $\text{Me}_6\text{-TREN}$ was added to obtain a homogeneous polymerization solution. The polymerization was carried out at room temperature and 500 MPa. The molecular weight of the produced PS homopolymer exceeded 2,000,000 in 12 h. It should be noted that without the addition of $\text{Me}_6\text{-TREN}$, the polymerization hardly proceeded. A detailed study on the ATRP using a homogeneous $\text{CuCl}/\text{Me}_6\text{-TREN}$ catalytic system in non-polar solvents is in progress in our laboratory. The ligand-exchange procedure was further applied to the sequential block polymerization of St with PMMA macroinitiator prepared by HP-ATRP. Figure 6-5a shows the GPC traces before and after the block copolymerization for 12 h. In contrast to Figure 6-3d, the GPC trace shifted to the high-molecular-weight region and showed a narrow size distribution, as expected by the homogenous and high-performance catalytic system with $\text{Me}_6\text{-TREN}$ and hence the enhanced polymerization rate. Thus, the obtained $\text{PMMA-}b\text{-PS}$ was characterized as $M_n = 2.63 \times 10^6$, $M_w/M_n = 1.29$, and $f_{\text{PS}} = 57 \text{ mol\%}$ by GPC and NMR. A high block efficiency (96%) was also confirmed by the GPC trace, which showed a small shoulder corresponding to the first segment: the difference between the normalized UV and RI data approximately corresponds to the uninitiated macro-initiator. In addition to a AB-type BCP, a ABA-type BCP, $\text{PS-}b\text{-PMMA-}b\text{-PS}$, can also be obtained

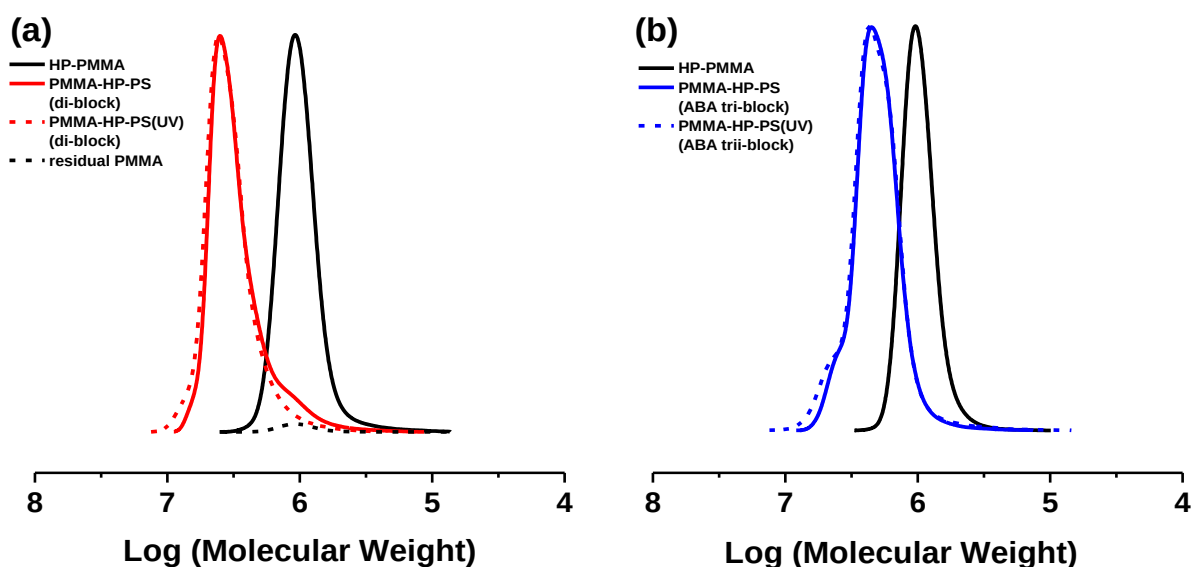


Figure 6-5. GPC traces of PMMA macro-initiator with one or two functional groups (black line) and the products obtained in the sequential procedure by ATRP of St (block copolymerization) at room temperature and 500 MPa for 12 h. The solid and dashed curves represent the data by RI and UV detection, respectively, and the dotted curve is obtained as the difference between the normalized RI and UV data of the products. The feed composition is (a) 1st: 2 g, St: 3 g, anisole: 3 g, Me₆-TREN: 0.023 g, (b) 1st: 1 g, St: 1.5 g, anisole: 4.5 g, Me₆-TREN: 0.012 g.

by similar technique (see Figure 6-5b), characterized as $M_n = 1.95 \times 10^6$, $M_w/M_n = 1.18$ by GPC. The shoulder in the high molecular weight region of the peak in Figure 6-5b was attributed to small amounts of polymer radical-polymer radical termination reaction. To the best of our knowledge, this is the first report on the synthesis of a BCP with a molecular weight on the order of 10^6 by LRP.

6-4. Conclusion

A feasible synthetic route to high-molecular-weight BPCs, PMMA-*b*-PS, was successfully established with two breakthroughs by ATRP at high pressure. One of the key points to the success of this reaction was the sequential polymerization procedure, which does not otherwise afford a high block efficiency. The macro-initiator prepared by HP-ATRP and isolated lost its ability to reinitiate the ATRP, although the reason for the same is unclear. The other key feature was the ligand exchange procedure, which provided a homogenous

CuCl/Me₆-TREN system even in a non-polar solvent. This resulted in an increased polymerization rate of St even at room temperature, as opposed to the conventional case that causes a serious problem in the form of thermal initiation and affords a significantly contaminated homopolymer via the block copolymerization.

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Chapter 7

Controlled Synthesis of Ultrahigh-Molecular-Weight ABA Type Block Copolymer and Fabrication of Ionic Gel

7.1 Introduction

ABA triblock copolymers (triBCPs), as containing solvent-insoluble A end-segments and solvent-soluble B middle-segment, are well-known for the ability to form a physical crosslink structure in a selective solvent. When solvating in a selective solvent at dilute concentration, the A segments aggregate as core particles to form a micelle structure where the soluble B segments behave as loop structure on the shell part of micelles. When at significant high concentration, the ratio of loops decreases and thus forms the crosslink/bridge structure with showing a gel behavior. In the last two decades, preparation of the physically-crosslinked gels with many kinds of selective solvents, such as oils,¹ heptane,² xylene,³ water⁴ and so on, morphology structure and physical properties of the gels, e.g. thermos-stability, rheology, were widely reported.

As a new choice of selective solvent, ionic liquids (ILs) have been developing for fabricating ionic gels. Recently, some polymers, e.g. poly(styrene-*b*-ethylene oxide-*b*-styrene) (SOS), poly(styrene-*b*-methyl methacrylate-*b*-styrene) (PS-*b*-PMMA-*b*-PS) (SMS), have been reported for the fabrication of ionic gels,⁵ in which ionic gels were demonstrated with high ion-conductivity and expected to be applied as the electrolytes for some electrical devices, e.g. lithium ion batteries, electric double layer capacitors and solar cells, etc.⁶ However, there were very less works focusing on the effect of molecular weight of polymer gels. This would be attributed to the difficult of synthesis for high molecular weight polymer. As known, a factor of molecular weight deeply affects the viscoelastic behavior of polymer chains in an unrestrained condition (melted state or solvated in solution), which is consider to reflect to a restrained condition (network structure).⁷ In the previous chapters, the polymerization techniques – high pressure and ionic liquid solvent effects - for

synthesizing high-molecular-weight polymers were introduced. For synthesis of block copolymers, the author successfully synthesized ultrahigh molecular weight PMMA-*b*-PS by applying high pressure effect to ATRP as described in Chapter 6. In this study, in spite of the success of high pressure polymerization for synthesizing BCPs, the author investigated the feasibility of ionic liquid solvent, *N,N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI), as the reaction medium for ATRP to synthesize a high-molecular-weight triBCP. The obtained triBCPs were then solvate into the selective solvent of DEME-TFSI to fabricate gel structures. In this work, small-angle X-ray scattering (SAXS) measurement as well as rheological experiments of formed gels are characterized in parallel to understand their microphase-separation structures and gelation behaviors in terms of molecular weights.

7-2. Experimental

7-2-1. Materials

Methyl methacrylate (MMA) and styrene (St) were obtained from Nacalai Tesque Inc., Japan and purified by passing through a column filled with activated basic alumina to remove inhibitor. Copper chloride (CuCl, 99.9%, Wako Pure Chemical Industries, Ltd., Japan) was washed with glacial acid to remove any soluble oxidized impurities, filtered off, washed with ethanol and diethyl ether, and dried. Ethylene bis(2-bromoisobutyrate) (2F-BIB) was synthesized according to ref-8. Copper dichloride (CuCl₂, 98%, Nacalai Tesque), 4,4'-dinonyl-2,2'-bipyridine (dN-bipy, >97.0%, Wako), *N,N*-diethyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI, Kanto Chemical Co., Inc., Japan), anisole (99.0%, Wako), methanol (MeOH, 99.8%, dehydrated, Wako) and sodium methoxide (MeONa, >95%, Wako) were used as received.

7-2-2. Polymerization and Characterization

All sample preparations were carried out in a glove box purge with argon, and all chemicals were deoxygenated before use in a glove box. Table 7-1 summarizes the detailed condition of polymerization. PMMA macroinitiator was synthesized by the ATRP as follows: the reaction mixture containing MMA, 2F-

Table 7-1. Polymerization conditions of ATRP for synthesis of ABA triblock copolymers

Run No.	Initiator	Monomer	Catalysts, CuCl/L ₂ / CuCl ₂ /L ₂	solvent	Temp. (°C)	Time (hr)	Pressure (MPa)
1	2F-BIB (0.31 mM)	MMA (3.1 M)	10 mM / 0.2 mM	DEME-TFSI (75 wt%)	60	1	0.1
(b)	PMMA (0.18 mM)	St (4.7 M)	47 mM / 1.0 mM	anisole (50 wt%)	110	20	0.1
2	2F-BIB (0.13 mM)	MMA (3.1 M)	5.2 mM / 0.1 mM	DEME-TFSI (75 wt%)	60	6	0.1
(b)	PMMA (0.065 mM)	St (4.7 M)	47 mM / 1.0 mM	anisole (50 wt%)	110	14	0.1
3	2F-BIB (0.56 mM)	MMA (5.7 M)	9.4 mM / 0.2 mM	DEME-TFSI (50wt%)	60	2	0.1
(b)	PMMA (0.22 mM)	St (4.7 M)	47 mM / 1.0 mM	anisole (50 wt%)	90	48	0.1
4	2F-BIB (1.6 mM)	MMA (9.4 M)	16 mM / 0.3 mM	bulk	70	4	0.1
(b)	PMMA (0.16 mM)	St (4.7 M)	24 mM / 1.2 mM	anisole (50 wt%)	100	22	0.1
5	2F-BIB (1.6 mM)	MMA (4.8 M)	8.1 mM / 0.2 mM	anisole (50 wt%)	60	2	0.1
(b)	PMMA (0.79 mM)	St (4.7 M)	24 mM / 1.3 mM	anisole (50 wt%)	100	23	0.1
6	2F-BIB (0.10 mM)	MMA (3.1 M)	5.4 mM / 0.3 mM ^a	DEME-TFSI (75wt%)	60	4.5	0.1
7	2F-BIB (0.48 mM)	MMA (4.8 M)	32 mM / 0.7 mM ^a	anisole (50 wt%)	60	2	500
(b)	PMMA solution (2g)	St (4g)	-	anisole (4g)	100	12	0.1
8	2F-BIB (0.48 mM)	MMA (4.8 M)	32 mM / 0.7 mM ^a	anisole (50 wt%)	60	2	500
(b)	PMMA solution (2g)	St (4g)	-	anisole (4g)	100	12	0.1

^a Catalysts applied as CuBr/L₂ and CuBr₂/L₂ for high-pressure ATRP.

BIB, Cu(I)Cl/L₂, Cu(Cl)₂/L₂ and/or DEME-TFSI (75 wt%) or anisole (50 wt%) was placed in a Schlenk tube and then heated in an oil bath thermostated at 60 or 70°C, where L represents dN-bipy. The produced PMMA was purified by repeated precipitation from chloroform into methanol, the precipitates were filtered off and dried in vacuum. The second (block) polymerization of St was carried out by the ATRP at 90-110°C in the reaction mixture of St, the purified PMMA macroinitiator, Cu(I)Cl/L₂, Cu(Cl)₂/L₂, and anisole (50 wt%). The obtained polymer was purified and isolated by repeated precipitation as above described. In some cases, an additional reprecipitation from chloroform into heated cyclohexane (40-50°C) was carried out to remove polystyrene homopolymer possibly produced and contaminated due to thermal initiation of St monomers. Finally, no trace of polystyrene homopolymers was confirmed by the gel permeation chromatographic (GPC) analysis. Some samples with a high-molecular-weight PMMA segment were synthesized by the high-

pressure ATRP as referred in Chapter 6: the first polymerization (the preparation of PMMA segment) was carried out at 60°C and 500 MPa for 2 h. After the polymerization was complete, St and anisole were added to the polymerization solution without exposure to the air and stirred until the solution became homogeneous. Then, the sequential block copolymerization was carried out at 100°C and ambient pressure for 12 h.

At each step, the polymerization solutions were analyzed by NMR to estimate the monomer conversion and by GPC to determine the molecular weight and its distribution. GPC analysis was carried out to determine the M_n , M_w and PDI of the free PMMA with a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30-cm mixed columns (Shodex GPC KF-806L, exclusion limit = 2×10^7), and a differential refractometer (Shodex RI-101). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 0.8 mL/min. The M_n and PDI were estimated by the calibration prepared by PMMA standards (Polymer Laboratories, $M_p = 1.31 \times 10^3$ - 1.64×10^6) and then complemented by polystyrene standards (Polymer Laboratories, $M_p = 1.93 \times 10^3$ - 1.32×10^7). ^1H (300 MHz) NMR spectra were recorded on JEOL/AL300 spectrometer.

In order to cleave the produced polymer at the initiating site (the ester linkage of 2F-BIB), the transesterification reaction was carried out according to ref. 9. Typically, SMS sample (50 mg) were dissolved in dry THF (5 g), to which methanol (5g) and 25 wt% MeONa/MeOH (4 drops) were slowly added, and then the mixture was heated at 80°C for 24 hr. After the reaction, the sample was neutralized with diluted acetic acid and then analyzed by GPC to determine the molecular weight and its distribution.

7-2-3. Preparation of DEME-TFSI solution of SMS

Preparation of DEME-TFSI solution of SMS samples was carried out by typically solvating SMSs into a solvent mixture containing DEME-TFSI (0.5 g) and a cosolvent of THF (2-3 g) in a prescribed polymer fraction. The mixture solution was placed in a glass vial and kept standstill in the atmosphere for 1-2 days until the THF cosolvent was evaporated. The SMS/DEME-TFSI solution was put in a vacuum oven at 80°C for 2-3 hr to completely remove the remained THF and then annealed at 160°C for 1 day.

7-2-4. Small-Angle X-Ray Scattering (SAXS) Measurement

Small-angle/ultra-small-angle X-ray scattering (SAXS/USAXS) measurement was performed at the beamlines BL40B2 and BL19B2 in SPring-8 (Harima, Hyogo, Japan) as well as using NANO-Viewer (Rigaku Co., Tokyo, Japan). In BL40B2 and BL19B2, SAXS profiles were measured on a CMOS camera with 2048×2048 pixels of a $43.1\text{-}\mu\text{m}$ pixel size (C11440-22C; Hamamatsu Photonics, Shizuoka, Japan) coupled to an image intensifier system (V7735P; Hamamatsu Photonics, Shizuoka, Japan) and a two dimensional hybrid pixel array detectors, Pilatus 2M (pixel apparatus for the Swiss Light Source) with 1475×1679 pixels of a $172\text{ }\mu\text{m}$ pixel size, respectively. NANO-Viewer was equipped with PILATUS 100K (Rigaku) as a detector, which has 487×195 pixels of a $172\text{-}\mu\text{m}$ pixel size. The X-ray wavelength (λ) was 0.19 nm (BL40B2), 0.069 nm (BL03XU), and 0.154 nm (NANO-Viewer). Sample-to-detector distance was approximately 4.3 m (BL40B2), 42 m (BL03XU), and 1.3 m (NANO-Viewer). The scattering vector, $q = (4\pi/\lambda) \sin\theta$, where θ is the scattering angle, was calibrated using collagen for the experiment in SPring-8 and silver behenate for the experiment by NANO-Viewer as standard samples. The scattered intensities are expressed as a function of the scattering vector, $q = (4\pi/\lambda) \sin\theta$, where θ is the scattering angle. The q -range was calibrated using collagen and silver behenate as standard samples for the experiments in SPring-8 and by NANO-Viewer, respectively. SAXS experiments with heat treatment were carried out with NANO-Viewer (Rigaku) in a temperature range of $30\text{-}180^\circ\text{C}$, constructed with a sample-to-detector distance of 380 mm , and calibrated by cholesterol. The temperature condition was controlled by Thermo plus EVO DSC8230 (Rigaku).

7-2-5. Rheometer Measurement

Rheological measurement was performed on a Bohlin C-VOR shear rheometer (Malvern Instrument Ltd., England) with a parallel plate (25 mm diameter) employed. A gap size was set to be $300\text{ }\mu\text{m}$ for all the measurement. The storage and loss moduli were measured with a strain of 5% in the frequency range of $0.1\text{-}100\text{ rad s}^{-1}$ and in the temperature range of $27\text{-}200^\circ\text{C}$. After the dynamic shear measurement, a strain test was performed in the strain range of $1\text{-}5000\%$ at a frequency of 1 rad s^{-1} at 27°C . The sample specimen were prepared by directly casting the polymer solution containing SMS, DEME-TFSI and a cosolvent of THF on the employed plate and then evaporating most of THF in air for 12 h . Before the measurement, samples were

Table 7-2. Molecular weight characteristics of synthesized SMSs

Run No.	Sample	$M_{n, \text{PMMA}}^a$	$M_{n, \text{PS}}^b$	M_w/M_n^a	f_{PS}
1	PMMA-309k	309000	-	-	-
1b	SMS-519k	309000	210000 ^c	1.34	0.405
2	PMMA-812k	812000	-	1.22	-
2b	SMS-824k	812000	12000	1.31	0.015
3	PMMA-275k	275000	-	1.22	-
3b	SMS-282k	275000	7000	1.24	0.025
4	PMMA-231k	221000	-	1.18	-
4b	SMS-231k	221000	9000	1.21	0.039
5	PMMA-43k	43000	-	1.17	-
5b	SMS-54k	43000	11000	1.13	0.204
6	PMMA-921k	921000	-	1.20	-
7	SMS-1172k ^d	949000	-	1.17	-
7b		949000	223000	1.26	0.190
8	SMS-1350k ^d	1078000	-	1.23	-
8b		1078000	272000	1.34	0.201

^a $M_{n, \text{PMMA}}$ and M_w/M_n analyzed by GPC and calibrated by PMMA standards. ^b $M_{n, \text{PS}}$ determined by NMR measurement. ^c $M_{n, \text{PS}}$ determined by GPC with RI detector. ^dSMS synthesized by the high-pressure polymerization method referred to Chapter 6.

put in a vacuum oven at 80°C for 2-3 hr to completely remove the remained THF and then annealed at 160°C for 1 day.

7-3. Results and discussion

7-3-1. Synthesis of ABA triBCP with the use of ionic liquid solvent:

Table 7-2 summarizes the molecular characteristics of SMS samples synthesized under the condition in Table 7-1 and used for the structure/property study. First of all, the author evaluated the end functionality of PMMA macroinitiator synthesized in DEME-TFSI and hence the block efficiency of thereby obtained SMS. It should be noted that good end-functionality and block efficiency was previously confirmed in the other polymerization systems.

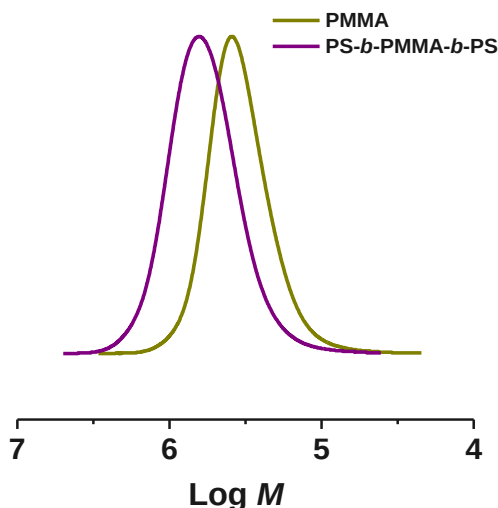


Figure 7-1. GPC traces of PMMA macroinitiator and the product of block polymerization for St. at 110°C after 20 hours.

Figure 7-1 shows the GPC traces before and after the block polymerization: the first and second (block) polymerization was carried out under the conditions of runs no. 1 and 1b, respectively, in Table 7-1. The PMMA macroinitiator, i.e., the B block segment in SMS, had $M_n = 3.09 \times 10^5$ and $M_w/M_n = 1.27$. After the block polymerization, the GPC trace was shifted to the higher molecular-weight region with a narrow distribution, giving $M_n = 5.19 \times 10^5$, $M_w/M_n = 1.34$. No shoulder peak was detectable at the original position corresponding to the macroinitiator. This suggests the well-controlled polymerization and sufficiently high block efficiency. This should be finally concluded by cleaving SMS at its center part (originally initiating site of 2F-BIB) and analyzing thus obtained polymers (see Figure 7-2). Figure 7-3 shows the GPC traces obtained using (a) refractive index (RI) and (b) ultraviolet (UV) detectors before and after the transesterification (cleaving) reaction. By cleaving, the molecular weight decreased to almost half of the original value with keeping a narrow polydispersity, giving $M_n = 2.68 \times 10^5$, $M_w/M_n = 1.35$. More importantly, the RI and UV (an absorption wavelength of 254 nm) detectors, which can detect both segments and only the polystyrene segment, respectively, gave almost the same GPC traces. This indicates equal propagation of PS from both ends of PMMA macroinitiator.

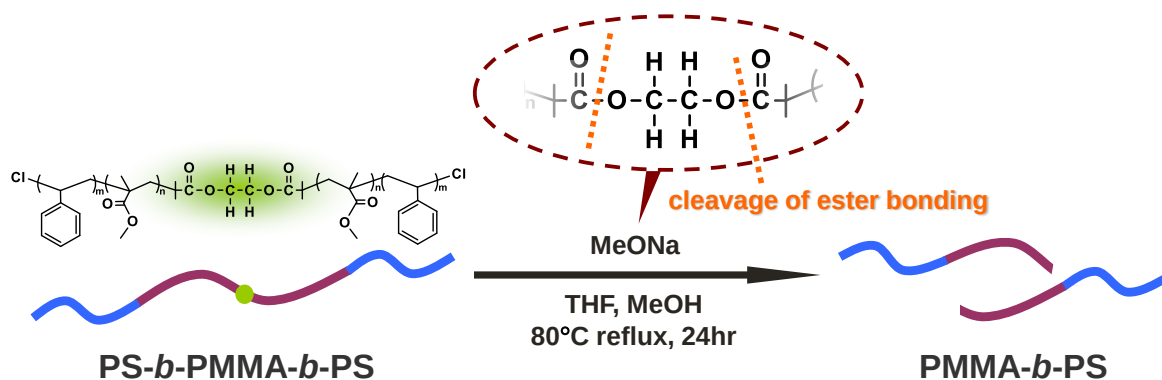


Figure 7-2. Schematic illustration of transesterification reaction for a PS-*b*-PMMA-*b*-PS.

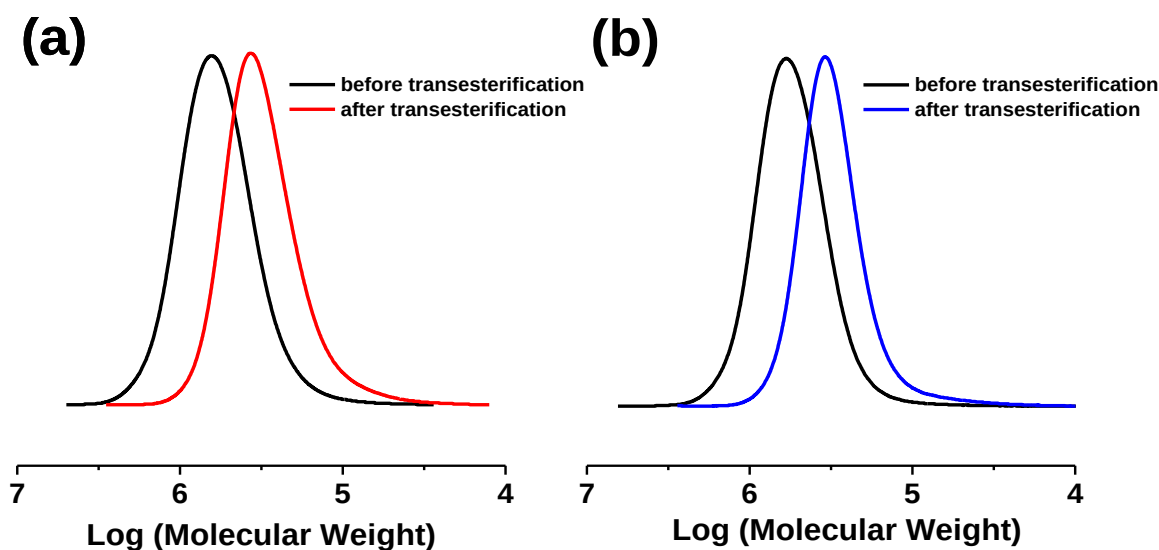


Figure 7-3. GPC traces of PS-*b*-PMMA-*b*-PS before and after transesterification reaction by (left) RI and (right) UV detectors.

7-3-2. Formation of gels by ABA triBCP in ionic liquid

Figure 7-4 displays the photographs of the gel/sol states in DEME-TFSI containing (a) SMS-54k and (b) SMS-820k at polymer fractions from 0.5 to 10 wt%. These two SMS samples have almost the same molecular weight of PS segment but different molecular weights of PMMA segments. The figure suggests that SMS-54k formed a gel at polymer concentration above 3 wt%, while SMS-824k formed a gel in all the studied range of polymer concentration even as low as 0.5 wt%. The PS segment insoluble in DEME-TFSI forms an aggregate (core) by micro-phase separation, and the PMMA segment soluble in DEME-TFSI forms a loop on a core and a bridge between cores. When increasing polymer concentration, the fraction of bridge

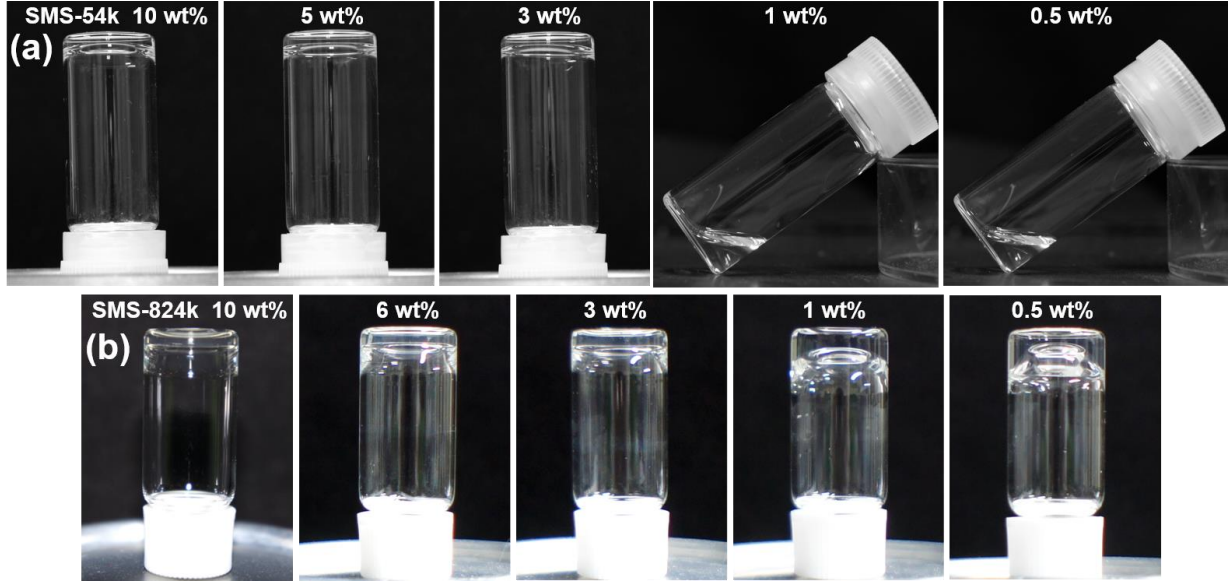


Figure 7-4. Photographs of (a) SMS-54k and (b) SMS-824k gels at a polymer concentration: 10, 5(6), 3, 1 and 0.5 wt%

increased and formed a gel above the critical concentration. As expected, the higher the chain length of PMMA segments, the critical concentration of gelation decreased. In other word, a high-molecular-weight PMMA segment has higher performance to gel the solvent.

7-3-3. Structure Characterization by SAXS measurements

The core structure in the gel formed by SMS was determined by SAXS measurements at room temperature. Figure 7-5(a-c) shows the SAXS and USAXS experimental data of SMS-824k, -282k and -54k gels at a polymer fraction of 10 wt% and the fitting data based on Percus-Yevick equation for hard sphere model.¹⁰ These profiles were fitted using Percus-Yevick hard-sphere model to evaluate the core-diameter of particles. For a system of N identical spherical particles, the scattered intensity $I(q)$ is described as follows:

$$I(q) = N[\langle F(q) \rangle^2 S(q) + \langle F(q)^2 \rangle - \langle F(q) \rangle^2] \quad (7-1)$$

where $F(q)$ and $S(q)$ are the form factor and the interface factor of the particle of the polystyrene domain, respectively. $F(q)$ is given by

$$F(q) = \rho_e V \cdot \frac{3[\sin(qR) - qR \cos(qR)]}{(qR)^3} \quad (7-2)$$

where ρ_e , R and $V=(4/3)\pi R^3$ are the electron density, the radius, and the volume of polystyrene domain,

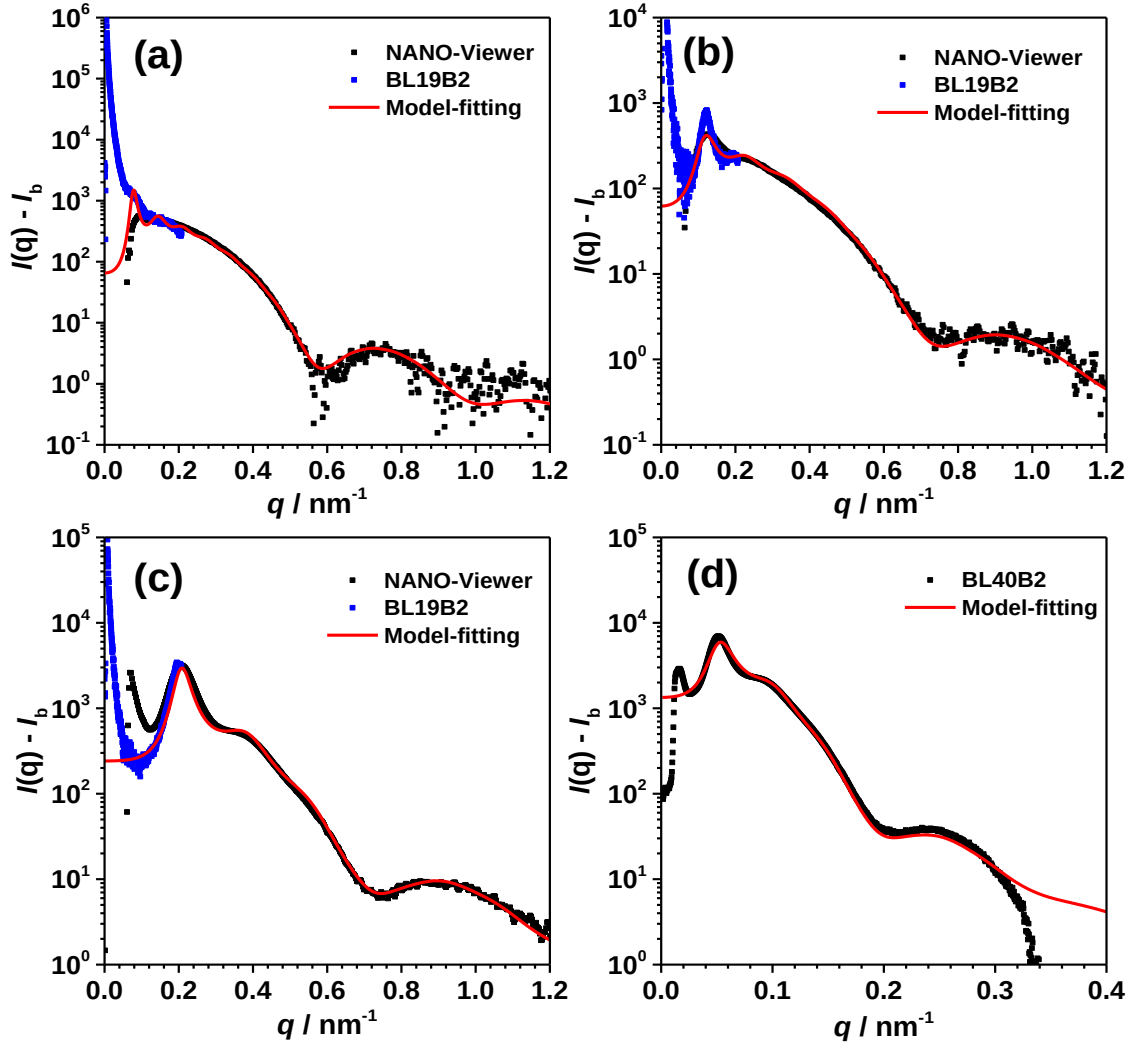


Figure 7-5. SAXS and USAXS profiles of (a) SMS-824k, (b) SMS-282k, (c) SMS-54k gels and USAXS profile of (d) SMS-1172k gel at polymer fraction of 10 wt% measured at room temperature.

respectively. $S(q)$ is written by

$$S(q) = \frac{1}{1 - \rho_n C(q)} \quad (7-3)$$

$$C(q) = -4\pi \int_0^{2R_{HS}} \left[\alpha + \beta \left(\frac{r}{2R_{HS}} \right) + \gamma \left(\frac{r}{2R_{HS}} \right)^3 \right] \frac{\sin(qr)}{qr} r^2 dr \quad (7-4)$$

where ρ_n , and R_{HS} are the number density and the radius of the hard-sphere, and α, β, γ are given by as follows:

$$\alpha = \frac{(1 + 2\varphi)^2}{(1 - \varphi)^4} \quad (7-6)$$

$$\beta = -\frac{6\varphi(1 + \varphi/2)^2}{(1 - \varphi)^4} \quad (7-7)$$

Table 7-3. Result of SAXS measurement for SMS gels

Sample	R_{HS} / nm	$2R_{HS}$ / nm	φ	R_0 / nm	σ / nm
SMS-824k, 10 wt% ^a	50	100	-	7.7	0.55
SMS-282k, 10 wt% ^a	25	50	0.25	5.9	0.75
SMS-54k, 10 wt% ^a	18.7	37.4	0.45	6.0	0.75
SMS-1172k, 10 wt% ^b	62	124	0.35	21.6	3.1
SMS-1172k, 5 wt% ^b	75	150	0.30	21.0	3.0
SMS-1172k, 3 wt% ^b	93	186	0.42	15.2	6.0
SMS-1172k, 1 wt% ^b	138	276	0.49	14.5	7.0
SMS-1172k, 0.5 wt% ^b	162	324	0.40	20.0	3.8

^aResult measured by SAXS with NANO-Viewer system @ Kyoto Univ. and USAXS @ BL19B2 in SPring-8.

^bResult measured by USAXS @ BL40B2 in SPring-8.

$$\gamma = \frac{\varphi(1 + 2\varphi)^2}{2(1 - \varphi)^2} \quad (7-7)$$

where φ is the hard-sphere volume fraction.

From the profiles, the radius of PS cores (R_0) can be determined from the peaks at $q = 0.6\sim 0.8 \text{ nm}^{-1}$. In addition, for the SMS-231k and -54k gels, the radius of hard spheres (R_{HS}) can be determined from the peaks at $q = 0.1\sim 0.2 \text{ nm}^{-1}$. By hard sphere model, the inner part of PS core and the outer part of PMMA chains are considered as a hard sphere, and the value of $2R_{HS}$ indicates the distance between two nearest cores. Since the R_{HS} of SMS-824k was too low to detect by SAXS measurement, USAXS experiment was carried out to measure the signals at low q range. Table 7-3 shows the calculation data for the tested ionic gels. The R_0 values for SMS-824k, -231k and -54k gels were calculated as 7.7, 5.9 and 6.0 nm, respectively, which shows a near value no matter a wide change of the $M_{n, PMMA}$. In contrast, with increasing the $M_{n, PS}$ for SMS-1172k ($M_{n, PMMA}$: 9.49×10^5 , $M_{n, PS}$: 2.23×10^5), the R_0 increased to 21.4 nm (Figure 7-6 and Table 7-3). This result exhibits that the core size was not affected by the molecular weight of middle PMMA but deeply dominated by the molecular weight of PS ends. On the other hand, the $2R_{HS}$ value shows good relationship with $M_{n, PMMA}$, which was inferred directly due to chain length of bridged PMMA segments. Figure 7-6 shows the SAXS profiles of the 10 wt% SMS-824k and SMS-54k gels obtained in a thermal condition from 30°C to

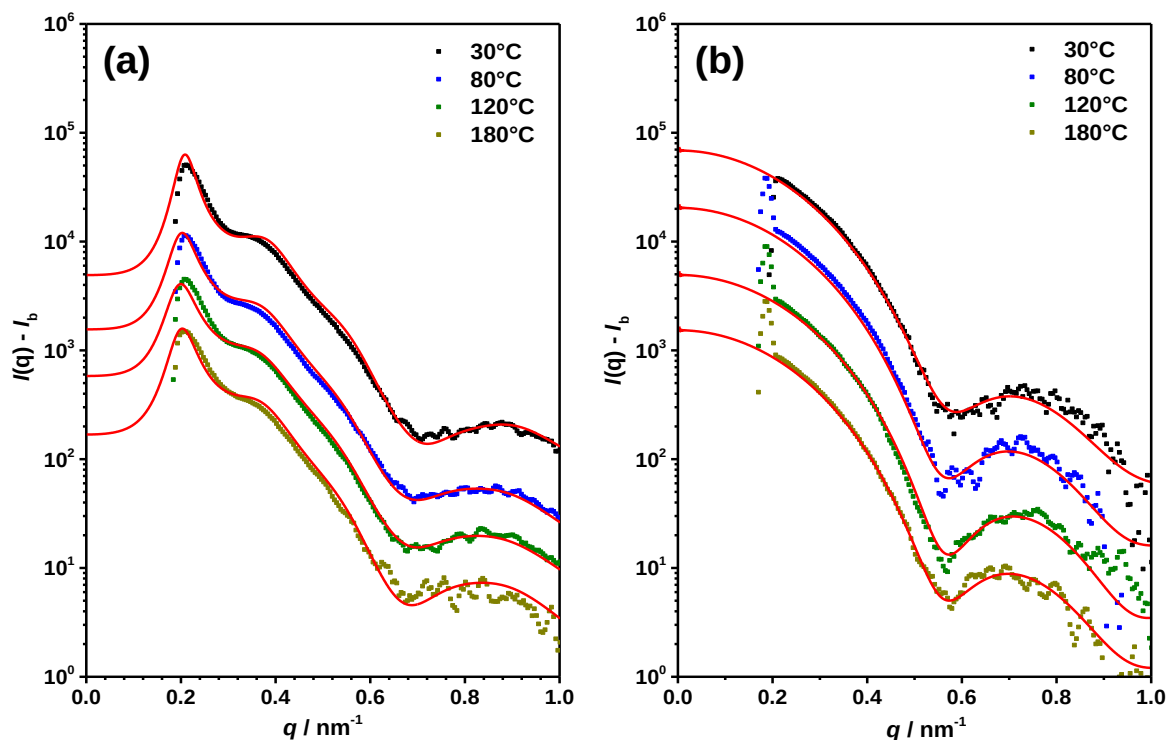


Figure 7-6. SAXS profiles of (a) SMS-824k and (b) SMS-54k gels at polymer fraction of 10 wt% measured at a temperature condition of 30, 80, 120 and 180°C.

180°C. The peak for both gels at $q = 0.6\sim 1.0 \text{ nm}^{-1}$ which represents the structure factor of the aggregated cores remained similarly with the increasing temperature, indicating a thermal-independent gel structure when at a high temperature environment up to 180°C.

Figure 7-7 shows the polymer fraction dependence of USAXS profile for SMS-1172k gel at room temperature. Noted that SMS-1172k/DEME-TFSI solution shows a gel structure when polymer fraction was above 1 wt%, whereas it exhibits a sol state when the fraction decreased to 0.5 wt%. The values of R_0 and R_{HS} were similarly calculated by the fitting of hard sphere model as shown in Table 7-3. At 0.5 wt%, the PS core size R_0 and distance between two nearest cores $2R_{HS}$ were calculated as 20 and 324 nm, respectively. With increasing the polymer fraction, the distance decreased to 124 nm. Whereas the core size exhibited consistent value in this fraction range (from sol to gel state). From this result, we may understand the mechanism of SMS/DEME-TFSI+cosolvent for forming gel structure as: With the cosolvent evaporating from the solution mixture, the SMSs start to aggregate due to the decreasing solubility; as the SMS fraction

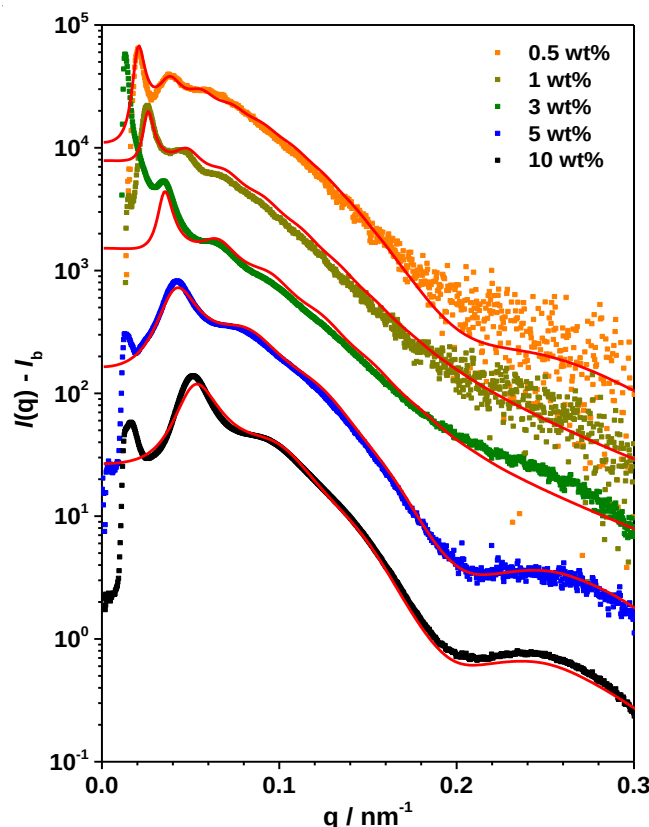


Figure 7-7. USAXS profiles of SMS-1172k gel at a polymer fraction from 0.5 wt% to 10 wt% measured at room temperature.

was higher than one critical concentration, the crosslink structure formed among for the aggregated particles due to the decreasing distance. This result shows good agreement with the result of SMS/[Li(G4)][TFSA] ionic gel report by Watanabe et al.²¹⁾.

7-3-4. Rheological property of ionic gels:

Dynamic rheological measurements for SMS ionic gels were performed at 10 wt% polymer fraction. Figure 7-8 shows the storage (G') and loss (G'') moduli of SMS-824k, -231k and -54k gels, where $M_{n, PS}$ was fixed as $\sim 10^5$ and $M_{n, PMMA}$ was 8.12×10^5 , 2.75×10^5 and 4.30×10^4 , respectively (as shown in Table 7-2), in a oscillation frequency range of 0.1-100 rad/s at three temperature (T) conditions of 28, 120 and 180°C. For these three gels when at room temperature (28°C), the G' exhibited greater values than G'' , indicating the formation of gel. Similar with other ionic gel reports using low molecular weight triBCPs ($M_n < 10^5$), the G'

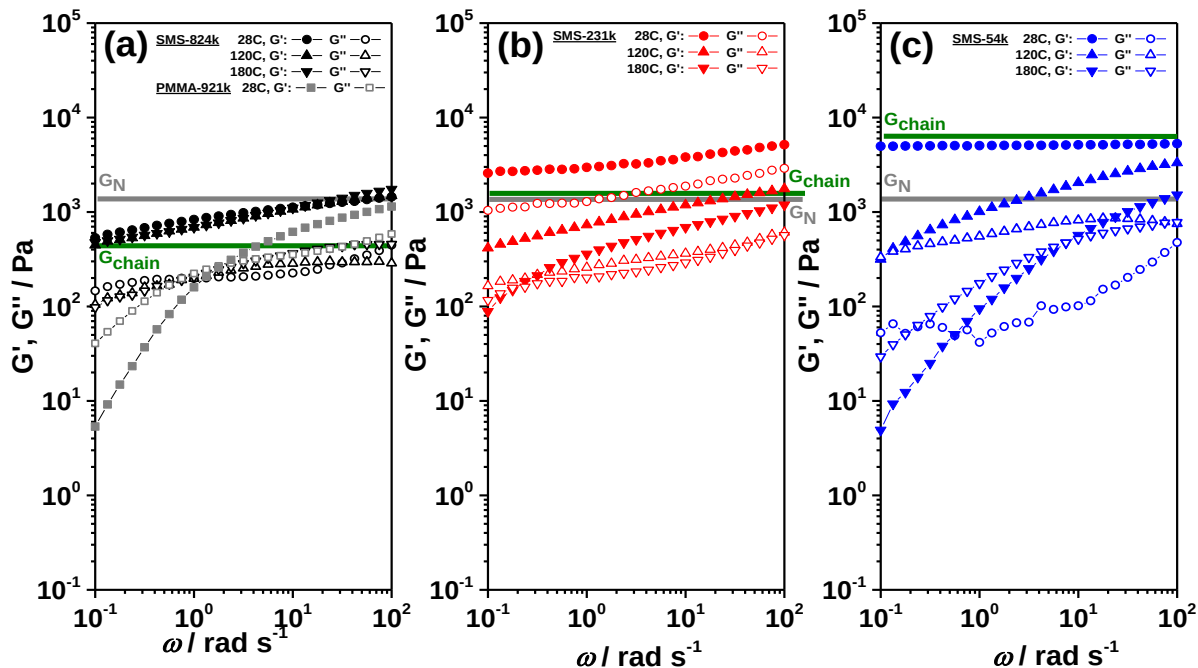


Figure 7-8. Frequency dependences of G' and G'' for (a) SMS-824k (b) SMS-231k and (c) SMS-54k gels at polymer fraction of 10 wt% at 28, 120 and 180°C, and for (a) PMMA-921k at polymer fraction of 10 wt% at 28°C.

value of SMS-54k gel exhibited the rubber regime for the flat region in this frequency range. With increasing the temperature, G' and G'' got close to each other and finally behaved as a fluid ($G'' > G'$) when at 180°C (see Figure 7-8c). Generally, the reverse in values for G' and G'' for a gel could be due to the happen of order-disorder transition (ODT), which indicates the dissolution for the PS cores and equally mixing of BCP chains. However, according to the SAXS experiment results as shown in Figure 7-6, gel structures were clarified as thermal-independent in temperature range of 30-180°C, which means the temperature of ODT should be at least high than 180°C. The flowable behavior for SMS-54k gel when at high temperature was attributed to a thermal movable crosslink, in which PS chains were slowly moving in and out of core particles. On the other hand, with increasing the molecular weight of middle PMMA, G' and G'' values of SMS-824k gel showed no change, indicating somehow the PMMA bridge chains can hardly escape from the crosslinks at high temperature when molecular weight of PMMA block was significantly large. In addition, a relaxation in G'

for SMS-824k gel was observed in this frequency range, which revealed different oscillation behavior between the gels. Here, the G moduli belong to the bridge chain (no influence from chain entanglement) (denoted as G_{chain}) and chain entanglement (G_N) were calculated by the following equation.

$$n = \rho / M_{n, \text{PMMA}} \quad (7-8)$$

$$G = n R T \quad (7-9)$$

where ρ represents the density, R and T are the gas constant and temperature. For the situation of entangled chains of 10 wt% PMMA solution, the entanglement molecular weight M_e ($M_{e, \text{PMMA}} = 256000$, referenced from ref.11) was applied to equation 7-8. The values of G_{chain} and G_N were calculated as $G_{\text{chain}} = 6465, 1580$ and 430 Pa for SMS-54k, -231k and -824k gels, respectively, and $G_N = 1366$ Pa, as shown in green dash lines for G_{chain} and grey dash lines for G_N in Figure 7-8. For SMS-54k gel, the measured value of G' was similar with the G_{chain} which is much larger than the G_N , indicating a non-chain-entangled network structure. In contrast for SMS-824k gel, the measured value of G' showed near value with the G_N at high frequency, and slightly reduced to close to the G_{chain} with the decreasing frequency, which revealed the existence of entangled chains in this network. The relaxation of G' was ascribed to the junction fluctuation of the entangled chains. A good evidence can be shown for the result of PMMA-921k/DEME-TFSI solution (Figure 7-8a, grey symbols). Since the near molecular weight of PMMA segments, PMMA-920k/DEME-TFSI exhibited a fluid characteristic when at low frequency; whereas, a gel behavior when at high frequency was observed, where the G' showed a similar value with the G' of SMS-824k gel and also G_N , which revealed that the G' was dominated by the entangled chains. For SMS-231k gel, it was considered as the intermediate state between SMS-54k and -824k gels.

Figure 7-9(a-c) shows the temperature dependence of G' and G'' values for these three gels at a frequency of 1 rad/s in a temperature range of 28-200°C. As described above, the G' and G'' values of SMS-54k gel intersected at the temperature around 150°C, indicating the gel-sol transition (Figure 7-9c). Over 150°C, the G'' value exceeded the G' value and behaved as a viscous fluid. Whereas, with increasing the molecular weight of middle PMMA, thermal effect on gel structure exhibited less and less. Especially for

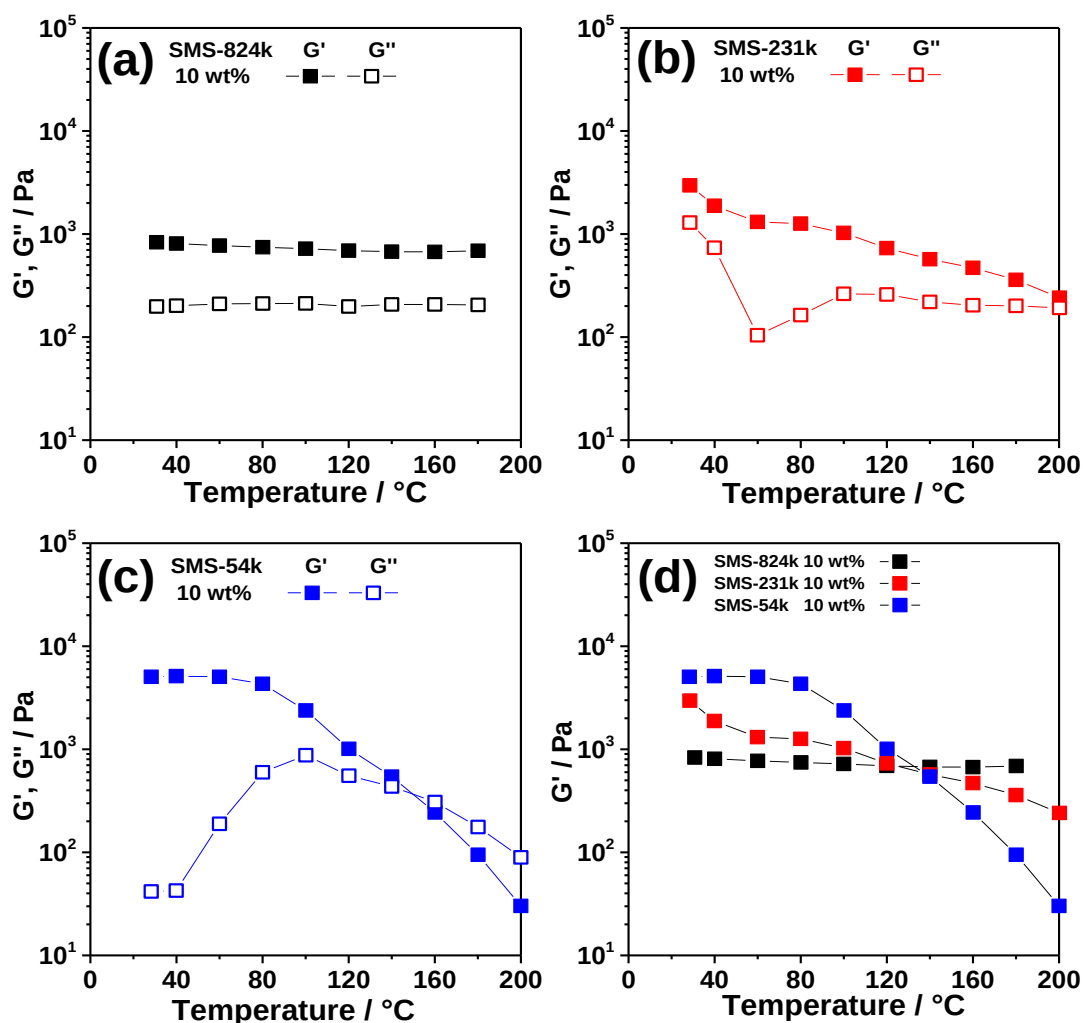


Figure 7-9. Temperature dependences of G' and G'' for (a) SMS-824k, (b) -231k and (c) -54k gels with 10 wt% polymer contents at 1 rad/s. (d) shows the temperature dependences of G' for the three samples.

SMS-824k gel, G' and G'' against T plots showed two parallel lines, and both G' and G'' remained constant values even at the temperature of 180°C. This result revealed that molecular weight of middle PMMA strongly influenced the gel-sol transition behavior which was never found in the reports using low molecular weight polymers. The dependence of molecular weight of PMMA might be ascribed to affinity between PS and PMMA which might be probably explained by the χN parameter, where χ is the Flory-Huggins parameter and N is the degree of polymerization. As the molecular weight was low (N was low, leading a low χN), PS

and PMMA would tend to mix with each other in ionic liquid solvent when T is higher than glass transition temperature (T_g), resulting in the gel-sol transition. In contrast, as the molecular weight of middle PMMA increased (high N and thus high χN), PS would stay separation from the PMMA/ionic liquid phase even at high temperature ($T > 150^\circ\text{C}$).

The G' against T plots of these three gels were summarized in Figure 7-9d. When at room temperature, SMS-824k gel shows the lowest G' value among these three gels. The lower G' value is attributed to the lower density of the bridging cores. As known, the G' modulus is deeply influenced by the crosslinking density of the gel. Despite of the similar weight fraction of the SMS polymer, polymers with higher molecular weight led a lower number of polymer chains, resulting in smaller amounts of PS cores and thus lower crosslinking density.

Figure 7-10 shows the strain dependence of the G' and G'' moduli of these three gels. With increasing the strain, G' modulus of SMS-54k gel firstly exhibited a flat region until the strain reached near 200%. When the strain was over 200%, both G' and G'' values started to decrease, which revealed that the bridge chains started to escape from the crosslinks due to the mechanical tension; the G' and G'' moduli of SMS-54k gel then intersected at the strain of $\sim 300\%$, which means that at such strain the bridge chains can hardly maintain the network structure, leading a liquid behavior over the intersection point (Figure 7-10c). In contrast for SMS-824k gel, G' and G'' similarly decreased from strain of $\sim 100\%$, however the intersection of G' and G'' extended to $\sim 5000\%$, which was even 17 times larger than the SMS-54k gel. Most interestingly, G' exhibited a second flat region at strain = $1000 \sim 2000\%$, which were never obtained from other low-molecular-weight gels. A Measurement with oscillation frequency with a strain of 5% for SMS-824k gel was carried out during the strain process to monitor the structure change in crosslinks. The monitored values of G' and G'' at frequency of 1 rad/s were plotted in Figure 7-10(a)(blue symbol line). Even proceeding a highly strained deformation around the second flat region (strain $< 2000\%$), SMS-824k gel was found to be able to recovery to its initial state, which was never discover from a gel formed by low-molecular-weight BCPs. As the strain was over 2000%, the network structure started to be destroyed and cannot recovery to the initial state even

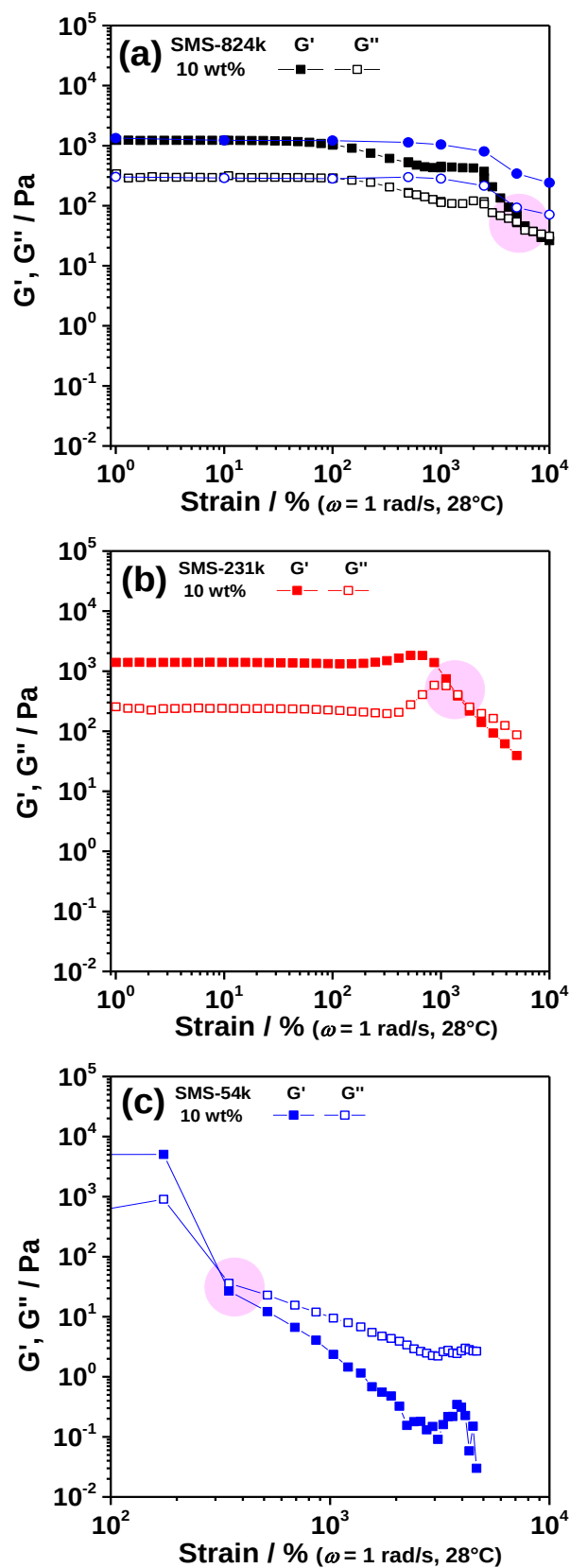


Figure 7-10. Strain dependences of G' (close symbol) and G'' (open symbol) for (a)SMS-824k (black lines), (b)SMS-231k and (c)SMS-54k gels with 10 wt% polymer contents at 28°C and 1 rad/s, and (a)oscillation monitor test of SMS-824k gel (blue line) at 28°C and 1 rad/s with a 5% strain.

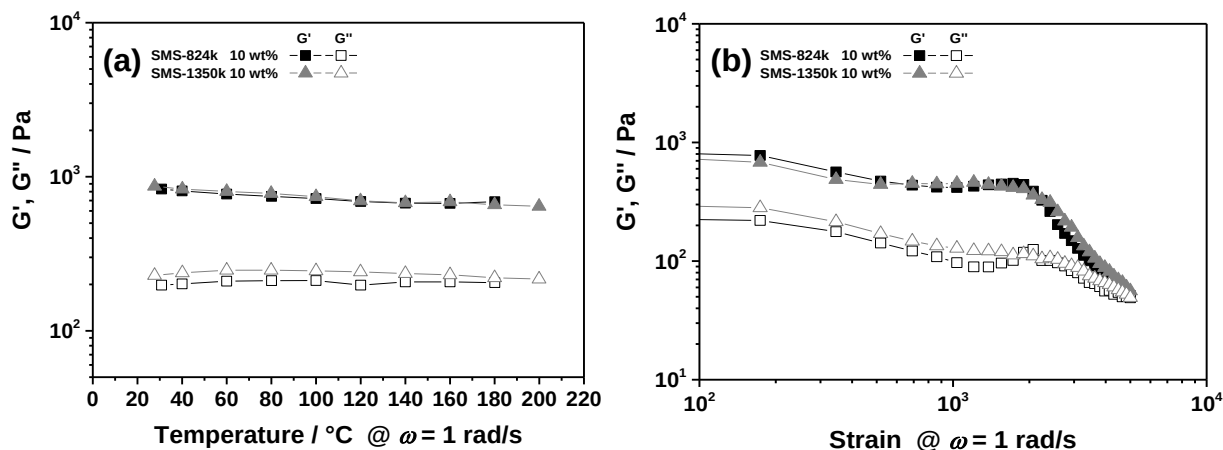


Figure 7-11. (a)Temperature and (b)strain dependences of G' and G'' for SMS-824k and -1350k gels with 10 wt% polymer contents at 1 rad/s.

through a thermal treatment. Although the detail of the crosslink structure and rheological behavior at the second flat regime is still remained debatable, the decreased in G' and G'' at this regime was ascribed to the moved entanglements which lowered the applied stress. This result confirmed a network structure with excellent toughness when applying high-molecular-weight polymer to the bridge chains.

The influence of M_n of the PS ends on the viscoelasticity property was also investigated. Figure 7-11 shows the rheological test result of SMS-824k and SMS-1350k gels at a frequency of 1 rad/s at 10 wt% polymer fraction against the factors of (a) temperature and (b) strain. Apparently, the change of $M_{n, PS}$ between SMS-824k and SMS-1350k gels shows no influence on their rheological properties. Watanabe et al. reported a different sol-gel transition behavior for the ionic gels using low molecular weight SMS polymers.^{5d} In their case, SMS with higher molecular weight of PS blocks shows better thermal stability, where 2 kinds of molecular weight (2.31×10^4 and 3.65×10^4 , M_n of the middle PMMA as 1.89×10^4) were used. In this study, the result was suggested be deeply affected the effect of entangled PMMA chains which dominates the rheological properties of the gels, resulting in elimination of influence from molecular weight change of PS ends.

Figure 7-12 shows the schematic illustration for rheological behavior of a gel in relationship with molecular weight of PMMA bridge. For a gel containing low molecular weight of PMMA bridges, the

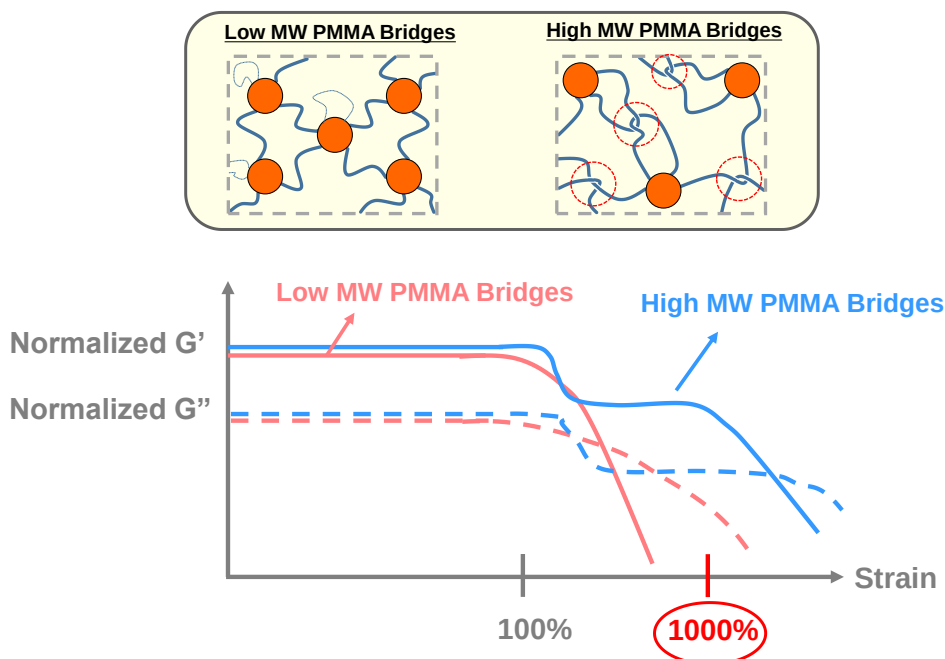


Figure 7-12. Schematic illustration for a gel formed by tciBCPs in terms of the molecular weight of PMMA bridges and their rheological properties in strain condition.

crosslinks were mainly formed by the micro-phase separation core particles. In contrast, with increasing the molecular weight of PMMA bridges, two kinds of crosslinks, micro-phase separation core particles and polymer chain entanglements exist, and the rheological property was dominated by polymer chain entanglements. The difference in their crosslinking structure also brought about different rheological property, especially in strain deformation condition, a gel formed by high-molecular-weight was firstly discovered with the tough, high strength property.

7-4. Conclusion

Synthesis of high-molecular-weight ABA-type triblock copolymers, PS-*b*-PMMA-*b*-PS was investigated with applying ionic liquid solvent, DEME-TFSI to ATRP. Transesterification reaction along with GPC analysis demonstrated the equal addition of styrene monomer to the two functional groups of PMMA macroinitiator, which revealed the successful formation of an ABA-type triblock copolymer. Fabrication of ionic gels was achieved by solvating PS-*b*-PMMA-*b*-PS into DEME-TFSI, which is soluble

for middle PMMA and insoluble for PS ends. The increase in molecular weight of middle PMMA brought about a wide range of gel-producible concentration, in which such a low polymer fraction of 0.5 wt% can even form a gel structure. For synthesis of high-molecular-weight block copolymers, ATRP was performed with the use of ionic liquid solvent or under high pressure. By SAXS measurement, the micro-phase separation structure of the ionic gels was demonstrated that the size of core particles/crosslinks was dominated by molecular weight of PS ends, and molecular weight of middle PMMA was dominant of the distance between the particles. Rheological data indicated that molecular weight of middle PMMA affects the thermo-viscoelastic behavior of the gels very much. As the molecular weight of middle PMMA increased to near 10^6 , the ionic gel exhibited good thermos-stability for no gel-sol transition was observed. For such gel, a relaxation of G' was measured during the dynamic oscillation experiments. This was due to the junction fluctuation of the entangled chains, which is generally observed for high-molecular-weight polymers. In addition, an increased strength was confirmed for bearing a high strain even up to 5000%, in which regime a strained network structure was found to be able to recovery to the initial state with excellent toughness. This discovery is expected to provide a new method to design the network structure of a gel.

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Summary

Two kinds of materials were studied, which naturally divided this thesis into two parts. Studies of concentrated polymer brushes (CPBs) including synthesis techniques and their tribological properties were introduced in **Chapter 2** to **Chapter 5**. In **Chapter 6** and **Chapter 7**, the synthesis of block copolymers (BCPs) and their application in gels were described.

In **Chapter 1**, the background, purposes, and outline of this thesis were described.

In **Chapter 2**, the surface-initiated atom transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) under a high pressure of 500 MPa was investigated. When changing the feed ratio of copper bromide and copper dibromide ($[\text{CuBr}]/[\text{CuBr}_2]$), the $[\text{CuBr}]/[\text{CuBr}_2]$ ratio dependence on the polymerization rate showed good linearity. The equilibrium constant K_{AT} at 500 MPa was 1.5×10^{-6} , indicating good control of the polymerization system. The high pressure effect was successfully conferred to SI-ATRP, leading to a dramatic increase in the thickness of prepared poly(methyl methacrylate) (PMMA) brushes, which showed a maximum thickness up to $2 \mu\text{m}$ despite of a relative low graft density of 0.24 chains/ nm^2 . With increasing $[\text{CuBr}_2]$, a concentration dependence on the graft densities was observed, in which the graft density increased finally to 0.36 chains/ nm^2 in this study. This result is attributed to the decrease of lifetime of propagating radicals and thus eliminated steric hindrance of graft chains. A “cut-off” experiment, in which the brush layers were successfully collected as films, combined with gel permeation chromatography (GPC) analysis, demonstrated similar molecular weights between free polymers and graft polymers even in high pressure conditions. The optimum polymerization condition in this chapter provides the method for synthesizing CPBs of PMMA with thickness and graft density of about $1 \mu\text{m}$ and 0.34 chains/ nm^2 , respectively.

In **Chapter 3**, the author investigated the synthesis of PMMA brushes with large thicknesses in ambient pressure by applying SI-ATRP of MMA in an ionic liquid solvent, N,N-diethyl-N-(2-methoxyethyl) ammonium bis(trifluoromethane sulfonyl) imide (DEME-TFSI). Compared with dimethyl sulfoxide and

anisole, enhancement of the polymerization rate by using DEME-TFSI as the solvent medium was achieved. By applying the pulsed-laser polymerization technique combined with size exclusion chromatography analysis, the propagation rate constant k_p and termination rate constant k_t of MMA containing 75 wt% DEME-TFSI at 60 °C were measured as 1.70×10^3 and 2.79×10^7 , respectively. A thickness of up to 700 nm was successfully achieved for PMMA brushes prepared in DEME-TFSI, even at ambient pressure. The concentration dependence of the deactivator catalyst, copper dichloride (CuCl_2), was also verified in this system according to the results in **Chapter 2**. High $[\text{CuCl}_2]$ resulted in a high graft density of 0.42 chains/ nm^2 , however it also lowered the polymerization rate, resulting in a relatively low thickness of 400 nm. When applying similar conditions with a slightly increased pressure of 50 MPa, the thickness was successfully enhanced to 600 nm with a graft density of 0.39 chains/ nm^2 , indicating the feasibility for combining the high pressure and ionic liquid solvent effects.

In **Chapter 4**, the frictional properties of PMMA brushes on the microscopic scale were investigated by atomic force microscope measurements in toluene. The degree of swelling in toluene for samples with a dry state thickness in the range of 200–900 nm was measured at a constant value of 0.4. For a PMMA brush with a thickness of 1 μm , the friction in boundary lubrication exhibited a relatively high frictional coefficient μ compared with low thickness CPBs. The increased friction was ascribed to the increased interpenetration between the confronted brushes occurring on the topmost surfaces with a thickened unequal part. However, such interpenetration did not hinder the brushes from displaying their super lubrication with a normal force independent μ , of 7×10^{-4} . In hydrodynamic lubrication, the change in film thickness did not affect the friction in this regime. According to a previous report by the author's group, in which the hydrodynamic friction deeply affected by the swelling degree of the brushes, it indicated that friction in this regime was dominated by a film thickness-independent hydrodynamic lubrication layer when the confronted brushes contacted each other.

In **Chapter 5**, the author measured the frictional properties of PMMA brushes in a macroscopic scale by a rotatory type tribometer in DEME-TFSI. For confronted CPBs of PMMA with a small thickness of 66

nm, μ was measured in the order of 10^{-2} at a normal force of 1 N and increased to the order of 10^{-3} when the normal force increased to 2–4 N. Wear tracks at a depth of several μm observed by laser-microscope revealed the brushes were completely damaged during the test. In contrast, for CPBs with a thickness of 950 nm, an extremely low μ of the order of 10^{-3} was measured with the same normal force. It is the first successful measurement of the super lubrication between confronted CPBs on a macroscopic scale. In a measurement with a constant rotating frequency, the μ value showed no change even after 10000 rotatory cycles, indicating excellent durability. By a calculation with a Hertz model, it was confirmed that in such system CPBs can bear a contact pressure of 164 MPa.

In **Chapter 6**, synthesis of poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS) with ultrahigh molecular weight by ATRP under high pressure was investigated. As a common technique for synthesis of BCPs, the “macro-initiator method” was firstly applied, in which the synthesized first PMMA block was followed by a re-precipitation purification and then collected to be used a macro-initiator for the second block polymerization of PS. However, when PMMA was prepared by HP-ATRP as a macro-initiator and isolated, the ability to reinitiate ATRP was lost, although the reason is unclear. The key to successful block copolymerization was the combination of sequential polymerization. Firstly, synthesized PMMA was sequentially applied to the second block polymerization, which led to successful initiation as well as high block efficiency for the second block polymerization. Then, ligand exchange procedures promoted a rapid polymerization of styrene as the second monomer, even at room temperature. By this technique, ultrahigh molecular weight diblock copolymers of PMMA-*b*-PS and triblock copolymers of PS-*b*-PMMA-*b*-PS were successfully synthesized and characterized with $M_n = 2.63 \times 10^6$ and 1.95×10^6 and $M_w/M_n = 1.29$ and 1.18, respectively.

In **Chapter 7**, ionic liquid solvent effect was applied to synthesis of triblock copolymer, PS-*b*-PMMA-*b*-PS for achieving high molecular weight. In the synthetic process, PMMA was prepared by ATRP in DEME-TFSI via the macro-initiator method, and then applied to the second block polymerization of St. The synthesized product was proceeded through a transesterification reaction to separate itself into two segments.

Along with GPC analysis the equal addition of styrene monomer to the two functional groups of PMMA macroinitiator was demonstrated, indicating the successful synthesis of an ABA triblock copolymer. With solvating the PS-*b*-PMMA-*b*-PS into DEME-TFSI, an ionic gel was formed with the occurred micro-phase separation, in which the insoluble PS segments aggregated as the crosslinks. For PS-*b*-PMMA-*b*-PS consisted of high-molecular-weight PMMA segments, ionic gel can be formed in a polymer fraction as low to 0.5 wt%. For the formed gels, small-angle X-ray scattering (SAXS) along with rheological measurement was carried out to investigate their microphase-separation structures and viscoelastic behaviors in terms of molecular weights. By SAXS measurement, the size of crosslinks and the distance between themselves were confirmed to be dominant of molecular weight of PS ends and middle PMMA, respectively. For their rheological properties, a gel formed with high-molecular-weight middle PMMA was found to exhibit specific structure for entangled bridge chain conformation, and viscoelastic behavior for the high thermal stability, high strain tolerance, and excellent toughness.

List of Publication

Chapter 2.

- (1) Controlled Synthesis of Concentration Polymer Brushes with Extraordinarily Large Thickness by High-Pressure Atom Transfer Radical Polymerization

Hsu, S. -Y.; Kayama, Y.; Ohno, K.; Fukuda, T.; Tsujii, Y. *Macromolecules*, submitted.

Chapter 3.

- (2) Controlled Synthesis of Concentration Polymer Brushes with Large Thickness by Atom Transfer Radical Polymerization in Ionic Liquid Solvent Medium

Hsu, S. -Y.; Ohno, K.; Tsujii, Y. *Polymer*, submitted.

Chapter 4.

- (3) Atomic Force Microscopic Study on Tribological Property of “Thick” Concentration Polymer Brushes

Hsu, S. -Y.; Nomura, A., Ohno, K.; Tsujii, Y., to be submitted.

Chapter 5.

- (4) Excellent Resiliency and Lubrication of “Thick” Concentration Polymer Brushes in Macroscopic-Scale Contact

Hsu, S. -Y.; Ohno, K.; Tanabe, T., Kurihara, K.; Sato, T.; Tsujii, Y. *Adv. Materi. Interfaces*, submitted.

Chapter 6.

- (5) Controlled Synthesis of Ultrahigh-Molecular-Weight Block Copolymer by High-Pressure Atom Transfer Radical Polymerization

Hsu, S. -Y.; Ohno, K.; Tsujii, Y. *Polym. Chem.*, submitted.

Chapter 7.

- (6) Controlled Synthesis of High-Molecular-Weight ABA Triblock Copolymers by Atom Transfer Radical Polymerization and their Formation of Ionic Gels

Hsu, S. -Y.; Ishige, R.; Nakanishi, Y.; Ohno, K.; Watanabe, H.; Tsujii, Y., to be submitted.

Other Associated Publications.

- (7) Uniaxial Extensional Flow Behavior of Comb-Shaped Poly(methyl methacrylate)

Ogura, K.; Morioka, K.; Tsujii, Y.; **Hsu, S. -Y.**; Wagner, M. H. *RheolActa* **2015**, 54, 637-645.

- (8) Rheological Characterization of H-Shaped Poly(methyl methacrylate)

Ogura, K.; Morioka, K.; **Hsu, S. -Y.**; Tsujii, Y.; Wagner, M. H. *RheolActa* **2015**, 54, 793-804.

- (9) Radical Propagation Rate Constants of Vinylcarbazole Derivatives Measured by Pulsed-Laser Polymerization Technique

Hsu, S. -Y.; Sakakibara, K.; Tsujii, Y.; Tani, K.; Ohoka, M.; Yamamoto, M., to be submitted.

- (10) Controlled Synthesis of 4-Arm Star-Block Copolymers Toward Ionic Gel with Homogeneous Network Structure

Hsu, S. -Y.; Kida, K.; Ishige, R.; Nakanishi, Y.; Sakakibara, K.; Tsujii, Y., to be submitted.

- (11) Good Lubrication of Polymeric Monolith with Different Pore Sizes in Different Solvents

Sakakibara, K.; **Hsu, S. -Y.**; Yasuda, S.; Ishibashi, D.; Ishizuka, N.; Tanabe, T.; Kurihara, K.; Tsujii, Y., to be submitted.

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