Precise Synthesis and Characterization of Polyelectrolyte Brushes with Cationic Side Chains

石川，達也

https://doi.org/10.15017/1398359

出版情報：九州大学，2013，博士（工学），課程博士
バージョン：
権利関係：全文ファイル公表済
Precise Synthesis and Characterization of Polyelectrolyte Brushes with Cationic Side Chains

カチオン性高分子電解質ブラシの精密合成と特性解析

Tatsuya Ishikawa

July, 2013
## Contents

Chapter 1  General Introduction  
1.1  Polyelectrolytes  
1.2  Lubrication of Biosystems  
1.3  Polymer Brushes  
   1.3.1  Neutral Polymer Brushes in Tribology  
   1.3.2  Polyelectrolyte Brushes  
1.4  Purpose of the Present Study and Contents  
References  

Chapter 2  Controlled Atom Transfer Radical Polymerization of Methacrylate Monomers in Protic Solvents  
2.1  Introduction  
2.2  Experimental  
   2.2.1  Materials  
   2.2.2  Polymerization Procedure  
   2.2.3  Procedure for a Halogen Exchange Model Reaction  
   2.2.4  Characterization  
2.3  Results and Discussion  
   2.3.1  ATRP of MMA  
   2.3.2  Halogen Exchange Reaction  
   2.3.3  ATRP of MEImCl  
2.4  Conclusions  
References
Chapter 3  Effect of Salt Concentration on Chain Conformation of a Polyelectrolyte in Aqueous Solutions 43

3.1 Introduction 44

3.2 Experimental 47

3.2.1 Materials 47

3.2.2 Molecular Weight Characterization 48

3.2.3 Dynamic Light Scattering 48

3.2.4 Small-Angle X-Ray Scattering 51

3.3 Results and Discussion 53

3.3.1 Molecular Weight Characterization 53

3.3.2 Salt-Concentration Dependence of the Hydrodynamic Radius 55

3.3.3 Molecular Weight Dependence of Chain Dimensions of PMTAC in Aqueous NaCl Solutions 56

3.3.4 Data Analysis and Comparison with Theory 58

3.3.4.1 Scattering Function 58

3.3.4.2 Molecular Weight Dependence of the Radius of Gyration 61

3.3.4.3 Molecular Weight Dependence of the Hydrodynamic Radius 64

3.3.4.4 Local Conformation of the PMTAC Chain 66

3.4 Conclusions 67

References 69

Chapter 4  Effect of Salt Concentration on Chain Conformation on High-Density Polyelectrolyte Brushes in Aqueous Solutions by Small-Angle X-ray Scattering 72

4.1 Introduction 73

4.2 Experimental 74
4.2.1 Materials 74
4.2.2 Immobilization of the Surface Initiator 74
4.2.3 Surface-initiated Atom Transfer Radical Polymerization of MTAC from BHE-SiNPs 75
4.2.4 Measurements 76

4.3 Results and Discussion 77
4.3.1 Preparation of PMTAC-SiNP 77
4.3.2 Estimation of Core Radius of SiNPs 79
4.3.3 Chain Dimensions of Grafted PMTAC Chain in Aqueous NaCl Solutions 80
4.3.4 Theoretical Analysis of Brush Thickness: Daoud–Cotton-Type Scaling Model 90

4.4 Conclusions 94

References 95

Chapter 5 Tribological Behavior of a Polymer Brush with Ionic Liquid Moiety 97
5.1 Introduction 98
5.2 Experimental 101
5.2.1 Materials 101
5.2.2 Characterization 104
5.2.2.1 Size Exclusion Chromatography 104
5.2.2.2 Differential Scanning Calorimetry 104
5.2.2.3 X-ray Photoelectron Spectroscopy 105
5.2.2.4 Contact Angle Measurement 105
5.2.2.5 Surface Analysis and Thickness of Polymer Brush 105
Chapter 1

General Introduction
1.1 Polyelectrolytes

Polyelectrolytes are polymers containing ionizable groups in their side chains or main chains. Polyelectrolytes play important roles in both industry and nature because they constitute many biological macromolecules such as tubulin, actin, lubricin, and DNA. From an industrial point of view, quaternary-ammonium-group-containing polymers derived from aminoalkyl (meth)acrylates are among the most extensively used polyelectrolytes in the chemical industry. These polymers have a broad range of industrial applications, for example, in the flocculation of particulate matter, the manufacture of fine paper, sludge dewatering, filtration, oil recovery, the cosmetic and related industries. An example of biomechanical systems using polyelectrolytes as biolubricants will be introduced below.

1.2 Lubrication of Biosystems

Friction is the force that resists the relative motions of solid surfaces, fluid layers, and material elements sliding against each other. Mechanical systems necessarily have frictional surfaces in their system. The function, performance, and reliability of a system are strongly affected by their frictional and wear-resistant properties, that is, the lubricating properties of the system. Friction and wear are dominated by interactions between surfaces moving relative to each other. The study of the science and technology of interacting surfaces in relative motion, and of related subjects and phenomena is known as tribology. The word tribology is derived from the Greek word *tribos*, which means “friction, rub, grind,” “to wear away,” or “science of friction.” Tribology is now considered to be a generic technology for engineering.
Given the rich diversity of life on our planet, it is easy to forget that all forms of life are essentially mechanical systems with multiple elements that need to slide easily past one other without being damaged, in order to effectively navigate their environment. Like artificial mechanical devices, the optimum performance and functionality of a biomechanical system needs effective lubrication of surfaces in relative motion. In many respects, the engineering challenges in managing friction and avoiding wear in artificial macro-, micro-, and nano-scale devices are not different from those faced by biological systems. Despite inherent limitations, nature has managed to create biolubrication systems exhibiting ultra-low friction coefficients, excellent wear resistance, and the capability to change environmental conditions that greatly exceed the performance of any artificial system devised so far. Nature therefore provides a useful template for new and innovative solutions to tribological problems. One of the most well-known and thoroughly investigated biolubrication systems is mammalian articular joints. To cope with high loading and shear stresses, nature often uses a variety of intermediately sized (~5–100 nm) surface-active biological lubricant molecules, typically lipids, short-chain polysaccharides, or glycoproteins whose protein backbones are decorated with large numbers of grafted sugar chains.\textsuperscript{6,7}

![Figure 1.1](image)

**Figure 1.1** Structure of proteoglycan aggregate found in the mammalian joints.
Mucins are the largest class of glycoprotein boundary lubricants, and they are found in abundance in articular joints. Figure 1.1 shows the structure of the proteoglycan aggregate that is a major component of cartilage joints.

Recent surface force apparatus (SFA) experiments investigating the lubrication behavior of lubricin, which is a mucin-like glycoprotein found in mammalian joints, showed that lubricin adsorbs to a variety of different types of surfaces in a unique and specific “loop” conformation to form protective polymer brush-like layers with extended loops and tails of thickness roughly 100 nm, as shown in Figure 1.2. In addition, the adsorbed lubricin layer lowers the frictional forces and protects the surfaces against wear, protects the substrates from adhering to each other, and prevents adsorption of other proteins, polymers, or wear debris.

Figure 1.2 Proposed physisorbed configurations of lubricin on (a) negatively charged surface, (b) hydrophobic surface, and (c) positively charged surface.

In SFA measurements, polymer brush-like behavior of lubricin was observed with normal and frictional forces, which support the idea that chemically immobilized polyelectrolyte brushes may serve as realistic models for biolubrication, and provide
novel biocompatible, low-friction, low-wear coatings for the surfaces of joint implants.\textsuperscript{11,12}

1.3 Polymer Brushes

1.3.1 Neutral Polymer Brushes in Tribology

Polymer chains end-grafted to a surface with a sufficiently high graft density are commonly referred to as polymer brushes. Chain conformation of end-grafted chains strongly depends on graft density $\sigma$, as indicated in Figure 1.3. The low-density grafted chains adopt a “mushroom” conformation with a coil dimension similar to that of ungrafted chains.

![Figure 1.3 schematic representations of polymer brushes.](image)

The densely grafted brush chains assume a highly extended conformation in good solvents because of the osmotic pressure and excluded volume effects among neighboring chains. The equilibrium thickness of the swollen brushes is determined by the balance between the osmotic pressure and extensional stress of the chains. Polymer brushes play important roles of both scientific and technological relevance, even beyond colloidal stabilization. Polymer brushes have a wide variety of potential applications
such as lubrication,\textsuperscript{13--15} tuning of adhesion\textsuperscript{16} and wetting properties,\textsuperscript{17} enzyme immobilization, improvement of biocompatibility,\textsuperscript{12} stimuli-responsive surfaces, and chromatography.\textsuperscript{18} In particular, polymer brushes on solid surfaces provide excellent lubrication in good solvents.\textsuperscript{13--15,19} They are able to support a significant load, but have extraordinarily low friction coefficients. The efficient lubrication of solvated brushes is attributed to the osmotic pressure of the compressed chains, together with weak interpenetration between the two opposite brushes.\textsuperscript{20}

Klein et al. have studied the normal and shear forces between opposing polystyrene (PS) brushes immersed in toluene using an SFA,\textsuperscript{21} although the brushes were prepared by the “grafting to” method. Note that the “grafting to” method gives a limited surface graft density because of the steric hindrance of the grafted chains. The brushes were found to function as an extremely efficient lubricant up to a moderate pressure because the interpenetration between opposing brushes was suppressed by configurational entropy effects.\textsuperscript{20--22} At much higher compressions, larger shear forces are observed because of the mutual interpenetration of the brushes and the elastic stretching of the chains when their tethered ends begin to move laterally.\textsuperscript{23} When the shear rate is increased to an extent where it is comparable to the relaxation rate of the chain segments, the opposing chains in the interfacial region do not become entangled; this is because of a self-regulating mechanism, resulting in lower shear forces. In a theta solvent, large shear forces can be detected even at milder levels of compression, because of changes in the strength of the frictional interactions,\textsuperscript{22} interpenetrating depths,\textsuperscript{24} and vitrification of the compressed polymer layers.\textsuperscript{25,26} Kilbey et al. have investigated the influence of polymer–solvent interactions on the frictional properties of PS brushes in cyclohexane at various temperatures.\textsuperscript{27}
During recent decades, various types of well-defined, high-density (or concentrated) polymer brushes have been prepared via a surface-initiated controlled radical polymerization technique, owing to the fast progress in controlled radical polymerization techniques. Tsujii et al. reported the frictional coefficient of high-density poly(methyl methacrylate) (PMMA) brushes (>0.5 chains nm\(^{-2}\)) in toluene remained low, at values lower than \(5 \times 10^{-4}\), over the whole range of loads studied. However, the frictional coefficient of low-density (semi-diluted) PMMA brushes (0.024 chains nm\(^{-2}\)) steeply increased with increasing normal load, approaching a constant value of about 0.1. Therefore, the graft density of polymer brushes is one of the dominant factors in determining the frictional properties of polymer brushes.

### 1.3.2 Polyelectrolyte Brushes

Polyelectrolyte chains densely end-grafted to a surface are called polyelectrolyte brushes.\(^{28}\) As stated in Section 1.1, the polymers constituting lubricin, which coats the cartilage in human and animal joints, are charged and form brush-like structures,\(^{6,10}\) thus lubrication and interactions among ion-containing polymer brushes have been extensively investigated both theoretically\(^{29-31}\) and experimentally.\(^{11,12,32-35}\) Polyelectrolyte brushes exhibit lower friction coefficients and monomer penetration than neutral brushes with identical graft densities, and polyelectrolyte brushes support a much higher normal load than neutral brushes for the same degree of compression.\(^{36}\) This is because an extra normal force contribution is provided by the counterion osmotic pressure that arises from polyelectrolyte brushes. The swollen structures of polyelectrolyte brushes under aqueous conditions are very important in understanding the frictional properties of polyelectrolyte brushes.
Polyelectrolyte brushes can be divided into two groups. One is *quenched* polyelectrolyte brushes, whose polyelectrolyte chains are strongly dissociated, e.g., poly(styrene sulfonic acid). Hence, the degree of dissociation of ionic monomer units of quenched polyelectrolyte brushes is independent of the system pH. The other is *annealed* polyelectrolyte brushes. The annealed polyelectrolyte brush consists of weak polyelectrolyte chains, e.g., poly(acrylic acid). The degree of dissociation of annealed polyelectrolyte brushes strongly depends on both the pH and ionic strength of the solution. Therefore, pH is a dominant variable and the brush shows pH-sensitive features.

In the cases of both quenched and annealed polyelectrolyte brushes, the swollen thickness of the brushes and interactions between charged segments are strongly affected by the ionic strength of the system. Helm and coworkers demonstrated that the brush thickness is independent of the salt concentration of the solution ($C_s$) in the region in which the external concentration is much lower than the concentration of counterions trapped in the brush, using X-ray reflectometry. In contrast, when $C_s$ exceeds the concentration of trapped counterions in the brush, the brush thickness decreases with increasing $C_s$, and is proportional to $C_s^{-1/3}$. Moreover specific interactions of the counterions must be considered to understand the swelling properties quantitatively. Direct visualization of highly stretched polyelectrolyte brush chains was first achieved for spherical polyelectrolyte brushes using cryogenic transmission electron microscopy. The basic theory of polyelectrolyte brushes is now gradually beginning to be understood.
1.4 Purpose of the Present Study and Contents

Almost all reports on chain conformations of polyelectrolyte brushes focus only on the changes in thickness of the brushes themselves, and are limited to brushes with moderate graft densities, less than about 0.1 chains nm\(^{-2}\). From a fundamental point of view, in order to understand the surface properties of polyelectrolyte brushes in depth, it is interesting and important to examine how the conformations of polyelectrolyte chains immersed in aqueous solution change when they form a high-density polyelectrolyte brush at an interface. Although the chain dimensions and chain conformations in aqueous solution of a few specific polyelectrolytes, for instance, sodium poly(styrene sulfonate), poly(acrylic acid), and poly(2-vinylpyridinium) salts, have been extensively investigated by many researchers, fundamental data on the other typical polyelectrolyte chains, such as polymers with quaternized ammonium groups are still limited. Additionally, precise (direct) synthesis of polyelectrolytes and polyelectrolytes brushes is still a difficult, despite the rapid progress in living radical polymerization techniques.

Against this background, the following subjects are discussed in this thesis:
1) precise synthesis of polyelectrolytes and polyelectrolyte brushes via a controlled radical polymerization technique;
2) differences among chain dimensions and conformations of polyelectrolytes and polyelectrolyte brushes in aqueous solutions;
3) tribological properties of polyelectrolyte brushes.

The basic concept of this thesis is presented in Figure 1.4.

In Chapter 2, the methods for the direct synthesis of well-defined polyelectrolytes from electrolyte monomers in polar protic solvents by a metal-catalyzed living radical polymerization are discussed. The use of polar protic solvents as reaction media is
inevitable for the synthesis of polyelectrolytes, because the solubilities of polyelectrolytes are quite limited in polar solvents, which usually cause unfavorable side reactions in the metal-catalyzed living radical polymerization.

In Chapter 3, single chain dimensions and chain conformations of well-defined cationic polyelectrolytes in aqueous NaCl solutions are studied by dynamic light scattering and small-angle X-ray scattering. Changes in the local chain conformations of polyelectrolytes, depending on the ionic strength of the solution, is first revealed on the basis of a helical worm-like chain theory.

In Chapter 4, the chain dimensions and chain conformations of cationic polyelectrolyte brushes immobilized on silica nanoparticles in aqueous NaCl are studied by small-angle X-ray scattering. The differences between the chain conformations of unbound polyelectrolyte and polyelectrolyte brushes are compared and discussed.

In Chapter 5, the synthesis of a new type of polyelectrolyte brush, inspired by room-temperature ionic liquids, is described. Ionic liquids are known to be ideal candidates for versatile lubricants that can be used even under very severe conditions such as extremely high temperatures and in a vacuum. The tribological properties of polyelectrolyte brushes with ionic liquid moieties are determined and discussed.
Figure 1.4 The basic concept of this thesis.
References

(DOI: 10.1039/c3py00146f)


Chapter 2

Controlled Atom Transfer Radical

Polymerization of Methacrylate Monomers in Protic Solvents
2.1 Introduction

As mentioned in the previous chapter, it is necessary to synthesize polyelectrolytes directly from electrolyte monomers via controlled radical polymerization in order to obtain well-defined polyelectrolyte brushes. Atom transfer radical polymerization (ATRP) is one of the most powerful controlled radical polymerization techniques for the synthesis of polymeric materials with predetermined molecular weights, low polydispersities, and controlled chain architectures.\(^1\) ATRP and other controlled radical polymerizations are based on establishing a rapid dynamic equilibrium between a minute amount of growing free radicals and a large majority of dormant species. The contribution of the termination reaction will therefore be small (less than a few percent of the total number of chains) under appropriate conditions.

ATRP is controlled by equilibrium between propagating radicals and dormant species, predominately in the form of initiating alkyl halides/macromolecular species \((P_nX)\). The dormant species periodically react with the rate constant of activation \((k_{act})\) with transition metal complexes in their lower oxidation state \((Mt^m/L)\) which acts as activators to intermittently form growing radicals \((P_n^\cdot)\) and deactivators–transition metal complexes in their higher oxidation state \((X–Mt^{m+1}/L)\). Here, \(Mt^m\) represents the transition metal species in oxidation state \(m\) and \(L\) is a ligand.
The deactivator reacts with the propagating radical in a reverse reaction ($k_{\text{deact}}$) to re-form the dormant species and the activator. ATRP is a catalytic process and can be mediated by many redox-active transition metal complexes (Cu$^\text{I}$/L and X–Cu$^\text{II}$/L system has been the most often used transition metal but other studied metals include Ru, Fe, Mo, Os, etc.).

ATRP can be applied to a large variety of monomers, and can be carried out either in the bulk, in solution, or in heterogeneous media. Recently, room-temperature ionic liquids (ILs) have been attracting much attention as novel “green” reaction media because they have many interesting properties such as negligible volatility, low flammability, and reusability. Because of their unique physical properties, both the thermodynamics and kinetics of reactions carried out in ILs are different from those in conventional solvents.$^2$ ILs have already been used as reaction media for conventional radical polymerizations as well as controlled radical polymerizations such as ATRP,$^3,4,5,6$ reverse ATRP,$^7$ activators regenerated by electron transfer (ARGET) ATRP,$^8$ reversible addition and fragmentation (RAFT) polymerization,$^9,10$ organotellurium-mediated living radical polymerization (TERP),$^{11}$ and nitroxide-mediated polymerization
Most of these demonstrated polymerization of non-ionic monomers such as methyl methacrylate (MMA), styrene, and acrylonitrile. The polymerization rate in ILs is usually higher than in the bulk or in conventional solvents because of the polarity of ILs, which contributes to stabilization of a transition state involving a polar polymer-end radical and a monomer. Also, the termination rate in ILs decreases with increasing viscosity of the medium.

Recently, our research group reported the precise synthesis of ionic polymers, poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] (PMTAC) and poly[3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammonatopropanesulfonate] (PMAPS) via ATRP, using a mixture of imidazolium ILs with chloride anions and 2,2,2-trifluoroethanol (TFE) as the solvent. In a previous study, ILs were used as additives. TFE is known to be a thermodynamically better solvent for PMAPS than aqueous salt solutions are. Thereby, the ATRP of those corresponding ionic monomers in ILs/TFE proceeded in a homogeneous state to produce polymers with predictable molecular weights (in the range $10^4$–$10^5$ g mol$^{-1}$) and narrow molecular-weight distributions ($M_w/M_n = 1.12$–1.13). In contrast to the above-mentioned previous studies using ILs as solvents, we found that the rate of polymerization of ionic monomers was significantly reduced by the addition of a small amount (several weight percent) of
imidazolium chloride. However, the role of imidazolium chloride remains unclear. In general, ATRP of ionic monomers is performed only in polar protic solvents, including water, because of the limited solubilities of ionic monomers.\textsuperscript{16} ATRP in polar protic solvents is usually fast, and yields polymers with relatively broad molecular weight distributions, indicating loss of control. This is because several side reactions\textsuperscript{17} occur in the presence of protic solvents: solvolytic displacement of the halogen atom from an initiator or a dormant polymeric species, disproportionation of the Cu\textsuperscript{I}-based ATRP catalyst, and solvolysis of the ATRP deactivator Cu\textsuperscript{II}L\textsubscript{n}X (L = ligand, X = Br, Cl, etc.) These side reactions can lower the concentration of the deactivator, leading to increase the concentration of radical species and then fast polymerization and loss of control. The reduction in the concentration of the deactivator in aqueous media can be suppressed by the addition of halide salts to regenerate the dissociated Cu\textsuperscript{II}–X species.\textsuperscript{18} As a result, the deactivation rate increases, and the ATRP proceeds in a controlled manner. On the other hand, mixed halide initiation systems, R–X/Cu–Y (R = alkyl groups; X, Y = Cl or Br), have been used to improve control of ATRP.\textsuperscript{19,20} Halide exchange during ATRP reactions especially by the bromide initiator/copper chloride system, provides faster initiation, slower propagation, and thus better control.\textsuperscript{19} In our previous studies, we used a mixed halide system such as R–Br/CuBr and imidazolium
chlorides. We observed a reduction in the polymerization rate and much better control of ATRP. These results implied that well-controlled ATRP in protic solvents can be achieved by simultaneously using the two above-mentioned effects, i.e., regeneration of the lost deactivator and the halide exchange reaction.

In the work described in this chapter, ATRP of MMA in TFE combined with various types of organic salts with chloride anions was carried out to demonstrate the effects of imidazolium chlorides and other organic salts on ATRP, to establish a method for controlling ATRP in protic solvents. In addition, a methacrylate monomer containing an imidazolium chloride moiety was synthesized and polymerized by ATRP without organic salts, to produce a well-defined poly(imidazolium salt) directly.

2.2 Experimental

2.2.1 Materials

Copper(I) bromide [CuBr, Wako Pure Chemical Industries, Ltd. (Wako), Osaka, Japan, 99.9%] was purified by successive washing with acetic acid and ethanol and dried under vacuum. Ethyl 2-bromoisobutyrate [EBiB, Tokyo Chemical Inc. (TCI), Tokyo, Japan, 98%], ethyl 2-chloropropionate (ECIP, TCI, 97%), triethylamine (TCI, 99.0%), and \( N,N,N',N',N' \)-pentamethyldiethylenetriamine (PMDETA, TCI, 98%) were dried and distilled over \( \text{CaH}_2 \) before use. 2-Propanol (\( \text{PrOH}, \text{Wako}, 99.7\% \))
was distilled over magnesium ribbon. 2,2’-Bipyridyl (bpy, Wako, 99.5%), TFE (TCI, 99.0%), 1-ethyl-3-methylimidazolium chloride (EMImCl, Aldrich, 98.0%), 1-hexyl-3-methyl- imidazolium chloride (HMImCl, Kanto Chemical Co., Inc., Tokyo, Japan, 98.0%), 1-ethylpyridinium chloride (EtPyCl, TCI, 98%), lithium chloride (Wako, 99.0%), tetrabutylammonium chloride (TBACl, TCI, 98%), 1-butyl-3-methylimidazolium bromide (BMImBr, Merck Chemicals, 98%), 2-bromoisobutyryl bromide (Aldrich, 98%), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP, Wako, 99%), and 1-hexanol (Wako, 97%) were used without further purification.

Dichloromethane (Kishida Chemical, 99.5%) was purified by passing it through the columns of a glass contour solvent system (Nikko Hansen & Co., Ltd., Osaka, Japan) under a high-quality argon gas atmosphere. 2-Chloroethyl methacrylate was synthesized by reacting 2-chloroethanol and methacryloyl chloride in the presence of pyridine in dichloromethane at 273 K, according to the previously reported method.\(^\text{21}\)

**Synthesis of Hexyl 2-bromoisobutyrate (HBiB)**

Bromoisobutyryl bromide (109 mmol) was added dropwise to a stirred solution of 1-hexanol (104 mmol) and triethylamine (132.7 mmol) in dry dichloromethane (60 mL) under a nitrogen atmosphere with cooling in an ice bath. The solution was stirred overnight at room temperature (Scheme 2.1).
After filtration to remove the hydrochloric salt, the reaction solution was washed with 0.1 N HCl, water, and saturated NaHCO$_3$, and dried over anhydrous MgSO$_4$. After filtration, the organic layer was concentrated under reduced pressure. The product was distilled under reduced pressure to give HBiB as a colorless liquid (87.6 mmol, 84%).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 0.90 (t, 3H, CH$_2$CH$_3$, $J = 7.0$ Hz), 1.32 (m, 4H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.39 (m, 2H, CH$_3$CH$_2$CH$_2$CH$_2$), 1.68 (m, 2H, OCH$_2$CH$_2$), 1.93 (s, 6H, BrC(CH$_3$)$_2$), 4.17 (t, 2H, OCH$_2$, $J = 6.6$ Hz).

**Synthesis of 1-(2-Methcryloyloxy)ethyl-3-ethylimidazolium chloride (MEImCl)**

A mixture of 2-chloroethyl methacrylate (106 mmol) and 1-ethylimidazole (112 mmol) was stirred at 343 K for 48 h. During the reaction, a small amount of $p$-tert-butylcatechol (about 50 mg) was added to the reaction mixture to inhibit the thermal polymerization of the resulting monomer MEImCl (Scheme 2.2).
The resulting yellow viscous liquid was washed several times with hexane by decantation. The product was dissolved in ca. 10 mL of dichloromethane and poured into a large amount of hexane to give a precipitate. The product was collected and dried in vacuo to form a white powder in a yield of 24.7 g (101 mmol, 95%). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ (ppm) 1.40 (t, 3H, CH$_2$CH$_3$, $J = 7.4$ Hz), 1.83 (s, 3H, CH3), 4.22 (q, 2H, CH$_2$CH$_3$, $J = 7.3$ Hz), 4.45 (t, 2H, OCH$_2$CH$_2$, $J = 5.0$ Hz), 4.55 (t, 2H, OCH$_2$CH$_2$, $J = 5.0$ Hz), 5.70 and 6.03 (m, 2H, CH$_2$=), 7.87 (dd, 2H, N–CHCH–N, $J = 2.8$, 2.0 Hz), 9.52 (s, 1H, NCHN).

2.2.2 Polymerization Procedure

A typical protocol for ATRP of MMA in TFE was as follows. MMA/TFE solution (3.3 g) containing organic salts was charged in a glass tube, and degassed by repeated freeze–pump–thaw cycles. CuBr (0.002 mmol) and PMDETA (0.004 mmol) were introduced into another glass tube, and then the glass tube containing CuBr and PMDETA was degassed by several cycles of vacuum pumping and flushing with argon. A free ATRP initiator EBiB (0.002 mmol) diluted with TFE, was added to the catalyst, to immediately give a homogeneous solution with a characteristic blue color. The copper catalyst solution was degassed by repeated freeze–pump–thaw cycles and then
injected into the monomer solution. The resulting reaction mixture was again degassed
by repeated freeze–pump–thaw cycles to remove oxygen, and then the tube was sealed
under reduced pressure. The polymerization reaction was carried out by stirring in an oil
bath at 333 K for 24 h (Scheme 2.3). After a certain period of time, the reaction was
stopped by opening the glass vessel to the air. The reaction mixture was poured into a
large amount of methanol to recover the polymer.

Scheme 2.3 Atom Transfer Radical Polymerization of Methacrylate Monomers in TFE in the
Presence of Organic Salts

The ATRP of MEImCl was also carried out in a similar manner to that of MMA,
using CuBr/bpy as a catalyst instead of CuBr/PMDETA. The reaction mixture was
poured into a large amount of diethyl ether to precipitate the resultant polymer. The
MEImCl monomer was also insoluble in diethyl ether. The conversion of the MEImCl
monomer was determined by $^1$H NMR spectroscopy of the precipitates in
dimethylsulfoxide-$d_6$, using the ratio of integrated signals at 5.5–6.0 ppm, from the
monomer vinyl protons, and at 7.9–9.5 ppm, from the imidazolium protons of the polymer and monomer.

2.2.3 Procedure for a Halogen Exchange Model Reaction

In order to confirm whether the halogen exchange reaction occurs between propagating chain ends and added organic chloride salts, a halogen exchange model reaction was carried out under similar conditions as those for ATRP.

CuBr (0.167 mmol) and bpy (0.335 mmol) were added to a glass tube with a stopcock and dried by five cycles of vacuum pumping and flushing with argon. A solution of EMImCl (3.40 mmol), HBiB (0.44 mmol), and TFE (20 g) was injected into the glass tube. The resulting reaction mixture was degassed by three freeze–pump–thaw cycles, and then stirred in an oil bath at 333 K under an argon atmosphere (Scheme 2.4). The reaction was stopped by opening the glass tube to the air at room temperature. The reaction mixture was then condensed, using a rotary evaporator, and dried in vacuum to
remove the solvent. The reaction mixture was then dissolved in water and the product was extracted with hexane. The product was again dried under reduced pressure.

### 2.2.4. Characterization

The number-average molecular weights ($M_n$) and molecular-weight distributions ($M_w/M_n$) of PMMA and PMEImCl were determined by size-exclusion chromatography (SEC). SEC measurements for PMMA were carried out at 313 K on a TOSOH HLC–8220 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three analytical columns (TOSOH TSKgel Super H6000, 4000, and 2500), and a refractive index detector. Tetrahydrofuran (THF) was used as the eluent, at a flow rate of 0.6 mL min$^{-1}$. Poly(methyl methacrylate) standards were used to calibrate the SEC system. In the case of SEC measurements of PMEImCl, a multi-angle light-scattering (MALS) detector (Dawn Heleos II; Wyatt Technology Corp., Santa Barbara, CA, USA), operated at a wavelength of 658 nm, and a refractive index (RI) detector (RID-10A; Shimadzu, Kyoto, Japan) were used to determine the absolute $M_n$ and $M_w/M_n$ values. Aqueous acetic acid (0.5 M) containing sodium nitrate (0.2 M) was used as the eluent, at a flow rate of 0.8 mL/min at 313 K. Normalization of the MALS detectors and corrections for the delay volume between the MALS and RI detectors were performed.
using a sample of poly(ethylene oxide) (PEO) with $M_w = 2.22 \times 10^4$ and $M_w/M_n = 1.08$.

The Rayleigh ratio at a scattering angle of 90° was based on that of pure toluene. The polystyrene gel columns TSKgel G5000PWXL-CP × 2 and TSKgel G3000PWXL-CP (Tosoh Corp., Tokyo, Japan) are claimed to separate polymers with molecular weights in the ranges (PEO) from $5 \times 10^5$ to $4 \times 10^2$ and from $5 \times 10^4$ to $2 \times 10^2$ g mol$^{-1}$, respectively. The angular dependence of the scattered light was extrapolated to zero angle using the linear Berry fitting method. The specific refractive index increment ($dn/dc$) of PMEImCl in aqueous acetic acid (0.5 M) containing sodium nitrate (0.2 M) at 298 K was determined to be 0.1624 mL/g, using a differential refractometer (DRM-3000; Otsuka Electronics Co., Ltd., Osaka, Japan) at a wavelength of 633 nm.

NMR spectra were recorded in dimethyl sulfoxide-$d_6$ at 298 K, using a Bruker AV-400 spectrometer ($^1$H: 400.13 MHz, $^{13}$C: 100.61 MHz).

2.3 Results and Discussion

2.3.1 ATRP of MMA

Table 2.1 summarizes the $M_n$ values and molecular-weight distributions of the resulting PMMA obtained via ATRP, determined by SEC measurements. All the ATRPs were carried out in TFE, using copper halides and PMDETA as catalysts for 24 h at 333
K, with molar ratios of [MMA]:[initiator]:[CuBr]:[PMDETA] of 500:1:1:2. To investigate the influence of organic salts, ATRPs of MMA in TFE in the absence of organic salts were first conducted using ethyl 2-bromoisobutyrate (R–Br) and ethyl 2-chloropropionate (R–Cl) as initiators. In ATRP using R–Br (entry 1), only 14% conversion was obtained after 24 h and the observed $M_n$ was much higher than the calculated value, indicating poor initiation efficiency. When R–Cl was used as the initiator (entry 2), the monomer conversion increased to 48%. However, the molecular-weight distribution was rather broader than that obtained using the R–Br system, and the observed $M_n$ was still higher than the calculated one. These poor controls are probably attributable to side reactions caused by protic solvents, which reduce the concentration of the ATRP deactivator, as mentioned in the Section 2.1. Figure 2.1 shows kinetic plots for ATRP of MMA using R–Br and R–Cl in TFE at 333 K. Although a small improvement in control was observed in ATRP with the R–Cl system, the ATRPs did not proceed in a controlled manner. In addition, the ATRP with a mixed halide initiating system, R–Br/CuCl resulted in rather poor control (entry 3). We then conducted the ATRP of MMA with the R–Br initiator in the presence of an imidazolium ionic liquid, HMImCl, under similar conditions, and the effect of adding HMImCl was investigated (entries 4–9).
<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Copper Halide</th>
<th>Organic Salt</th>
<th>[Salt]/[Cu]</th>
<th>Conv.</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_n$/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EBiB</td>
<td>CuBr</td>
<td></td>
<td></td>
<td>14</td>
<td>6 900</td>
<td>24 100</td>
</tr>
<tr>
<td>2</td>
<td>EClP</td>
<td>CuBr</td>
<td></td>
<td></td>
<td>48</td>
<td>24 100</td>
<td>58 200</td>
</tr>
<tr>
<td>3</td>
<td>EBiB</td>
<td>CuCl</td>
<td></td>
<td></td>
<td>39</td>
<td>19 500</td>
<td>66 500</td>
</tr>
<tr>
<td>4</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>2</td>
<td>37</td>
<td>18 700</td>
<td>40 200</td>
</tr>
<tr>
<td>5</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>20</td>
<td>53</td>
<td>26 600</td>
<td>57 300</td>
</tr>
<tr>
<td>6</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>100</td>
<td>66</td>
<td>34 200</td>
<td>62 000</td>
</tr>
<tr>
<td>7</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>200</td>
<td>72</td>
<td>36 500</td>
<td>58 300</td>
</tr>
<tr>
<td>8</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>500</td>
<td>51</td>
<td>25 800</td>
<td>57 800</td>
</tr>
<tr>
<td>9</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>800</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>EClP</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>500</td>
<td>17</td>
<td>8 600</td>
<td>39 500</td>
</tr>
<tr>
<td>11</td>
<td>EBiB</td>
<td>CuBr</td>
<td>LiCl</td>
<td>99</td>
<td>63</td>
<td>31 800</td>
<td>79 700</td>
</tr>
<tr>
<td>12</td>
<td>EBiB</td>
<td>CuBr</td>
<td>EtPyCl</td>
<td>99</td>
<td>64</td>
<td>31 800</td>
<td>85 300</td>
</tr>
<tr>
<td>13</td>
<td>EBiB</td>
<td>CuBr</td>
<td>EtPyCl</td>
<td>490</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>EBiB</td>
<td>CuBr</td>
<td>TBACl</td>
<td>98</td>
<td>66</td>
<td>33 400</td>
<td>89 300</td>
</tr>
<tr>
<td>15</td>
<td>EBiB</td>
<td>CuBr</td>
<td>TBACl</td>
<td>499</td>
<td>75</td>
<td>37 400</td>
<td>63 400</td>
</tr>
<tr>
<td>16</td>
<td>EBiB</td>
<td>CuBr</td>
<td>HMImCl</td>
<td>500</td>
<td>88</td>
<td>44 300</td>
<td>46 600</td>
</tr>
<tr>
<td>17</td>
<td>EBiB</td>
<td>CuBr</td>
<td>BMImBr</td>
<td>499</td>
<td>9</td>
<td>4 500</td>
<td>24 600</td>
</tr>
</tbody>
</table>

$^a$Conditions: 15 wt% MMA in solution; [CuBr]$_0$/[PMDETA]$_0$/[MMA]$_0$/[EBiB]$_0$ = 1/2/500/1. $^b$The conversion was determined gravimetrically. $^cM_n$ (calcd) = [MMA]/[EBiB] $\times$ conversion/100 $\times$ (MW of MMA) + (MW of EBiB). $^d$The $M_n$ (obsd) was determined by SEC, calibrated with a series of PMMA standards using THF as the eluent.
Figure 2.1 Semilogarithmic kinetic plots for the ATRP of MMA using initiators of R–Br and R–Cl in TFE at 333 K. Conditions: 46 wt% MMA in solution; [CuBr]₀ : [PMDETA]₀ : [MMA]₀ : [EBiB]₀ = 1 : 2 : 500 : 1.

As can be seen from the data in Table 2.1, monomer conversion gradually increased with increasing molar ratio of HMImCl to CuBr from 2 to 500. Additionally, the values of $M_w/M_n$ decreased from 1.63 to 1.13 with increasing amounts of HMImCl. However, further increases in the amount of HMImCl caused the polymerization to stop almost completely under the present conditions (entry 9). Furthermore, PMMA with a narrow molecular weight distribution was also obtained when the R–Cl initiator was used, although the monomer conversion was quite low, 17%, even after 24 h, and the $M_n$ was much higher than expected (entry 10). These results suggest that the lost ATRP deactivator, Cu$^{II}$L₅X, in TFE was regenerated by the addition of HMImCl, leading to improved control of ATRP.
Addition of excess HMImCl produced a large excess of deactivator, therefore the polymerization stopped with [HMImCl]/[Cu] = 800 (entry 9). The typical blue color of the ATRP solution with CuBr/PMDETA gradually changed to a light green color with increasing amounts of HMImCl, reflecting regeneration of the deactivator. Decreases in the values of $M_w/M_n$ and increases in monomer conversion were also observed with other salts containing chloride anion (entries 11–15). Figure 2.2 shows the kinetic plots for the ATRP of MMA using R−Br with [HMImCl]/[Cu] = 500 and R−Br with [TBACl]/[Cu] in TFE at 333 K.

![Figure 2.2](image)

**Figure 2.2** Semi-logarithmic kinetic plots for the ATRP of MMA in the presence of HMImCl (open circle) and TBACl (open square) in TFE at 333 K. Conditions: 15 wt% MMA in solution; [CuBr]₀ : [PMDETA]₀ : [MMA]₀ : [EBiB]₀ = 1 : 2 : 500 : 1. The open triangle represents the same data for ATRP using R−Br as already shown in Figure 2.1.
It can be seen that the logarithmic monomer conversion index for ATRP with added chloride anions increased linearly with polymerization time, indicating that the number of active species was constant during polymerization. These results showed an improvement in control by addition of chloride salts. As can be seen in Figure 2.3, $M_n$ increased linearly with increasing conversion, and the values of $M_w/M_n$ were low, at around 1.1. However, although the values of $M_w/M_n$ were relatively low, the all observed $M_n$ values obtained by ATRP with halide salts were almost twice as high as the predicted $M_n$ values. Previous studies\textsuperscript{3,7,22} also showed that the ATRP in ionic liquids produced polymers with $M_n$ values higher than the theoretical $M_n$.

![Figure 2.3](image)

**Figure 2.3** Evolution of the number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) with conversion of ATRP of MMA in the presence of TBACl in TFE at 333 K. Conditions: 15 wt% MMA in solution; [CuBr]$_0$ : [PMDETA]$_0$ : [MMA]$_0$ : [TBACl]$_0$ : [EBiB]$_0$ = 1 : 2 : 500 : 500 : 1.
We supposed that the higher observed $M_n$ values were partly attributable to the experimental procedure. In the present study, the catalyst and initiator solutions were prepared and degassed by repeated freeze–pump–thaw cycles before injection into the monomer solutions. The initiator may be lost during this procedure, because the predicted $M_n$ was observed for entry 16, in which the initiator was introduced to a degassed solution of the catalyst and monomer just before heating the reaction mixture.

In contrast, the effect of additive was less pronounced when a bromide-anion-based imidazolium salt, BMImBr, was used instead of HMImCl (entry 17). The effect on ATRP of the addition of a bromide salt in the case of a homogeneous halide system, i.e., R–Br/CuBr/bromide salt, has already been reported by Matyjaszewski et al.\(^\text{23}\) Compared with their system, our ATRP system is a mixed halide system, i.e., R–Br/CuBr/chloride salt. We supposed that an additional effect of the halide exchange reaction between R–Br and chloride salts must influence the ATRP because better control was observed with the mixed halide system R–Br/CuBr/HMImCl than with R–Br/CuBr/BMImBr in the present study.

2.3.2 Halogen Exchange Reaction

To confirm whether the halogen exchange reaction occurs in the course of ATRP, we
carried out model studies. A solution of CuBr, bpy, EMImCl, and HBiB in TFE without a monomer, was heated at 333 K under an argon atmosphere. The progress of the halogen exchange reaction was monitored by $^1$H NMR spectroscopy, in terms of the relative concentrations of R–Br and R–Cl. Figure 2.4 shows the $^1$H NMR spectra obtained from the model study of the halogen exchange reaction.

![Figure 2.4](image)

Figure 2.4 $^1$H NMR spectra obtained from halogen exchange reaction model study in TFE at 333 K.

The $^1$H NMR spectra confirmed that HBiB was converted to hexyl 2-chloroisobutyrate (HClIb). The changes in the degree of halogen exchange with reaction time are shown in Figure 2.5. The halogen exchange reached equilibrium after around 30 min, as previously reported, and the equilibrium position was greatly toward the formation of HClIb because of the difference between the bond energies of C–Cl and C–Br.
It has been reported that halogen exchange in ATRP can occur either by a radical pathway (atom transfer) or by an ionic pathway (SN2 reaction). However, the halogen exchange reaction did not occur in the absence of a complex of CuBr and bpy. This showed that the halogen exchange reaction occurs by a radical pathway through the ATRP activation–deactivation mechanism, not by an ionic pathway. The additional chloride anion first associates Cu(I)(L)X complex to generate an ATRP deactivator, and then halogen exchange takes place via a radical pathway. It can be concluded that an increase in the concentration of the ATRP deactivator, Cu(I)(L)X₂, and halogen exchange between the initiator and the deactivator can occur simultaneously by the addition of chloride salts, resulting in excellent control of ATRP.
2.3.3 ATRP of MEImCl

To demonstrate the positive effects of additional organic chloride salts, we polymerized a methacrylate monomer containing an imidazolium chloride group by ATRP in TFE in the absence of additional organic salts. The cationic MEImCl monomer is soluble in water, methanol, and fluoroalcohols, but insoluble in most organic solvents. ATRP of MEImCl in TFE was carried out without additional organic salts at 333 K for 24 h. Table 2.2 summarizes the $M_n$ values and molecular-weight distributions of the resulting PMEImCl. ATRP of MEImCl in H$_2$O/iPrOH at 333 K for 24 h produced PMEImCl in 39% yield (entry 1).

Table 2.2 ATRP of MEImCl in 2,2,2-Trifluoroethanol at 333 K for 24 h$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conv. $^b$ (%)</th>
<th>$M_n \times 10^{-4}$ (g mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^c$</td>
<td>H$_2$O/iPrOH</td>
<td>39</td>
<td>9.55</td>
<td>25.8</td>
</tr>
<tr>
<td>2</td>
<td>HFIP</td>
<td>33</td>
<td>8.06</td>
<td>7.12</td>
</tr>
<tr>
<td>3$^f$</td>
<td>TFE</td>
<td>97</td>
<td>6.62</td>
<td>8.68</td>
</tr>
<tr>
<td>4</td>
<td>TFE</td>
<td>64</td>
<td>23.5</td>
<td>25.3</td>
</tr>
</tbody>
</table>

$^a$Conditions: 35 wt% MEImCl in solution; [CuBr]$_0$/[bpy]$_0$/[MEImCl]$_0$/[EBiB]$_0 = 2/4/1000/1$. $^b$Estimated by $^1$H NMR. $^c M_n$ (calcd) = [MEImCl]/[EBiB] × conversion/100 × (MW of MEImCl) + (MW of EBiB). $^d$The $M_n$ (obsd) was determined by SEC equipped with a multi-angle light-scattering detector, using acetic acid aqueous solution (500 mM) containing sodium nitrate (200 mM) as the eluent. $^e$H$_2$O/iPrOH = 1/1 (v/v). $^f$[CuBr]$_0$/[bpy]$_0$/[MEImCl]$_0$/[EBiB]$_0 = 1/2/300/1$. $^{g}$[CuBr]$_0$/[bpy]$_0$/[MEImCl]$_0$/[EBiB]$_0 = 3/6/1500/1$. 
However, the observed $M_n$ of the free polymer was much higher than the theoretical value, and the polydispersity index was rather broad, at $M_w/M_n = 1.37$, indicating poor control of ATRP of MEImCl in aqueous solution. Furthermore, the reaction mixture gradually became inhomogeneous as polymerization proceeded because of the low solubility of the resulting PMEImCl in H$_2$O/iPrOH.

Better control for ATRP of MEImCl was obtained when fluoro alcohols were used as the solvent (entries 2–4). ATRP of MEImCl in fluoro alcohols at 333 K afforded polymers with predictable molecular weights larger than $10^5$ g mol$^{-1}$ and narrower molecular-weight distributions ($M_w/M_n = 1.07–1.13$). Monomer conversion of 64% was achieved in TFE within 24 h, whereas conversion in HFIP was only 33%. Controlled ATRP of MEImCl can be obtained without addition of an organic chloride salt. This result is consistent with the results for ATRP of MMA, which proceeds in a well-controlled manner when an equimolar amount of organic chloride salt is added to MMA. A notable point in these results is that ATRP of a methacrylate monomer with an imidazolium moiety in the side chain proceeded in a controlled manner in fluoro alcohols, but was poorly controlled in aqueous solution.
**Figure 2.6** Semilogarithmic kinetic plot for the ATRP of MEImCl at 333 K in 2,2,2-trifluoroethanol (TFE). Conditions: 35 wt% MEImCl in TFE; 
\([\text{CuBr}]_0/[\text{bpy}]_0/[\text{MEImCl}]_0/[\text{EBiB}]_0 = 3/6/1500/1\).

**Figure 2.7** Evolution of the $M_n$ (open circle), theoretical line (dashed line), and molecular weight distribution (solid circle) with conversion for ATRP of MEImCl in TFE at 333 K. Conditions: 35 wt% MEImCl in TFE; 
\([\text{CuBr}]_0/[\text{bpy}]_0/[\text{MEImCl}]_0/[\text{EBiB}]_0 = 3/6/1500/1\).

Figure 2.6 shows the kinetic plot for ATRP of MEImCl in TFE at 333 K. The logarithmic monomer conversion index given by $\ln([M]_0/[M])$ increased linearly with
polymerization time from the initial stage up to 84 % conversion at 36 h, indicating that polymerization proceeded without crucial side reactions. As shown in Figure 2.7, as the monomer conversion increased, the \( M_n \) of poly(MEImCl) also increased linearly, maintaining a narrow molecular-weight distribution. The observed \( M_n \) values were in good agreement with the theoretical values. We can therefore conclude that a mixed halogen system such as an R–Br initiator and an additional chloride salt is very useful for controlled ATRP in protic solvents, especially in fluoro alcohols, as reported in the present study.

2.4 Conclusions

ATRP of MMA in the presence of organic chloride salts using alkyl bromide initiators was carried out in TFE at 333 K. The ATRP proceeded in a controlled manner to produce polymers with narrow molecular-weight distributions (\( M_w/M_n \approx 1.2 \)). The ATRP deactivator lost as a result of typical side reactions in protic solvents was regenerated by the added organic chloride salt. Furthermore, a halogen exchange reaction occurred between the alkyl bromide initiator and the regenerated ATRP deactivator, leading to better control of ATRP of MMA in TFE. The ATRP of a methacrylate monomer bearing an imidazolium chloride moiety also proceeded in a
well-controlled manner in fluoro alcohols, without any added organic chloride salts. We demonstrated that mixed halogen systems such as alkyl bromide initiators and organic chloride salts as additives were very effective for controlling ATRP in protic solvents, especially in fluoro alcohols.
References


(13) Kobayashi, M.; Terada, M.; Terayama, Y.; Kikuchi, M.; Takahara, A.


Chapter 3

Effect of Salt Concentration on Chain Conformation of a Polyelectrolyte in Aqueous Solutions
3.1 Introduction

In this chapter, chain dimensions and chain conformation of single cationic polyelectrolyte chains in aqueous solutions are discussed. As described earlier in Chapter 1, in order to deeply understand conformational properties of polyelectrolyte brushes, it is essential to know the conformational properties of unbound polyelectrolyte chain in aqueous solutions before studying polyelectrolyte brushes.

Polyelectrolytes are polymers containing ionizable groups that can dissociate into polyvalent macroions and counterions of opposite charge in polar solvents such as water.\(^1\) Electrostatic interactions between charges lead to complex intra- and intermolecular interactions that have strong consequences for both static and dynamic properties of polyelectrolyte solutions which are qualitatively different from those of neutral counterparts. Polyelectrolytes play an important role in nature because they constitute many of biological macromolecules such as tubulin, actin, and DNA. The molecular conformation of polyelectrolytes has been attracting research interests because of their fundamental importance in biological and biophysical processes. Thus, the response of polyelectrolytes to ionic strength of aqueous solutions has been intensively investigated.\(^2,3,4,5,6,7\) The high charge of the macroion produces a strong electric field which attracts these counterions. Due to the strong electric field of the macroion, a fraction of the counterions will be condensed on the macroion. This is the counterion condensation effect, which is first described by Oosawa\(^1\) and formalized by Manning for the case of an infinite line with constant charge density.\(^8\) The Manning–Oosawa (MO) model assumes that the polyelectrolyte chain can be replaced by an infinitely long cylinder because the local chain segments may be considered as a rigid rod due to the strong electrostatic repulsion of the charged groups. The MO model predicts a renormalization of the effective charge of the chain to a constant value, above
a condensation threshold at \( b = l_B \), where \( b \) is the average distance between charged monomers and \( l_B \) is the Bjerrum length defined by \( l_B = \frac{e^2}{\varepsilon k_B T} \) (\( \varepsilon \) is the dielectric constant of the solvent, \( e \) is the elementary charge, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature). This model is apparently capable of describing the experimental electrical properties of polyelectrolytes.\(^8,^9,^10\)

On the other hand, chain dimensions of polyelectrolytes are very sensitive to changes in charge density and ionic strength of the solution\(^11\) because of coulombic long-range interactions among charged groups. The understanding of dimensional properties of flexible polyelectrolytes is one of the very fundamental and important subjects in polymer physics but there is currently no consensus.\(^12\) As in the case of neutral polymer chain, the conformation of polyelectrolytes is conceivable to be determined by both short-range and long-range electrostatic interactions. The former interaction affects chain stiffness, \textit{i.e.}, local conformation. The stiffness parameter (\( \lambda^{-1} \)) of polyelectrolyte is considered as a sum of two contributions, or

\[
\lambda^{-1} = \lambda_0^{-1} + \lambda_{\text{el}}^{-1}
\]

where \( \lambda_0^{-1} \) is the intrinsic stiffness parameter, due to the original stiffness of the backbone and \( \lambda_{\text{el}}^{-1} \) is the electrostatic chain stiffness parameter, arising from the neighboring charges. According to the so-called Odijk-Skolnic-Fixman (OSF) theory,\(^13,^14\) \( \lambda_{\text{el}}^{-1} \) is given by the equation,

\[
\lambda_{\text{el}}^{-1} = \frac{l_g}{2\kappa^2 b^2}
\]

where \( \kappa^{-1} \) is the Debye-Hückel screening parameter. The latter, long-range interaction influences excluded volume effects. The excluded volume strength (\( B \)) of polyelectrolyte chains is also considered as a sum of non-electrostatic (\( B_0 \)) and electrostatic excluded volume strengths (\( B_{\text{el}} \)).\(^15\) The chain stiffness and the excluded

---

45
volume strength of polyelectrolytes are a function of ionic strength and in relation of the trade-off. Hence it is very difficult but essential to investigate ionic strength dependence of chain stiffness and excluded volume effects of polyelectrolyte chains separately. To determine the factors separately, the wormlike chain model of Kratky and Porod (KP) which is the simplest continuous (elastic wire) model have been used for a wide variety of polyelectrolytes.\textsuperscript{16,17,18,19,20} The KP chain model theory is applicable not only to stiff polymers but also to ordinary flexible polymers if the characteristic ratio $C_n$ increases monotonically to its coil-limiting value $C_\infty$ as the number of skeletal bonds $n$ in the chain is increased. The breakdown of the KP chain model, however, was reported for some flexible polymers especially for the molecular weight corresponding to oligomer.\textsuperscript{21} As a more general model, Yamakawa developed the helical wormlike (HW) chain\textsuperscript{22,23} which is an elastic wire model with bending and torsional energies. When its total potential energy is a minimum, the HW chain adopts a regular helical form. This model can be regarded as a hybrid of the three extreme forms of rod, random coil, and regular helix. The HW chain is capable of describing these three forms, as well as their intermediate conformations. The KP wormlike chain is considered to be a special case of the HW chain; the former has only the bending energy and its energy is minimized when its contour becomes a straight line. Thus the HW chain model enables us to know a local conformation of polymer chains more realistic.

In this chapter, we investigated the conformational properties of poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] (PMTAC) as a typical flexible cationic polyelectrolyte chain in aqueous NaCl solutions, especially focused on the change in the local chain conformation with varying ionic strength. On the experimental side, well-characterized samples including oligomers are required for a data analysis based on the HW theory. As far as we know, the experimental data
including oligomer samples are very limited in particular on polyelectrolytes so far. We have developed a direct synthesis of PMTAC by a controlled atom transfer radical polymerization (ATRP) of MTAC monomer in a mixture of 2,2,2-trifluoroethanol and an imidazolium-based ionic liquid as a solvent as described in Chapter 2 in detail. This ATRP gave PMTAC with predictable molecular weight and low polydispersity index ($M_w/M_n < 1.2$), thereby permitting the preparation of samples of PMTAC that are amenable to precise characterization. There are a few reports on the properties of PMTAC with high molecular weights in dilute aqueous solution, but the molecular weight distributions of the samples of PMTAC used in these studies were rather broad. In this chapter, we performed size exclusion chromatography (SEC) measurements with multiangle light-scattering (MALS) detector, dynamic light scattering (DLS), and small-angle X-ray scattering (SAXS) measurements on a series of samples of PMTAC with various molecular weights to elucidate the chain conformation of PMTAC in aqueous NaCl solution. The scattering function $P(q)$, the root-mean-square radius of gyration $<S^2>_z^{1/2}$, and the hydrodynamic radius $R_H$ in 0.05 M, 0.1 M and 0.5 M aqueous NaCl solutions were analyzed in terms of the HW chain with an excluded-volume effect.

3.2 Experimental

3.2.1 Materials

[2-(Methacryloyloxy)ethyl]trimethylammonium chloride (MTAC, Sigma-Aldrich, 80 wt% in H$_2$O) was concentrated by a vacuum pump and was dissolved in TFE. The MTAC/TFE solution was purified by alumina column chromatography and filtration by a membrane filter. Then the MTAC/TFE solution was reprecipitated into a large amount of diethyl ether for further purification. Seven samples of PMTAC were prepared by ATRP at 333 K in a mixture of 2,2,2-trifluoroethanol and an imidazolium ionic liquid as a
solvent using the same procedure described in Chapter 2. Details of the reaction conditions have been described elsewhere.\textsuperscript{24} Chemical structure of the PMTAC is presented in Figure 3.1. Each of the polymer samples was dissolved in deionized water and dialyzed against deionized water to remove unreacted monomer. The solutions were then concentrated in a rotary evaporator and filtered three times through 0.45-\(\mu\)m PTFE membrane filters. The solutions were freeze-dried and then further dried in vacuum at 333 K for 24 h. Deionized water (resistivity = 18.2 M\(\Omega\) cm) for sample preparation for the DLS and SAXS measurements was purified by using an arium 611UV system (Sartorius Stedim Biotech GmbH, Göttingen, Germany). All polymer solutions were prepared by a gravimetric method, and the polymer mass concentrations \(C_p\) (g/mL) and salt concentrations in the aqueous NaCl solutions were calculated.\textsuperscript{27}

![Chemical structure of PMTAC](image)

**Figure 3.1** Chemical structure of PMTAC.

### 3.2.2 Molecular Weight Characterization

The values of the weight-average molecular weight (\(M_w\)) and the \(M_w/M_n\) were determined by SEC equipped with a MALS detector. Details of experimental setup were already described in Chapter 2.

### 3.2.3 Dynamic Light Scattering

Dynamic light scattering (DLS) measurements for solutions of PMTAC in aqueous NaCl at 298 K were carried out at scattering angles between 30° and 150° by using a
goniometer system (CGS-3-TAC/LSE-5004; ALV-Laser Vertriebsgesellschaft m-b.H., Langen, Germany) with a He–Ne laser ($\lambda = 632.8$ nm) to determine the translational diffusion coefficient ($D$). For each series of measurements, four sample solutions with different polymer concentrations were used to eliminate the concentration dependence of $D$. The solutions were filtered through PTFE membranes with suitable pore sizes (usually 0.1 $\mu$m) into cylindrical quartz cells with an inner diameter of 8 mm. The apparent diffusion coefficient ($D_{app}$) for each solution with finite polymer concentration ($C_p$) was determined by applying the cumulant method to the normalized autocorrelation function. At sufficiently small values of $C_p$, $D_{app}$ may be expanded as follows:

$$D_{app} = D_0 \left(1 + k_D C_p + \ldots\right)$$

(3.3)

where $D_0$ and $k_D$ are the diffusion coefficient at infinite dilution and the concentration coefficient of the diffusion coefficient, respectively.

Figure 3.2 shows plots of values of the first cumulant $\Gamma$ relative to the square of the scattering vector $\Gamma/k^2$ against $k^2$ for the sample P2 in 0.5 M aqueous NaCl solution at 298 K.
298 K, where the magnitude of the scattering vector is defined by 

\[ k = \frac{4\pi n_0}{\lambda} \sin(\theta/2) \]

with \( n_0 \) being the solvent refractive index and \( \theta \) being the scattering angle. The values of \( \Gamma/k^2 \) is almost independent of \( k^2 \), so that we adopt as the value of \( D_{\text{app}} \) \([= (\Gamma/k^2)\text{ at } C_p = 0]\) at each finite \( C_p \) the mean value represented by the horizontal line. Figure 3.3 shows plots of \( D_{\text{app}} \) as a function of \( C_p \) for each sample of PMTAC (P1 to P7) in 0.05, 0.1, and 0.5 M aqueous NaCl solutions. As can be seen from the plots, the data points for each sample follow a straight line, and therefore the values of \( D_0 \) and \( k_D \) can be determined from the intercept and the slope, respectively.

**Figure 3.3** Polymer concentration dependence of \( D_{\text{app}} \) for samples of PMTAC in (a) 0.05 M, (b) 0.1 M, and (c) 0.5 M aqueous NaCl solution at 298 K.

From the values of the \( D_0 \) obtained from extrapolation of \( D_{\text{app}} \) to \( C_p = 0 \), the hydrodynamic radius \((R_{\text{hi}})\) for each sample was evaluated by means of the following equation:

\[
R_{\text{hi}} = \frac{k_B T}{6\pi\eta_0 D_0}
\]

\[(3.4)\]
where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \eta_0 \) is the viscosity of the solvent.

### 3.2.4 Small-Angle X-Ray Scattering

SAXS measurements on solutions of PMTAC in aqueous NaCl at room temperature were carried out at the BL40B2 beamline of the SPring-8 facility (Hyogo, Japan). Incident X-rays with a wavelength of 0.1 nm were used. The scattering vector \( (q) \) defined as \( (4\pi/\lambda)\sin(\theta) \), where \( \lambda \) is the wavelength and \( \theta \) is the scattering angle, was calibrated from the Bragg reflection of powdery silver behenate. The scattering intensity \( I(q) \) was detected by using an imaging plate with 3000 \times 3000 pixels to cover the range of scattering vectors from 0.02 to 7.0 nm\(^{-1}\). Two sample-to-detector distances of 1156 mm and 2164 mm were used. The excess scattering intensity \( \Delta I(q) \) was obtained as the difference between the value of \( I(q) \) for the solution and that of the neat solvent. Correction for the effect of absorption of X-rays by a given solution or solvent was performed by measuring the intensity of the incident X-rays and the scattering intensity of the X-rays. The solution of the sample was contained in a quartz capillary with an external diameter of 2 mm, and the capillary with the sample solution was capped with Teflon tape to prevent the solution from evaporating.

The excess scattering intensities were analyzed by means of a square-root plot based on the following equation:

\[
\left[ KC_p / \Delta I(q) \right]^{1/2} = \left[ \sqrt{M_w P(q)} \right]^{1/2} \left[ 1 + M_w A_2 P_2(q) / P(q) C_p + \ldots \right]
\]  

(3.5)

where, \( K \) is the optical constant, \( A_2 \) is the second virial coefficient, and \( P_2(q) \) represents the intermolecular interference. \( P(q) \) is the particle-scattering function and is determined experimentally by the following equation:
\[
\frac{1}{P(q)} = \frac{\left[ C_p/\Delta I(q) \right]_{C_p \to 0}}{\left[ C_p/\Delta I(q) \right]_{C_p \to 0}} (3.6)
\]

\[P(q) = 1 - \frac{1}{3} \langle S^2 \rangle_z q^2 + \ldots \]  

(3.7)

Figure 3.4 gives a typical scattering intensity profiles obtained from sample P1 in 0.5 M aqueous NaCl solution at various \( C_p \). The plot of \([C_p/\Delta I(q)]^{1/2}\) against \( C_p \) was fitted by a straight line and could be extrapolated to infinite dilution to give the value \([C_p/\Delta I(q)]_{C_p=0}^{1/2}\) (the open circle in Figure 3.4). At values of \( q \) above 1.1 nm\(^{-1}\), no significant concentration dependence of \([C_p/\Delta I(q)]^{1/2}\) was observed.

**Figure 3.4** Plots of the reduced scattering intensity at various polymer concentrations for sample P1 in 0.5 M aqueous NaCl solution at 298 K. The open circles were obtained by extrapolation to zero polymer concentration.
Figure 3.5 Berry plots for samples of PMTAC in (a) 0.05 M, (b) 0.1 M, and (c) 0.5 M aqueous NaCl solutions at 298 K. The solid line shows the initial slope. Data points are shifted vertically to different amounts for the viewing clarity.

We determined the value of $<S^2_z>^{1/2}$ from the intercept and the initial slope of the Berry plot $\{[C_p/\Delta I(q)]_{C_p=0}^{1/2} \text{ against } q^2\}$ in the Guinier region as shown in Figure 3.5 by applying the following equation, which can be derived from Eqs. (3.5) and (3.7):

$$\left[\frac{C_p}{\Delta I(q)}\right]_{C_p=0}^{1/2} = \left[\frac{C_p}{\Delta I(0)}\right]_{C_p=0}^{1/2} + \frac{1}{6}\left[\frac{C_p}{\Delta I(0)}\right]_{C_p=0}^{1/2} \left(S^2\right)_c q^2 + \ldots$$

(3.8)

3.3 Results and Discussion

3.3.1 Molecular Weight Characterization

For reliable SEC measurements of cationic polyelectrolytes, it is necessary to eliminate both ionic and hydrophobic interactions between the cationic polyelectrolyte and the packing material of the column. Stickler and Eisenbeiss controlled non-size-exclusion effects (ion inclusion, ion exclusion, and adsorption) by means of a special surface treatment of the stationary phase and by appropriate selection of the mobile phase. In the current study, to reduce hydrophobic and ionic interactions, we
used 0.5 M aqueous acetic acid containing 0.2 M sodium nitrate as a mobile phase in conjunction with columns with poly(methacrylate)-bearing cationic groups on their surfaces that are specially designed for the separation of cationic polyelectrolytes. The SEC absolute calibration curve for PMTAC is shown in Figure 3.6 with chromatograms of each PMTAC sample used in the present study. The $M_w$ and $M_w/M_n$ were calculated from the absolute calibration curve, and the results are listed in Table 3.1. The values of $<S^2>_z^{1/2}$ in the figure for samples of PMTAC with high $M_w$ ($> 1.6 \times 10^5 \text{ g mol}^{-1}$) were determined by SEC–MALS. The plot for $<S^2>_z^{1/2}$ shows a fairly linear relationship between $<S^2>_z^{1/2}$ and the retention volume, which can be expressed as $(S^2)_z^{1/2} \propto M_w^{0.58}$. These results confirm that reliable $M_w$ and $M_w/M_n$ values for samples of PMTAC are determined in the present SEC condition.

![Figure 3.6 SEC absolute calibration curve and $<S^2>_z^{1/2}$ (open squares) for PMTAC samples in 0.5 M aqueous acetic acid solution containing 0.2 M sodium nitrate. Open circles represent molar masses corresponding to maxima in the chromatogram. The SEC chromatograms for each PMTAC sample used in the present study are also shown.](image-url)
Table 3.1 Molecular Characteristics of PMTAC Samples as Determined by SEC-MALS, SAXS and DLS in 0.05 M, 0.1 M and 0.5 M Aqueous NaCl Solutions at 298 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w/10^3$ (g mol$^{-1}$)</th>
<th>$M_w/M_n$</th>
<th>$&lt;S^2&gt;_{z}^{1/2}$ (nm)</th>
<th>$R_H$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>P1</td>
<td>6.03</td>
<td>1.08</td>
<td>1.40</td>
<td>1.47</td>
</tr>
<tr>
<td>P2</td>
<td>12.9</td>
<td>1.11</td>
<td>2.39</td>
<td>2.51</td>
</tr>
<tr>
<td>P3</td>
<td>21.0</td>
<td>1.15</td>
<td>3.83</td>
<td>3.80</td>
</tr>
<tr>
<td>P4</td>
<td>42.1</td>
<td>1.15</td>
<td>7.33</td>
<td>6.70</td>
</tr>
<tr>
<td>P5</td>
<td>67.7</td>
<td>1.17</td>
<td>10.92</td>
<td>9.70</td>
</tr>
<tr>
<td>P6</td>
<td>90.1</td>
<td>1.19</td>
<td>13.0</td>
<td>11.5</td>
</tr>
<tr>
<td>P7</td>
<td>154</td>
<td>1.22</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

3.3.2 Salt-Concentration Dependence of the Hydrodynamic Radius

The dependence of $R_H$ of PMTAC in aqueous NaCl at 298 K on the concentration of salt ($C_s$) was investigated by using sample P6 ($M_w = 9.01 \times 10^4$ g mol$^{-1}$).

![Figure 3.7](image)

**Figure 3.7** Double-logarithmic plot of $R_H$ for P6 against the salt concentration ($C_s$) in aqueous NaCl solution at 298 K. The solid line is drawn as a guide for the eye.

The $R_H$ value decreased from 9 nm to 7 nm with increasing $C_s$, and then leveled off at 7 nm for $C_s$ above 0.5 M, as shown in Figure 3.7. In other words, the chain dimensions of
PMTAC were not affected by the presence of hydrated ions above 0.5 M. It is well known that the chain dimensions of decreases with increasing $C_s$. However, the value of the hydrodynamic radius in 0.5 M aqueous NaCl solution was the same that in a 1.0 M solution. This phenomenon was also observed in a single fully protonated poly(2-vinylpyridine) (P2VP) chain at $C_s < 1.5$ M.$^{29}$ On the other hand, re-expansion of P2VP coils adsorbed on mica surface from salt solutions with $C_s$ higher than 1.0 M was observed by in situ atomic force microscopy.$^{5,6,7}$ In turn, PMTAC is not salted out even in saturated aqueous NaCl in the present study.

Below, we discuss the difference of conformational properties of PMTAC in aqueous NaCl solutions with $C_s$ smaller than 0.5 M at 298 K.

### 3.3.3 Molecular Weight Dependence of Chain Dimensions of PMTAC in Aqueous NaCl Solutions

The values of $<S^2>_z^{1/2}$ and $R_H$ for PMTAC in aqueous NaCl obtained from SAXS and DLS are listed in Table 3.1. Figure 3.8 shows double logarithmic plots of the $<S^2>_z^{1/2}$ against $M_w$ for the PMTAC chain in 0.05 M (open circles), 0.1 M (open squares), and 0.5 M (open triangles) aqueous NaCl solutions. The data points are fitted by a straight line with values of exponent 0.85 for $C_s = 0.05$ M, 0.78 for $C_s = 0.1$ M, and 0.70 for $C_s = 0.5$ M. All these values of the exponent are higher than the limiting value of 0.6 for nonionic flexible chains in good solvents. The increase of the slope with decreasing $C_s$ is well-known phenomenon in many polyelectrolyte solutions, resulting from an increase of electrostatic repulsive interaction, which increases the chain stiffness and excluded-volume strength.
An interesting and remarkable observation to be noted in Figure 3.8 is that for $M_w > 2 \times 10^4$ g mol$^{-1}$ the values of $<S^2>_z^{1/2}$ simply increase with a decrease in $C_s$, but the values for $M_w < 2 \times 10^4$ g mol$^{-1}$ contrarily decrease with a decrease in $C_s$. The phenomenon of inversion in $C_s$ dependence of $<S^2>_z^{1/2}$ appeared more prominently in the $M_w$ dependence of $R_H$ for the PMTAC chain as shown in Figure 3.9. Obviously the phenomenon of inversion cannot be simply explained by changes in the
excluded-volume effect and chain stiffness. One plausible explanation is that a local conformation of PMTAC chain changes in response to $C_s$ of aqueous NaCl solutions.

### 3.3.4 Data Analysis and Comparison with Theory

#### 3.3.4.1 Scattering Function

To determine the local conformation of PMTAC chain in 0.05 M, 0.1 M and 0.5 M aqueous NaCl, we analyzed the scattering profile on the basis of the helical wormlike (HW) chain model proposed by Yamakawa and co-workers, who performed extensive investigations on chain conformation of poly(methyl methacrylate) (PMMA) in a theta state. It is known that the molecular weight dependence of $<S^2>_z^{1/2}$ and the scattering function for PMMA cannot be explained in terms of a Kratky–Porod (KP) wormlike chain; hence, the HW model has been applied to PMMA in theta solvents. The HW chain is a continuous wormlike chain with bending and torsional energies. When its total potential energy is a minimum, the HW chain adopts a regular helical form. The HW chain has four major model parameters: the constant curvature $\kappa_0$ and the torsion $\tau_0$ of the characteristic regular helix at the energy minimum, the stiffness parameter $\lambda^{-1}$, and the shift factor $M_L$, which is defined as the molecular weight per unit contour length. The stiffness parameter $\lambda^{-1}$ is defined as the bending force constant divided by $k_BT/2$.

The $\lambda^{-1}$ for the HW chain is related to the Kuhn statistical segment length ($A_K$)

$$A_K = c_\kappa \lambda^{-1} \quad (3.9)$$

with

$$c_\kappa = \frac{4 + \tau_0^2}{4 + \kappa_0^2 + \tau_0^2} \quad (3.10).$$
The schematic drawing of the conformations of the helical wormlike chain is shown in Figure 3.10. The term “helix” does not necessarily mean the helix in $\alpha$-helices, DNA, and the like. The real polymer chain may also be regarded as a wormlike chain randomly possessing complete or incomplete helical conformations to some extent, which can be determined by the stiffness parameter $\lambda^{-1}$ as can be seen in Figure 3.10.

**Figure 3.10** Schematic drawing of helical wormlike chains.

This model can be regarded as a hybrid of the three extreme forms of rod, random coil, and regular helix. The HW chain is capable of describing these three forms, as well as their intermediate conformations. The KP wormlike chain is considered to be a special case of the HW chain; the former has only the bending energy and its energy is minimized when its contour becomes a straight line. Thus the HW chain model enables us to provide a more realistic local chain conformation of polymers.

The theoretical scattering function of the HW model was compared to the experimental data of oligomer PMTAC (P1), to reduce the obscuration resulting from the excluded volume effect because the excluded volume effects become of practical significance when the Kuhn segment number $A_K L$ exceeds a value around 5. Hence the excluded-volume effects can be neglected for oligomeric samples. Figure 3.11 shows plots of the $q^2[C_p/\Delta I(q)]_{C_p,q=0}^{1/2}/[C_p/\Delta I(q)]_{C_p=0}^{1/2}$ against $q$ (in the form of the Kratky plot)
for P1 in 0.1 M and 0.5 M aqueous NaCl solution at 298 K. As can be seen in the figure, the Kratky plots show a remarkable oscillation, similar to that observed by Kirste and Wunderlich for a syndiotactic PMMA chain.\textsuperscript{33} This oscillation was attributed to the local chain conformation, that is, to helical sequences of PMMA. Unfortunately, reliable scattering profile for P1 in 0.05 M aqueous NaCl could not be obtained for $q > 1$ nm\textsuperscript{-1} due to the insufficient scattering contrast. To estimate the model parameters for the HW chain from the scattering profiles of PMTAC, we calculated the scattering function $F(q; L)$ for an HW chain of total contour length $L$ by means of empirical equations.\textsuperscript{34} The effect of the chain thickness (the thickness of the spatial distribution of scatterers around the HW chain contour) was considered by applying the touched spheroid model.\textsuperscript{35} [Eq. (50) in ref. 35]

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3_11.png}
\caption{Kratky plots for samples P1 in (a) 0.1 M and (b) 0.5 M aqueous NaCl solutions at 298 K and the theoretical curves for the helical wormlike chain with the parameter sets listed in Table 3.2.}
\end{figure}
For sample P1 at $C_s = 0.1$ M and 0.5 M, the best-fit theoretical curve calculated from Eq. (13) of ref. 34 was obtained when we used the parameter values listed in Table 3.2, where, $d$ is the cross-sectional diameter. The HW theory quantitatively reproduced the experimental curve for P1 in 0.1 M and 0.5 M aqueous NaCl with a characteristic oscillation in the range $q < 6$ nm$^{-1}$. The values of $M_L$ increased with decreasing $C_s$, and the average value of 700 nm$^{-1}$ yields 0.29 nm for the monomeric contour length $l$. This $l$ value is close to the value calculated on the assumption that the PMTAC molecule assumes the all-trans conformation.

<table>
<thead>
<tr>
<th>$C_s$ (M)</th>
<th>$\lambda^{-1} \kappa_0$</th>
<th>$\lambda^{-1} \tau_0$</th>
<th>$\lambda^{-1}$</th>
<th>$\lambda_K$</th>
<th>$M_L$ (g mol$^{-1}$ nm$^{-1}$)</th>
<th>$d$ (nm)</th>
<th>$d_{H}$ (nm)</th>
<th>$B$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5.2</td>
<td>3.0</td>
<td>7.5 ± 0.2</td>
<td>2.5 ± 0.06</td>
<td>740 ± 40</td>
<td>0.45</td>
<td>0.8</td>
<td>9.26 ± 0.9</td>
</tr>
<tr>
<td>0.5</td>
<td>5.5</td>
<td>2.4</td>
<td>7.0 ± 0.2</td>
<td>1.7 ± 0.05</td>
<td>650 ± 30</td>
<td>0.50</td>
<td>1.4</td>
<td>3.37 ± 0.5</td>
</tr>
</tbody>
</table>

### 3.3.4.2 Molecular weight Dependence of the Radius of Gyration

To demonstrate the validity of the parameters determined from the scattering profiles for P1 at $C_s = 0.1$ M and 0.5 M, we examined whether the HW chain model with these model parameters is capable of describing the molecular-weight dependence of $<S^2>_{z}^{1/2}$ for PMTAC at $C_s = 0.1$ M and 0.5 M.

The unperturbed mean-square radius of gyration $<S^2>_0$ of the HW chain with a contour length $L$ is calculated by applying the following expression:\textsuperscript{23}

$$
<S^2>_0 = \frac{r_0^2}{\lambda^2 v^2} \left( <S^2> \right)_0 + \frac{\kappa_0^2}{\lambda^2 v^2} \left[ \frac{\lambda L \cos \varphi - \frac{1}{r^2} \cos (2\varphi) + \frac{2}{r^4 \lambda L} \cos (3\varphi)}{r^4 (\lambda L)^2} \cos (4\varphi) + \frac{2}{r^4 (\lambda L)^2} e^{-2\lambda L} \cos (\lambda L + 4\varphi) \right] (3.11)
$$

with
The parameter $L$ is related to the molecular weight $M_w$ by the expression $L = M_w / M_L$. The unperturbed mean-square radius of gyration of the KP chain, $<S^2>_{0,KP}$, in Eq. 3.11 is calculated from the Benoit–Doty equation\textsuperscript{36}

\[ <S^2>_{0,KP} = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^4L} - \frac{1}{8\lambda^6L} \left[1 - \exp(-2\lambda L)\right] \]  

The values of $<S^2>_{2}^{1/2}$ determined by SAXS measurements contain contributions from the finite cross section of the polymer chain. For a continuous chain with a uniform circular cross section of diameter $d$, $<S^2>$ can be expressed as follows:\textsuperscript{37}

\[ <S^2> = <S^2>_{0} + \frac{d^2}{8} \]  

Here, we must consider the excluded-volume effects for the PMTAC chain in aqueous NaCl, although the excluded-volume effect of P1 was found to be negligible in the analysis of the scattering function. The excluded-volume effect on $<S^2>$ can be expressed in terms of the radius expansion factor $\alpha_s$ as follows:

\[ <S^2> = \alpha_s^2 <S^2>_{0} \]  

Here, $\alpha_s$ can be calculated by using the theoretical scheme of Yamakawa, Shimada, and Stockmayer (YSS)\textsuperscript{38,39} by applying the modified Domb–Barrett equation:\textsuperscript{40}

\[ \alpha_s^2 = \left[1 + 10^{-7.9} \left(\gamma \sigma - 5 \right) \right]^{1.45} \]  

where $\gamma$ is a scaled excluded-volume parameter, which takes into account the effects of excluded volume and chain stiffness, defined as follows:
with

\[ z = \left( \frac{3}{2\pi} \right)^{\nu^2} (\lambda B)(\lambda L)^{\nu^2} \]  

(3.20)

and

\[ K(\lambda L) = \frac{4}{3} - 2.711(\lambda L)^{-\nu^2} + \frac{7}{6}(\lambda L)^{-1} \]  

(for \( \lambda L > 6 \))

\[ = (\lambda L)^{-\nu^2} \exp \left[ -6.611(\lambda L)^{-1} + 0.9198 + 0.03516\lambda L \right] \]  

(for \( \lambda L \leq 6 \))  

(3.21).

Here, \( B \) is the excluded-volume strength defined by the expression \( B = \beta/b^2c_s^{\nu^2} \), where \( \beta \) is the binary cluster integral between beads with spacing \( b \).

The full curves in Figure 3.12 represent the theoretical values of \( <S^2>^{1/2} \) calculated from Eq. 3.17 using the model parameters listed in Table 3.2. The theoretical curves well agreed with the experimental data points with \( B = 9.26 \) nm for \( C_s = 0.1 \) M and \( B = 3.37 \) nm for \( C_s = 0.5 \) M.

![Figure 3.12 Molecular-weight dependence of \( <S^2>^{1/2} \) for PMTAC in 0.1 M and 0.5 M aqueous NaCl solutions at 298 K and literature values in 1.0 M aqueous NaCl solution (squares and diamonds). The solid curves represent the theoretical values for a helical wormlike chain with parameters listed in Table 3.2.](image)
We therefore concluded that the model parameters obtained from the scattering function for P1 were valid for PMTAC chain. The literature values\textsuperscript{25,26} of $<S^2>_z^{1/2}$ for PMTAC in a 1.0 M aqueous NaCl solution at 298 K are plotted in Figure 3.12 as square and diamond symbols. As mentioned in 3.3.2, we have already confirmed that the chain dimensions of PMTAC in both 0.5 M and 1.0 M aqueous NaCl solutions are identical. Hence we can compare our present data with the literature data. Note that the PMTAC samples used in the literature showed a high polydispersity; corrections for this polydispersity were thus applied by assuming a Schulz–Zimm distribution.\textsuperscript{41} The data point for the corrected literature values also fitted the theoretical curve for the HW chain. We found that the model parameters determined from the scattering profile for P1 in 0.1 M and 0.5 M aqueous NaCl solution are reasonable.

It can be assumed that parameter $B$ for polyelectrolyte chains consists of an intrinsic excluded-volume effect associated with the nonionic polymer backbone and electrostatic contributions. Yamakawa and co-workers reported $B$ values for atactic PMMA in the good solvents acetone, nitroethane, and chloroform.\textsuperscript{42} The $B$ values in acetone at 298 K, nitroethane at 303 K, and chloroform at 298 K are 0.22, 0.52, and 1.15, respectively. The values of $B = 9.26$ nm for $C_s = 0.1$ M and $B = 3.34$ nm for $C_s = 0.5$ M were much larger than those for neutral atactic PMMA, probably as a result of the contribution of electrostatic interactions in PMTAC. Also, the $B$ values in the present study are much larger than those of sodium poly(styrene sulfonate) in aqueous NaCl reported by Norisuye, et al.\textsuperscript{43}

### 3.3.4.3 Molecular Weight Dependence of the Hydrodynamic Radius

In addition to the analysis of $<S^2>_z^{1/2}$, we also confirmed that the molecular-weight dependence of the $R_H$ for PMTAC at $C_s = 0.1$ M and 0.5 M can be explained by means of
the HW chain model. The theoretical values of $R_{H}$ as a function of the molecular weight were calculated on the basis of the HW cylinder model.\textsuperscript{44} The hydrodynamic cylinder model for the HW chain is defined by introducing the diameter of the cylinder, $d_{H}$.

The value of $R_{H,0}$ for unperturbed HW cylinders may be expressed as follows:\textsuperscript{44}

$$R_{H,0}^{-1} = \frac{2}{L} f_{D} \left( \frac{\lambda L}{c_{\infty}}, \frac{\lambda d}{c_{\infty}} \right)$$

(3.22),

where $f_{D}$ is a known function of $\frac{\lambda L}{c_{\infty}}$ and $\frac{\lambda d}{c_{\infty}}$; $f_{D}$ is derived through the associated KP chain with a Kuhn length identical to that of the HW chain under consideration. The value of $R_{H}$ for a perturbed HW cylinder can be calculated from the expression

$$R_{H} = \alpha_{H} R_{H,0}$$

(3.23)

by using the Barrett equation\textsuperscript{45} for the hydrodynamic radius expansion factor $\alpha_{H}$ in the YSS scheme:\textsuperscript{38,39}

$$\alpha_{H} = \left( 1 + 6.02 \right)^{-0.1 \lambda_{0}^{-1}}$$

(3.24).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.13}
\caption{Molecular-weight dependence of $R_{H}$ for PMTAC in aqueous NaCl solutions at 298 K. The solid curves represent the theoretical values for a helical wormlike cylinder with the parameters listed in Table 3.2.}
\end{figure}
The solid lines in Figure 3.13 show the theoretical values of $R_H$ calculated from Eqs. 20, 21, and 22 for an HW cylinder with the model parameters listed in Table 3.2. The theoretical curves closely fit the experimental data points except for a lower molecular weight region of $M_w < 2 \times 10^4$ g mol$^{-1}$. From these results, we confirmed that the HW theory also consistently described the $M_w$ dependence of $R_H$ for PMTAC in 0.1 and 0.5 M aqueous NaCl solution, as well as the $M_w$ dependence of $<S^2>_z^{1/2}$.

3.3.4.4 Local Conformation of the PMTAC Chain

For an HW chain, the radius $R$ and the pitch $h$ of the characteristic helix at the minimum potential energy are given by the following expressions:

$$R = \frac{\kappa_0}{\kappa_0^2 + \tau_0^2}$$

(3.25)

and

$$h = \frac{2\pi\tau_0}{\kappa_0^2 + \tau_0^2}$$

(3.26).

For a solution of PMTAC in 0.1 M and 0.5 M aqueous NaCl at 298 K, we have $R = 1.08$ nm and $h = 3.93$ nm and $R = 1.07$ nm and $h = 2.93$ nm, respectively. From those values, we can draw schematics of the characteristic helices of HW chain model at the minimum potential energy for the PMTAC chain (Figure 3.14). Note that the actual conformation of the PMTAC chain in dilute solution differs from that of a regular helix because the regular structure is destroyed by thermal fluctuations in dilute solution. From the figure, it is seen that the characteristic helix for the PMTAC chain is elongated in the direction of helix axis with decreasing $C_s$. Namely, the PMTAC chain adopts slightly extended conformation with decreasing $C_s$. This is a result of an increase in short-range interactions caused by decreasing $C_s$. 

66
As mentioned in Section 3.1, the chain dimensions of polyelectrolytes are significantly influenced by short-range and long-range electrostatic interactions. By applying the HW chain model, these interactions can be analyzed more quantitatively to afford the information of the local chain conformation change of polyelectrolyte with \( C_s \). The values of \( R \) and \( h \) for the PMTAC chain in 0.5 M aqueous NaCl approach to the corresponding values for PMMA, for which \( R = 1.35 \) nm and \( h = 2.33 \) nm.\(^{46}\) This suggests that the local conformation of PMTAC chain in \( C_s = 0.5 \) M at 298 K is similar to that of PMMA chain, because the electrostatic repulsive interactions are remarkably suppressed at this \( C_s \).

### 3.4 Conclusions

The particle scattering function, the values of \( <S^2>_z^{1/2} \) and \( R_H \) for a series of samples of PMTAC in \( C_s = 0.05 \) M, 0.1 M and 0.5 M were measured at 298 K by means of SAXS and DLS. The scattering function and the molecular-weight dependence of \( <S^2>_z^{1/2} \) and
$R_H$ for the PMTAC chain were quantitatively described in terms of the HW chain model. The $R_H$ for PMTAC decreased with increasing salt concentration and then leveled off at salt concentrations above 0.5 M. From the analysis with the HW chain, we revealed that not only the chain dimensions but also the local conformation of PMTAC is strongly influenced by the ionic strength. We conclude that the HW chain is an appropriate model for understanding the solution behavior of the PMTAC chain in aqueous NaCl solutions.
References


(22) Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions*, Springer: Berlin, **1997**.


Chapter 4

Effect of Salt Concentration on Chain Conformation on High-Density Polyelectrolyte Brushes in Aqueous Solutions by Small-Angle X-ray Scattering
4.1. Introduction

Polyelectrolyte chains densely end-grafted to a surface form polyelectrolyte brushes. The polymers consisting of hyaluronan and lubricin, which coat the cartilage in human and animal joints, are charged, and they have brush-like structure. Thus, lubrication and interactions between ion-containing polymer brushes have been extensively investigated both theoretically and experimentally.

The swollen structures of polyelectrolyte brushes under aqueous condition are very important in understanding the frictional properties and other related surface properties of polyelectrolyte brushes. Despite many efforts, as described in Chapter 1, the conformations of polyelectrolyte chains in aqueous solutions are only partly understood. From a fundamental point of view, it is interesting to describe how the conformations of charged chains immersed in aqueous media change at interfaces.

In this chapter, the chain dimensions and chain conformations of cationic polyelectrolyte brushes immobilized on silica nanoparticles in aqueous NaCl were investigated using small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS). Such a colloidal system provides a good model of soft condensed matter, and various measurement techniques such as solution scattering methods, electron microscopy, optical techniques, and atomic force microscopy can be easily applied. The small-angle scattering technique is one of the most suitable methods for experimentally determining the radial density profile of brush chains (i.e., the swollen thickness of the brushes). In the work described in the following section, the scattering profiles of cationic polyelectrolyte brushes on silica nanoparticles, obtained from SAXS and USAXS, were analyzed using the core–corona model with interacting corona chains, to determine the swollen thickness of the brushes. Furthermore, the effect of curvature...
of the core, length of the grafted chain, and added salt concentration on the chain dimensions and chain conformations of polyelectrolyte brushes are discussed.

4.2. Experimental

4.2.1. Materials

Copper(I) bromide [CuBr, Wako Pure Chemical Industries, Ltd. (Wako), Osaka, Japan, 99.9%] was purified by the same procedure as described in Chapter 2. Commercially available 2,2’-bipyridine (bpy, Wako, 99.5 %), 2,2,2-trifluoroethanol [TFE, Tokyo Chemical Inc. (TCI), 99.0%], and tetrabutylammonium chloride (TBACl, TCI, 98%) were used without further purification. [2-(Methacryloyloxy)ethyl]trimethylammonium chloride (MTAC, Sigma-Aldrich 80 wt.% in H₂O) was purified according to the procedure in Chapter 3. The procedure used for the synthesis of (2-bromo-2-methyl)-propionyloxyhexyltriethoxysilane (BHE) has been described in previous papers.¹³,¹⁴ Silica nanoparticles (SiNPs) with nominal radii of 50 nm and 100 nm, dispersed in water (40 wt%), were kindly supplied by Nissan Chemical Industries Ltd., Tokyo, Japan. Deionized water (resistivity = 18.2 MΩ cm) for sample preparation for the SAXS measurements was purified using an Arium 611UV system (Sartorius Stedim Biotech GmbH, Göttingen, Germany).

4.2.2 Immobilization of the Surface Initiator

The typical procedure for immobilizing BHE on SiNPs was as follows.¹³,¹⁵ A commercially supplied SiNP suspension (13.6 mL) was collected in a 500 mL flask and diluted with 100 mL of ethanol. A mixture of ammonia solution (28% NH₃ aqueous solution, 10 mL) and ethanol (180 mL) was added dropwise to the SiNP suspension
with stirring, and the system was stirred for 6 h at 313 K. BHE (2 g, 4.8 mmol) diluted with ethanol (10 mL) was added dropwise to the suspension over 15 min, and the reaction mixture was continuously stirred for another 18 h at 313 K. The SiNPs with immobilized BHE (BHE-SiNP) were then purified by consecutive centrifugation and redispersion in ethanol. Finally, the BHE-SiNP suspension in ethanol was subjected to solvent exchange treatment to obtain a stock TFE suspension.

4.2.3 Surface-initiated Atom Transfer Radical Polymerization of MTAC from BHE-SiNPs

A mixture containing MTAC (1.2 g), TBACl (0.1 g), BHE-SiNP (0.12 g), and TFE (8.6 g) was charged in a glass ampule and then degassed by seven freeze–pump–thaw cycles. CuBr (0.02 mmol) was introduced into another glass tube with a stop-cock, and then degassed by three cycles of vacuum pumping and flushing with argon. A well-degassed TFE solution of bpy (0.04 mmol) was added to the glass tube containing CuBr, immediately giving a homogeneous solution with a characteristic red color. The CuBr/bpy solution was degassed by repeated freeze–pump–thaw cycles and then injected into the mixture of MTAC, TBACl, and BHE-SiNP in TFE. The resulting reaction mixture was again degassed by repeated freeze–pump–thaw cycles to remove oxygen, and the tube was sealed under reduced pressure. The polymerization reaction was carried out in an incubator shaker thermostated at 333 K (Scheme 4.1).

Scheme 4.1 Surface-initiated ATRP of MTAC from SiNP Surface
After a prescribed time, the reaction was stopped by opening the glass vessel to the air. The reaction mixture was poured into a large amount of a methanol/diethyl ether (1/1, v/v) to precipitate the PMTAC-grafted SiNPs (PMTAC-SiNPs) and to remove residual compounds. PMTAC-SiNP was purified by consecutive reprecipitation in a methanol/diethyl ether mixture and redispersion in methanol.

To determine the weight-average molecular weight ($M_w$) and polydispersity index ($M_w/M_n$) of the surface-grafted PMTAC, the PMTAC chains were isolated from the surface as follows. PMTAC-SiNP (25–50 mg) was dissolved in water (1 mL). A 10% HF aqueous solution (2 mL) was added to the PMTAC-SiNP suspension, and the resultant solution was stirred at room temperature for 12 h. The solution was allowed to stand for three weeks. After addition of 10% HF aqueous solution (1 mL), the solution was again allowed to stand for 3 weeks. The solution was neutralized with NaHCO$_3$ and centrifuged. The resultant supernatant solution was dialyzed in water to remove inorganic salt ions. The aqueous solution containing isolated PMTAC chains was freeze-dried, and then subjected to size exclusion chromatography (SEC).

### 4.2.4 Measurements

Thermogravimetric analysis (TGA) of PMTAC-SiNP was carried out using Perkin-Elmer Pyris TGA under a nitrogen atmosphere, at a flow rate of 20 mL min$^{-1}$. The temperature of the sample was first raised from room temperature to 373 K, then allowed to stand for 60 min, and then raised again at 10 K min$^{-1}$ to 1073 K.

The $M_w$ and $M_w/M_n$ values of the grafted PMTAC were determined by SEC equipped with a MALS detector. Details of experimental setup have already been described in Chapter 2.
To estimate the core radius \( R_c \) of the SiNPs and the radius of gyration of the grafted PMTAC, SAXS and USAXS were performed on PMTAC-SiNP in aqueous NaCl (concentration of PMTAC-SiNP: 0.1–0.3 wt%) at room temperature at the BL40B2 and BL19B2 beamlines, respectively, of the SPring-8 facility (Hyogo, Japan). Incident X-rays with a wavelength of 0.1 nm (BL40B2) or 0.07 nm (BL19B2) were used. The scattering vector \( q \) is defined as \( (4\pi/\lambda)\sin\theta \), where \( \lambda \) is the wavelength and \( \theta \) is the scattering angle. The scattering intensity \( I(q) \) was determined using an imaging plate with 3000 \( \times \) 3000 pixels and a PILATUS detector, for SAXS and USAXS, respectively. Two sample-to-detector distances of 2240 mm (SAXS) and 41 890 mm (USAXS) were used to cover the \( q \) range from \( 5 \times 10^{-3} \) to \( 5 \times 10^{-1} \) nm\(^{-1}\). The excess scattering intensity \( \Delta I(q) \) was obtained as the difference between the value of \( I(q) \) for the solution and that of the neat solvent. Correction for the effect of absorption of X-rays by a given solution or solvent was performed by measuring the intensity of the incident X-rays and the scattering intensity of the X-rays. The solution of the sample was contained in a quartz capillary tube with an external diameter of 2 mm. The tube was capped with Teflon tape. The normalized scattering intensities obtained from SAXS were slightly shifted for combination with those obtained from USAXS.

4.3 Results and Discussion

4.3.1 Preparation of PMTAC-SiNP

Surface-initiated ATRPs of MTAC from the surfaces of BHE-SiNPs with different \( R_c \) values were carried out in TFE at 333 K to obtain high-density spherical polyelectrolyte brushes. To determine the values of \( M_w \) and \( M_w/M_n \) for the brush chains, the grafted chains were cleaved from the SiNPs using aqueous HF solution. The SEC
curves of the cleaved grafted chains are shown in Figure 4.1. Although there is a high-molecular-weight shoulder present in the SEC trace of SP1, as can be seen in Figure 4.1(a), all the SEC curves showed a unimodal peak. This suggests that no crucial side reactions occurred in the course of surface-initiated ATRP.

Table 4.1 summarizes the characteristics of the PMTAC-SiNPs used in the present study. A series of PMTAC-SiNPs with \( M_w \) values from \( 5 \times 10^4 \) to \( 1 \times 10^5 \) were prepared by surface-initiated ATRP. The values of \( M_w/M_n \) were around 1.7, and were relatively higher than the previously reported values obtained by bulk ATRP of MTAC monomer under the same conditions.\(^{16}\)

The graft density \( (\sigma_0) \) of the PMTAC-SiNP can be expressed as follows:

\[
\sigma_0 = \frac{\rho N_A R_s}{3M_n \left( \frac{1}{w} - 1 \right)}
\]  

where \( \rho \), \( N_A \), \( M_n \), and \( w \) are the density of SiNPs (1.6 g/cm\(^3\)), Avogadro’s number, the number-average molecular weight, and the weight fraction of grafted polymer, respectively.
Table 4.1 Characteristics of PMTAC-SiNPs

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_c$ (^a) (nm)</th>
<th>$M_w/10^3$ (^b) (g mol(^{-1}))</th>
<th>$M_w/M_n$ (^b)</th>
<th>$W_p$ (^c) (wt%)</th>
<th>$\sigma_0$ (^d) (chains nm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP1</td>
<td>50.7</td>
<td>1.87</td>
<td>24.6</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>SP2</td>
<td>60.4</td>
<td>1.75</td>
<td>31.0</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>SP3</td>
<td>56.0</td>
<td>1.67</td>
<td>37.1</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>SP4</td>
<td>85.0</td>
<td>1.62</td>
<td>41.6</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>SP5</td>
<td>108</td>
<td>1.72</td>
<td>45.2</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>LP1</td>
<td>53.4</td>
<td>1.72</td>
<td>17.6</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>LP2</td>
<td>96.4</td>
<td>1.66</td>
<td>23.1</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>LP3</td>
<td>86.4</td>
<td>1.68</td>
<td>27.3</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>LP4</td>
<td>119</td>
<td>1.63</td>
<td>35.4</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) $R_c$ denotes the core radius of SiO\(_2\); and the values of $R_c$ were estimated from SAXS measurements, as discussed later. \(^b\) The values of $M_w$ and $M_w/M_n$ were estimated by SEC-MALS measurements. \(^c\) Weight fraction of grafted polymer layer ($W_p$) was determined by TGA. \(^d\) $\sigma_0$ denotes the graft density of PMTAC at the surface of the SiO\(_2\) core.

As can be seen from the Table 4.1, the values of $\sigma_0$ are nearly constant, independent of $R_c$, and approximately equal to 0.22 chains nm\(^{-2}\). This value is much higher than the graft density of polyelectrolyte brushes used in previous studies.\(^{17,18}\) High-density polyelectrolyte brushes were therefore obtained using surface-initiated ATRP from the SiNP surfaces.

4.3.2 Estimation of Core Radius of SiNPs

To estimate the $R_c$ values of the SiNPs, USAXS and SAXS were performed on suspensions of BHE-SiNPs with two different core radii (nominal $R_c = 50$ nm and 100 nm) in TFE. Figure 4.2 shows the experimental excess scattering intensity $\Delta I(q)$ profiles of BHE-SiNPs in TFE; these show characteristic fringes from the primary particles, the form factor from the particles. These profiles were well expressed by the form factor of a sphere with a Schulz size distribution,\(^{19,20}\) as indicated by the solid curves in the figure.
The mean core radii and the root-mean-square deviation were estimated to be $53.0 \pm 3.9$ nm and $96.4 \pm 4.8$ nm, respectively.

Figure 4.2 Excess scattering intensity profiles of silica nanoparticles (SiNP) with a core radius ($R_c$) of (a) 53.0 nm and (b) 96.3 nm in 2,2,2-trifluoroethanol (TFE) at room temperature obtained through USAXS and SAXS measurements. Solid lines depicted in figure are fitting curves by a form factor of a spherical particle with a Schulz distribution in size.

4.3.3 Chain Dimensions of Grafted PMTAC Chains in Aqueous NaCl Solutions

Figures 4.3 and 4.4 show the experimental scattering profiles of PMTAC-SiNPs with $R_c = 53.0$ and 96.4 nm in aqueous NaCl solutions ($C_s = 0.05, 0.1, 0.5$ M). To estimate the swollen thickness of the grafted PMTAC layer, the profiles were fitted using a spherical core–shell model with interacting self-avoiding corona chains, proposed Pedersen et al.\textsuperscript{21-23} The form factor of the core–shell model contains four different terms corresponding to scattering from the spherical core and the corona chains, and terms from core–corona and corona–corona interferences. It can be written as
\[
P(q) = \left[ N \Delta Z_{\text{e,core}}^2 P_{\text{core}}(q) + N \Delta Z_{\text{e,chain}}^2 P'(q) \right]^{-1} + N \left[ N - P'(0) \right] \Delta Z_{\text{e,chain}}^2 S_{\text{chain-chain}}(q) \left( \Delta Z_{\text{e,core}} + \Delta Z_{\text{e,chain}} \right)^{-2} \quad (4.2)
\]

where \( N \) is the number of grafted polymer chains on the SiNP, and \( \Delta Z_{\text{e,core}} \) and \( \Delta Z_{\text{e,chain}} \) are the excess electron density of the core and the chain, respectively. \( P_{\text{core}}(q) \) is the self-correlation term of the spherical core with a Schulz distribution, as described in Section 4.3.2. \( P'(q) \) is the effective single chain form factor, expressed by

\[
P'(q) = \frac{P_{\text{PWC}}(q)}{1 + \nu P_{\text{PWC}}(q)} \quad (4.3)
\]

where \( P_{\text{PWC}}(q) \) and \( \nu \), respectively, are the scattering functions for a perturbed worm-like chain of finite thickness, \(^{24}\) and a parameter that increases with increasing concentration within the corona and is related to the chain–chain interactions within the corona. The parameter \( \nu \) is approximated as follows\(^{21}\)

\[
\nu = 1.4 \left[ \frac{N s^2}{4(R_c + s)} \right]^{1.04} \quad (4.4)
\]

Here, \( s \) is the radius of gyration of the grafted polymer chain. Note that the scattering functions of worm-like chains, \( P_{\text{PWC}}(q) \), for PMTAC in aqueous NaCl solutions have already been determined in Chapter 3.

The interference terms for a smooth core–corona interface are

\[
S_{\text{core-chain}}(q) = \frac{3}{(qR_c)^3} \left[ \sin(qR_c) - qR_c \cos(qR_c) \right] A_{\text{chain}}(q) \quad (4.5)
\]

and

\[
S_{\text{chain-chain}}(q) = A_{\text{chain}}(q)^2 \quad (4.6)
\]

where
\( A_{\text{chain}}(q) = \frac{4\pi \int \rho_{\text{chain}}(r) \sin(qr) r^2 dr}{4\pi \int \rho_{\text{chain}}(r) r^2 dr} \)  

(4.7)

\( A_{\text{chain}}(q) \) is the normalized Fourier transform of the configurationally average radial density distribution \( \rho_{\text{chain}}(r) \) of the corona chains. In the present study, the corona profile, \( \rho_{\text{chain}}(r) \), is calculated using Spline3 function,\(^{21}\) given by

\[
\rho_{\text{chain}}(r) = \frac{\rho_1(r) + a_1 \rho_2(r) + a_2 \rho_3(r)}{1 + a_2 + a_3}
\]

(4.8)

where \( a_1 \) and \( a_2 \) are fitting parameters. In the fitting processes, \( a_1 \) and \( a_2 \) were found not to be critical in corona profiles in the present study. Therefore, \( a_1 \) and \( a_2 \) are assumed to be zero to eliminate the number of parameters and obscuring of the resultant parameters.

For details of the calculation of \( \rho_{\text{chain}}(r) \), see ref. 21.

The excess electron densities of the core and chain are calculated from the known compositions of core and corona chains as follows:

\[
\Delta Z_{e,\text{core}} = N_A \rho_{\text{SiNP}} \frac{n_{e,\text{SiNP}}}{M_{\text{SiNP}}} - N_A \rho_{\text{brush}} \frac{n_{e,\text{brush}}}{M_{\text{brush}}}
\]

(4.9)

and

\[
\Delta Z_{e,\text{chain}} = N_A \rho_{\text{brush}} \frac{n_{e,\text{brush}}}{M_{\text{brush}}} - N_A \rho_{\text{solv}} \frac{n_{e,\text{solv}}}{M_{\text{solv}}}
\]

(4.10)

where \( n_{e,\text{SiNP}}, n_{e,\text{brush}}, \) and \( n_{e,\text{solv}} \) are the number of electrons of the SiNP, monomer unit of the brush chain, and solvent, respectively; \( \rho_{\text{SiNP}}, \rho_{\text{brush}}, \rho_{\text{solv}}, M_{\text{SiNP}}, M_{\text{brush}}, \) and \( M_{\text{solv}} \) are the densities of SiNP, brush, and solvent, and the molecular weights of SiNP, brush, and solvent, respectively. Here, the density of the polymer brush in the solvent (\( \rho_{\text{brush}} \)) is defined as

\[
\rho_{\text{brush}} = (1 - \nu_{\text{brush}} \rho_{\text{solv}}) \rho_{\text{solv}} + \rho_{\text{solv}}
\]

(4.11)
where $v_{\text{brush}}$ is the partial specific volume of the polymer brush chain, which is determined by fitting the SAXS profile. However, it is difficult to determine the accurate concentration of polymer brushes, $C_{\text{brush}}$, because of the swollen brush structure. The apparent concentration of polymer brushes in the solvent, $C_{\text{brush, app}}$ was therefore used instead of $C_{\text{brush}}$, defined as follows:

$$C_{\text{brush, app}} = \frac{3M_{n,\text{brush}}N}{4\pi N_A \left[ (2s + R_c)^3 - R_c^3 \right]}$$

(4.12)

Kikuchi et al. reported that the values of $v_{\text{brush}}$ of zwitterionic polymer brushes were in accordance with those of corresponding isolated zwitterionic polymers. The partial specific volume for isolated PMTAC chain, $v_{\text{PMTAC}}$ was therefore used for the $v_{\text{brush}}$. As described in Chapter 3, the values of worm-like chain model parameters for PMTAC chains in aqueous NaCl solution have already been determined. Furthermore, the values of $R_c$ have also been estimated. Accordingly, the fitting parameter is now only the radius of gyration of the grafted polymer layer, $s$. 

83
Figure 4.3 SAXS profiles for PMTAC-SiNP having different molecular weight in aqueous NaCl solutions at $C_s =$ (a) 0.05 M, (b) 0.1 M, and (c) 0.5 M at room temperature. The $R_c$ is 96.4 nm.
Figure 4.4 SAXS profiles for PMTAC-SiNP having different molecular weight in aqueous NaCl solutions at $C_s = (a) 0.05 \text{ M}, (b) 0.1 \text{ M}, \text{ and } (c) 0.5 \text{ M}$ at room temperature. The $R_c$ is 53.0 nm.
As can be seen in Figures 4.3 and 4.4, the experimental SAXS profiles were well reproduced by the core–shell model with interacting corona chains. The data are not shown in the figures, but the SAXS profiles cannot be expressed by a simple rigid sphere model with a Schulz size distribution.

Figure 4.5 Typical radial excess electron density profiles for the PMTAC-SiNP (LP4) in aqueous NaCl solutions at Cs = (a) 0.05 M, (b) 0.1 M, and (c) 0.5 M.

Figure 4.5 shows typical radial profiles of excess electron density for LP4 in aqueous NaCl solutions, obtained from fitting of scattering profiles. With decreasing Cs, the PMTAC brushes gradually extended as a result of increasing electrostatic repulsion among quarternary ammonium groups. Similar trends were observed for other PMTAC-SiNP samples; the fitting results of are listed in Table 4.2. Figure 4.6 shows the plots of swollen brush thickness, \( h (= 2s) \), against the weight-average degree of polymerization, \( N_w \), for PMTAC-SiNPs with different \( R_c \) values in aqueous NaCl solutions.
Table 4.2 Radii of Gyration for PMTAC-SiNPs in Aqueous NaCl Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_c$ (nm)</th>
<th>$M_w/10^3$ (g mol$^{-1}$)</th>
<th>$M_w/M_n$ $^b$</th>
<th>$s$ (nm) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$C_s = 0.05$ M</td>
<td>0.1 M</td>
</tr>
<tr>
<td>SP1</td>
<td>50.7</td>
<td>1.87</td>
<td>12.1</td>
<td>11.8</td>
</tr>
<tr>
<td>SP2</td>
<td>60.4</td>
<td>1.75</td>
<td>14.6</td>
<td>13.9</td>
</tr>
<tr>
<td>SP3</td>
<td>56.0</td>
<td>1.67</td>
<td>17.6</td>
<td>16.8</td>
</tr>
<tr>
<td>SP4</td>
<td>85.0</td>
<td>1.62</td>
<td>19.6</td>
<td>18.2</td>
</tr>
<tr>
<td>SP5</td>
<td>108</td>
<td>1.72</td>
<td>23.0</td>
<td>21.0</td>
</tr>
<tr>
<td>LP1</td>
<td>53.4</td>
<td>1.72</td>
<td>33.8</td>
<td>15.4</td>
</tr>
<tr>
<td>LP2</td>
<td>96.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LP3</td>
<td>70.0</td>
<td>1.66</td>
<td>43.2</td>
<td>19.7</td>
</tr>
<tr>
<td>LP4</td>
<td>86.4</td>
<td>1.68</td>
<td>53.0</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>1.63</td>
<td>70.4</td>
<td>31.1</td>
</tr>
</tbody>
</table>

$^a$ $R_c$ denotes a core radius of SiO$_2$. $^b$ The values of $M_w$ and $M_w/M_n$ were estimated by SEC-MALS measurements. $^c$ Radius of gyration for grafted polymer chain.

Figure 4.6 Plots of $h$ against $N_w$ for PMTAC-SiNP with $R_c = (a)$ 96.4 nm and (b) 53.0 nm in aqueous NaCl solutions. Filled symbols represent the $2R_g$ values for isolated PMTAC chain in aqueous NaCl solutions determined in Chapter 3. The dashed line shows the theoretical values of fully stretched (all-trans) chain. The solid curve represents the literature values$^{26}$ for high-density poly(methyl methacrylate) brushes ($\sigma_0 = 0.6–0.7$ chains nm$^{-2}$) on SiNP with $R_c = 65$ nm in acetone at 303 K.

The broken lines in the figure show the theoretical values of fully stretched (all-trans conformation) chains, assuming that the chain contour length per monomer unit of
PMTAC chain is 0.25 nm. The values of $h$ were more than twice those of unbound PMTAC single chains at all $C_s$ values, and were as large as ca. 50% of the full contour length of the PMTAC. These results implied a highly extended structure of PMTAC brushes. The solid curve in the figure corresponds to the experimental values of swollen brush thickness determined by dynamic light scattering for high-density ($\sigma_0 = 0.6–0.7$ chains nm$^{-2}$) PMMA brushes on SiNPs ($R_c = 65$ nm), reported by Ohno et al.$^{26}$ Despite the large difference between the graft densities of PMTAC-SiNP (0.22 chains nm$^{-2}$) and PMMA-SiNP (0.6–0.7 chains nm$^{-2}$), the brush thicknesses are comparable to each other. Furthermore, the $h$ values for PMTAC-SiNP at $C_s = 0.05$ M exceeded those of high-density PMMA-SiNP. The values of $h$ for PMTAC-SiNP decreased with increasing $C_s$ because of the screening effect of electrostatic repulsive interactions among the charges on PMTAC chains, as well as unbound PMTAC chains, in aqueous NaCl solution. Thus, it can be concluded that the electrostatic repulsion among PMTAC chains and the osmotic pressure from counterions confined in the brush layer largely contributed to the swelling behavior of PMTAC-SiNP.

According to Ohno et al., the double logarithmic plot of $h$ versus $M_w$ for PMMA-SiNP gave an approximately linear relationship, showing that $h$ was proportional to $M_w^b$ with $b = 0.83$. PMTAC-SiNP with $R_c = 96$ nm gave a similar relationship to that with PMMA-SiNP, but the value of $b$ was higher than that of PMMA-SiNP. The values of the exponent were 0.92 for $C_s = 0.05$ M, 0.88 for $C_s = 0.1$ M, and 0.85 for $C_s = 0.5$ M. Note that all these values are higher than those of unbound single PMTAC chains, as discussed in Chapter 3 (0.85 for $C_s = 0.05$ M, 0.78 for $C_s = 0.1$ M, and 0.70 for $C_s = 0.5$ M). The exponential law is valid for most kinds of dilute polymer solutions. The values of the exponent are related to the chain conformation of
the polymer. For example, the limiting values of the exponent for random coils are 0.5 (in the theta state) and less than 0.6 (in a good solvent), respectively. The exponent for rod-like polymers usually exceeds 1.0.\textsuperscript{27,28} Therefore, the high values of the exponent for PMTAC-SiNP, around 1.0, indicated a highly extended conformation of grafted-PMTAC chains i.e. rod-like macromolecules.

In contrast, the value of $h$ decreased by roughly half when $R_c$ decreased from 96.4 nm to 53.0 nm, as shown in Figure 4.6(b). This is because the effective graft density ($\sigma_{\text{eff}}$) decreases with decreasing core radius and increasing radial distance from the core surface. The $\sigma_{\text{eff}}$ is expressed using the radial distance $r$ from the core center as follows:

$$\sigma_{\text{eff}} = \sigma_0 \left( \frac{R_c}{r} \right)^2$$

(4.13)

Figure 4.7 shows the radial distance dependence of the calculated values of $\sigma_{\text{eff}}$ for PMTAC-SiNPs with different $R_c$ values. The curvature effects on $\sigma_{\text{eff}}$ are found to be very large.

![Figure 4.7](image)

**Figure 4.7** Dependence of $\sigma_{\text{eff}}$ of PMTAC-SiNP with different $R_c$ on the radial distance from the SiNP core surface.
4.3.4 Theoretical Analysis of Brush Thickness: Daoud–Cotton-type Scaling Model

To understand the observed brush thickness, \( h \), and the values of the exponent \( b \) in detail, the observed experimental values were compared to those obtained from a Daoud-Cotton (DC) scaling model. The modified DC scaling model proposed by Ohno et al. was used.

The DC model was initially proposed to determine the conformation of a star-shaped polymer, by taking into account the radial variations in monomer concentration. The modified DC model consists of a spherical core of radius \( R_c \), and \( f \) graft chains of the same length are radially extended out. The effective graft density, \( \sigma_{\text{eff}} \), decreases with increasing radial distance, according to equation (4.13). When \( \sigma_{\text{eff}} \) is large enough (generally \( \sigma_0 > 0.1 \) chains \( \text{nm}^{-2} \)), the polymer brushes are in the high-density brush regime, where the excluded-volume effect is screened out (chain expansion factor, \( \alpha = 1 \)). As \( r \) increases beyond the crossover radius, \( r_c \), the polymer brushes enter the intermediate-density brush regime (generally, \( 0.01 < \sigma_0 < 0.1 \)), where \( r_c \) is expressed by

\[
    r_c = R_c \sigma_0^{*} \nu^{-1} \quad (4.14)
\]

with

\[
    \nu' = (4\pi)^{1/2} \nu \quad (4.15)
\]

Here, \( \nu \) is the excluded-volume parameter, as defined by the DC model, and \( \sigma_0^{*} \) is the dimensionless graft density (surface coverage), given by \( \sigma_0^{*} = \sigma_0 s_m \), where \( s_m \) is the cross-sectional area of the grafted chain. The values of \( s_m \) for PMTAC were calculated on the basis of the cross-sectional diameters of PMTAC in aqueous NaCl solutions.
determined in Chapter 3; $\sigma_0^*$ is approximated by $\sigma_0^* = fl_m^2/4\pi r_0^2$, where $l_m$ is the chain contour length per monomer unit (0.25 nm), leading to the following expressions for the thickness, $h$, of the brush layer on the particle for different cases. A schematic image of the modified DC model is shown in Figure 4.8.

![Figure 4.8 Schematic image of the modified DC model with a crossover from high-density brush regime to intermediate-density brush regime, where $R_c$, $h$, and $r_c$ are the core radius, brush thickness, and crossover radius, respectively.](image)

**Case 1:** $R_c < r_c$ and $r < r_c$. The whole brush layer is in the high-density brush regime, the relation between brush thickness and graft density is given by

$$h\left[1 + \left(\frac{h}{2R_c}\right)^2\right] = aL_c\sigma_0^*$$

where $a$ is a proportionality constant of the order of unity, and $L_c$ is the full length of the grafted chain.

**Case 2:** $R_c \geq r_c$. The whole brush layer is in the intermediate-density brush regime. We have

$$\left(h + R_c\right)^{\gamma_3} - R_c^{\gamma_3} = A$$

with
\[ A = (5/3) a L_c r_0^{2f} \sigma_0^{*v} \nu^{v/3} \]  

**Case 3: \( R_c < r_c < r \).** The brush layer has a crossover from the high-density brush regime to the intermediate-density brush regime; we have

\[ (h + R_c)^{2f} = A \left[ 1 + \left( 5 + \sigma_0^{*v} \nu^{v/3} \right) \left( \frac{R_c}{10a L_c \sigma_0^{2f/3}} \right) \right] \]

Therefore, the modified DC model predicts that the universal plot of \( h[1+(h/2R_c)] \) against \( L_c \sigma_0^{*1/2} \) will give a straight line, regardless of chain length, graft density, and surface curvature, if the system is in the high-density regime. Here, \( a \) and \( \nu^* \) are the fitting parameters.

Figure 4.9 gives the double logarithmic plots of \( h[1+(h/2R_c)] \) against \( L_{c,w} \sigma_0^{*1/2} \) for PMTAC in aqueous NaCl solutions with different \( C_s \) values. The subscript “w” of \( L_{c,w} \) denotes the weight-average chain contour length of the grafted PMTAC. The fitting parameters are summarized in Table 4.3. As indicated by the solid lines in the figure, PMTAC-SiNP with \( R_c = 96.4 \) nm was in the high-density brush regime at any \( C_s \).
Table 4.3 Fitting Parameters for Modified DC model Used in Figure 4.8

<table>
<thead>
<tr>
<th>$R_c$ (nm)</th>
<th>$C_s$ (mol/L)</th>
<th>$a$</th>
<th>$\nu^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.0</td>
<td>0.05</td>
<td>1.36</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.07</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.01</td>
<td>0.189</td>
</tr>
<tr>
<td>96.4</td>
<td>0.05</td>
<td>1.60</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1.53</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.32</td>
<td>–</td>
</tr>
</tbody>
</table>

The differences in $a$ are probably caused by electrostatic interactions among PMTAC chains, which are not considered in the modified DC model in the present study.

In contrast, PMTAC-SiNP with $R_c = 53.0$ nm is in the high-density brush regime only at $C_s = 0.05$ M. In other words, long range electrostatic interactions among PMTAC chains, such as electrostatic repulsion, enable PMTAC-SiNP to be in the high-density brush regime, although the $\sigma_{\text{eff}}$ largely decreases to less than or close to that of an intermediate brush regime with increasing brush thickness. However, PMTAC-SiNPs with $R_c = 53.0$ nm at $C_s = 0.1$ M and 0.5 M no longer obey the DC model for a high-density brush regime, presumably because of a decrease in $\sigma_{\text{eff}}$ attributed to an increase in curvature and screening of electrostatic interactions by added salt ions. For PMTAC-SiNP with $R_c = 53.0$ nm at $C_s = 0.1$ M and 0.5 M, the data points were well fitted by the DC model, with a crossover from a high-density brush regime to an intermediate-density brush regime.

Therefore, it can be concluded that the relationship between brush thickness and molecular weight of grafted chains is qualitatively explained by the modified DC model. From the model, it is confirmed that the crossover from a high-density regime to an intermediate-density regime, which is closely related to the degree of swelling and
various surface properties of polymer brushes, occurs as the added salt concentration of the solution increases.

### 4.4 Conclusions

In the work described in this chapter, high-density cationic polyelectrolyte brushes with different molecular weights were prepared on SiNPs with a core radii of 53 nm and 96 nm. The chain dimensions for cationic polyelectrolyte brushes in aqueous NaCl solutions were characterized by synchrotron radiation SAXS and USAXS. The swollen brush thickness, $h$, decreased with increasing added salt concentration, and similar trends were also seen in isolated cationic polyelectrolyte chains, as described in Chapter 3. The values of $h$ were more than twice those of unbound single cationic polyelectrolyte chains at all $C_s$ values, and were as large as ca. 50% of the full contour length of the cationic polyelectrolyte chain. The double logarithmic plot of $h$ versus $M_w$ for PMTAC-SiNP with $R_c = 96$ nm gave a linear relationship, showing that $h$ was proportional to $M_w^b$, with $b = 0.92$ for $C_s = 0.05$ M, 0.88 for $C_s = 0.1$ M, and 0.85 for $C_s = 0.5$ M. The high values of the exponent, around 1.0, indicated a highly extended conformation of grafted cationic polyelectrolyte chains, i.e., rod-like macromolecules. The relationship between brush thickness and molecular weight of the grafted chain was qualitatively explained by the modified DC model. It was confirmed that the crossover from a high-density regime to an intermediate-density regime occurs as the added salt concentration of the solution increases. Such a transition is thought to be closely related to the degree of swelling and various surface properties of the polymer brushes.
References


Chapter 5

Tribological Behavior of a Polymer Brush with Ionic Liquid Moiety
5.1 Introduction

In the work described in this chapter, a novel high-density polyelectrolyte brush bearing an ionic liquid moiety has been prepared in order to take advantage of both of their excellent tribological properties as will be described below. The tribological properties of the brushes were characterized by reciprocating tribometer under various conditions.

Since the use of room-temperature ionic liquids as novel lubricants was first reported by Liu and coworkers in 2001,\textsuperscript{1,2,3} ionic liquids have attracted considerable attention as a new class of lubricants.\textsuperscript{4,5} This is because of their unique properties such as negligible volatility, low flammability, high thermal stability,\textsuperscript{6} a low melting point, and a wide liquid range.\textsuperscript{7} These characteristics are derived from ionic interactions between large organic cations and inorganic or organic non-coordinating anions, which together form salts with melting points below room temperature.\textsuperscript{8} Ionic liquids are expected to be ideal candidates for new lubricants under severe conditions such as ultrahigh vacuum and extreme temperatures.\textsuperscript{9,10} The tribological properties of some ionic liquids have been evaluated extensively. Ionic liquids exhibited excellent friction reduction, better wear resistance, and high load capacity than conventional lubricants such as synthetic hydrocarbons and fluoroether polymers.\textsuperscript{1} The tribological properties of ionic liquids largely depend on the chemical structure of the organic cations and anions.\textsuperscript{11} Liu and coworkers proposed that ionic liquids could be easily adsorbed on the sliding surfaces of frictional pairs because of their polar structure. These liquids can form an effective boundary film, which would reduce friction and wear.\textsuperscript{1,2,3} Xiao and coworkers measured film thicknesses of ionic liquids at high pressures up to 3 GPa in real-time employing relative optical interference intensity measurement method.\textsuperscript{12} The film thicknesses of ionic liquids were thicker than those of silicone oils of similar
viscosities, indicating better film-forming ability of ionic liquids. Liu and coworkers further suggested that a tribochemical reaction between an ionic liquid and a friction surface under severe contact conditions forms surface protective films, which was confirmed by Mori and his co-workers.\textsuperscript{13,14,15} However, some tribochemical reactions involving the decomposition of the ionic liquid would cause corrosive wear. In the case of an N-alkyl imidazolium derived ionic liquid, it has been reported that imidazolium with a short alkyl chain and a reactive anion, such as tetrafluoroborate BF\textsubscript{4}\textsuperscript{−} or hexafluorophosphate PF\textsubscript{6}\textsuperscript{−}, increased wear through tribocorrosive attack on steel and aluminum surfaces.\textsuperscript{16} One of the reasons for the increased wear is that BF\textsubscript{4}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−} produce corrosive hydrogen fluoride upon hydrolysis, which can damage frictional systems.\textsuperscript{17} Jiménez et al. reported that trifluoromethanesulfonate or 4-methylbenzenesulfonate anions can reduce tribocorrosion and, consequently, friction and wear, despite the presence of the short alkyl chains of the imidazolium cation.\textsuperscript{18} In contrast, BF\textsubscript{4}\textsuperscript{−} of imidazolium cations with longer chains results in lower friction and wear compared to the corresponding PF\textsubscript{6}\textsuperscript{−} salt.\textsuperscript{18,19} The pressure viscosity coefficient of ionic liquids is also an important factor in the formation of a lubrication film.\textsuperscript{20} Therefore, the lubrication film for hydrodynamic lubrication and the boundary layer on the friction surface are important for reducing friction and wear using ionic liquids as well as conventional oil-base lubricants.

Here, another type of boundary film consisting of a high-density polymer brush with an ionic liquid moiety is proposed to improve the tribological properties of ionic liquids. It is expected that the high-density polymer brush bearing ionic liquid moiety would assist the retention of ionic liquids between the sliding pairs and work as an effective lubrication layer in combination with an ionic liquid. Therefore, a high-density polymer
brush bearing ionic liquid moieties such as imidazolium salts can be expected to act as a
good boundary layer.

Actually, several types of poly(ionic liquid) brushes have already been synthesized. Yu and coworkers prepared a poly(1-ethyl-3-(2-methacryloyloxyethyl)imidazolium chloride) brush on a gold surface and investigated its swelling/collapsing behavior in different electrolyte solutions and also its electrochemical properties.\(^{21}\) Yang and coworkers prepared a polystyrene brush with an imidazolium hexafluorophosphate unit in the side chain by SI-ATRP.\(^{22}\) They found that the surface wettability of the poly(ionic liquid) brushes could be controlled by exchanging their counter anions. Hao and coworkers prepared brush-like poly(ionic liquids)-grafted multiwalled carbon nanotubes (MWCNTs-g-PILs). They evaluated the tribological property of MWCNTs-g-PILs as additives in the base lubricant 1-methyl-3-butylimidazolium hexafluorophosphate, confirming that MWCNTs-g-PILs were excellent anti-wear and friction-reducing additives.\(^{23}\)

In this study, a novel poly(methacrylate) brush bearing an \(N\)-alkylimidazolium ionic liquid unit in the side chain was prepared on a silicon wafer by SI-ATRP. In order to achieve low friction surface and inhibit corrosive wear, a combination of an \(n\)-butyl group and bis(trifluoromethanesulfonyl)imide (TFSI) was selected as the \(N\)-alkyl chain for the imidazolium and counter anions. Subsequently, the macrotribological properties of poly[1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)-imide] (PMIS) brushes in a dry nitrogen atmosphere, water, methanol, and an ionic liquid were investigated by ball-on-plate type tribometer. A tribotest on a non-ionic poly(\(n\)-hexyl methacrylate) (PHMA) brush surface was also carried out as a control experiment.
5.2 Experimental

5.2.1 Materials

Copper(I) bromide [CuBr, Wako Pure Chemical Industries, Ltd. (Wako), Osaka, Japan, 99.9%] was purified by the same procedure as described in Chapter 2. Acetonitrile (Wako, 99.5%), ethyl 2-bromoisobutylate [EB, Tokyo Chemical Inc. (TCI), Tokyo, Japan, 98%), n-hexyl methacrylate (TCI, 98%), pyridine (Wako, 99.5%), and (−)-sparteine (TCI, 98%) were dried and distilled over CaH₂ before use. Anisole was stirred with small pieces of sodium at 373 K for 6 h, followed by distillation from sodium under reduced pressure. Commercially available 2,2′-bipyridyl (Wako, 99.5%), 2-bromoethanol (TCI, 95%), N-butylimidazole (Wako), methanol (Wako, 99.5 %), toluene (Wako, 99.8 %), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Wako, 98 %), and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI, Kanto Chemical Co., Tokyo, Japan, 98%) were used without further purification. Dichloromethane was the same as used in Chapter 2. Surface-initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE) was the same as used in Chapter 4. Silicon (111) wafers (SUMCO Corp., Tokyo, Japan) were cleaned by washing with freshly prepared piranha solution (H₂SO₄/H₂O₂ = 7/3, v/v) at 373 K for 1 h followed by exposure to vacuum ultraviolet-ray (VUV) generated from an excimer lamp (UER20-172V, USHIO Inc., Tokyo, Japan, λ = 172 nm) for 10 min under reduced pressure (30 Pa). The BHE monolayer was immobilized on the silicon wafer by chemical vapor adsorption technique. Deionized water used for contact angle measurement was purified by the Simpli Lab (Nihon Millipore Ltd., Tokyo, Japan). 2-Bromoethyl methacrylate was synthesized by the reaction of 2-bromoethanol and methacryloyl chloride in the presence of pyridine in dichloromethane at 273 K, as shown in Scheme 5.1.
Synthesis of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bromide (MIB)

The mixture of 2-bromoethyl methacrylate (109 mmol) and N-butylimidazole (110 mmol) was stirred at 313 K for 4 days. During the reaction, small amount of p-tert-butylichlorocatechol (50 mg) was added to the reaction mixture to inhibit the thermal polymerization of the resulting monomer MIB. Reaction mixture was dissolved in ca.10 mL of dichloromethane and was poured into a large amount of hexane to give a precipitate. The product was collected and dried in vacuo to form a high-viscous pale-yellow liquid in a yield of 30.16 g (95 mmol, 87%). $^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ (ppm) 0.87 (t, 3H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.20 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.74 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.82 (s, 3H, CH$_3$), 4.17 (m, 2H, OCH$_2$), 4.47 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 4.52 (m, 2H, OCH$_2$CH$_2$), 5.71 and 6.01 (s, 2H, CH$_2$=), 7.84 (m, 2H, N-CH=CH-N), 9.32 (s, 1H, N-CH=N).

Scheme 5.1 Synthesis of MIS Monomer

Synthesis of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis(trifluoromethane-sulfonyl)imide (MIS)

The mixture of LiTFSI (87 mmol) and MIB (95 mmol) diluted with deionized water (130 mL) was stirred at 298 K for 36 h to give a liquid-liquid phase separation. The organic layer containing the ionic liquid was isolated with a separating funnel and diluted with dichloromethane. The solution was washed with water three times, mixed with activated carbon powder, and allowed to stand in a light-resistant container.
overnight. After filtration, the product was concentrated by evaporator and was dried under reduced pressure to afford 39.8 g of MIS (77 mmol, 88%) as a viscous liquid.

$^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta$ (ppm) 0.87 (t, 3H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.20 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.74 (m, 2H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.82 (s, 3H, CH$_3$), 4.17 (t, 2H, OCH$_2$), 4.47 and 4.52 (q, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$, OCH$_2$CH$_2$), 5.71 and 6.01 (s, 2H, CH$_2$=), 7.80 (m, 2H, N-CH=CH-N), 9.23 (s, 1H, N-CH=N); $^{13}$C NMR (DMSO-$d_6$, 75 MHz): 13.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 18.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 18.8 (CH$_3$), 31.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 48.2 and 48.8 (NCH$_2$CH$_2$), 62.8 (OCH$_2$), 122.9 (CH$_2$=), 123.2 and 127.0 (N-CH=CH-N), 135.5 (CH$_2$=C), 137.1 (N-CH=N), 166.4 (C=O)

**Polymer brush preparation**

A few sheets of the silicon wafers with immobilized BHE, CuBr (0.045 mmol), and bpy (0.091 mmol) were introduced into a well-dried glass tube with a stopcock, which was degassed by seven cycles of vacuum pumping and flushing with argon. Degassed acetonitrile (4.4 mL), MIS (8.54 g, 17 mmol), and ethyl 2-bromoisobutylate (free initiator, 0.025 mmol) in a separate Schlenk flask were added to a catalyst in the glass tube. The polymerization solution was degassed by a repeated freeze-and-thaw process to remove the oxygen. The polymerization reaction was conducted at 318 K for 73 h under argon to simultaneously generate PMIS brush from the substrate and free PMIS from ethyl 2-bromoisobutylate (Scheme 5.2). The reaction was stopped by opening the glass vessel to air, and the reaction mixture was poured into chloroform to precipitate the free polymer. The polymer solution was passed through the alumina column using THF to remove the catalysts. The silicon wafers were washed with acetonitrile using a Soxhlet apparatus for 12 h to remove the free polymer adsorbed on their surface, and were dried under reduced pressure for 2 h.
PHMA brush was also prepared in a similar manner using (−)-sparteine and anisole, as a ligand and a solvent, respectively.

5.2.2 Characterization

5.2.2.1 Size Exclusion Chromatography (SEC)

SEC equipped with a multi-angle light scattering (MALS) on the unbound PMIS was performed to determine the absolute molecular weight and molecular weight distribution with a SHIMADZU liquid chromatography system as described in Chapter 2. Three polystyrene gel columns of Shodex GF-310 HQ × 2 + GF-510 HQ were claimed to separate the polymers. Methanol/water (9/1, v/v) containing acetic acid (0.5 M) and sodium nitrate (0.2 M) was used as an eluent at a flow rate of 0.6 mL min⁻¹.

5.2.2.2 Differential Scanning Calorimetry (DSC)

DSC measurement was conducted using an EXSTAR6000 (SEIKO Instruments Inc., Chiba, Japan). Samples of ca. 5 mg were used in tests. They were sealed in aluminium
pans and heated at a heating rate of 10 K min\(^{-1}\) in a temperature range of 173 to 473 K. The glass transition temperature (\(T_g\)) was determined from a third scan.

### 5.2.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out on an APEX (ULVAC-PHI, Inc., Kanagawa, Japan) at 10\(^{-6}\) Pa using a monochromatic Al-K\(\alpha\) X-ray source of 150 W. All XPS data were collected at a take-off-angle of 45°, and a low-energy (25 eV) electron flood gun was used to minimize sample charging. The survey spectra (0–1000 eV) and high-resolution spectra of C\(_{1s}\), O\(_{1s}\), F\(_{1s}\), N\(_{1s}\), S\(_{2p}\), and Si\(_{2p}\) were acquired at pass energies for the analyzer of 100.0 eV and 25.0 eV, respectively. X-ray beam was irradiated onto an area with a diameter of ca. 0.2 mm.

### 5.2.2.4 Contact Angle Measurement

The static contact angles of water and EMImTFSI on silicon wafers were recorded with a drop shape analysis system, DSA10 Mk2 (KRÜSS Inc., Hamburg, Germany), equipped with a video camera. A droplet of 2.0 mL was used for contact angle measurement. Angles from different spots were measured 10 times and statistically compiled.

### 5.2.2.5 Surface Analysis and Thickness of Polymer Brush

AFM observations were carried out with an SPI4000 (SII NanoTechnology Inc., Chiba, Japan) using a Si\(_3\)N\(_4\) tip on a cantilever with a spring constant of 0.09 N m\(^{-1}\) under vacuum. The thicknesses of the polymer brushes on the silicon substrates were evaluated by an imaging ellipsometer (Nippon Laser and Electronics Lab., Aichi, Japan)
equipped with a YAG laser ($\lambda = 532.8$ nm). Optical micrographs were obtained using an Eclipse E400 (Nikon Corporation, Tokyo, Japan).

5.2.2.6 Macroscopic Friction Test Using a Ball-on-Plate Tribometer

Macroscopic friction tests on polymer brushes were carried out on a conventional ball-on-plate type reciprocating tribometer, (Tribostation Type32, Shinto Scientific Co. Ltd., Tokyo, Japan) The test involves sliding a glass ball probe on the substrates at a reciprocating distance of 20 mm and a rate of $1.5 \times 10^{-3}$ m s$^{-1}$. Tests were conducted in a dry nitrogen atmosphere, water, methanol, and EMImTFSI under a normal load of 0.49 N at room temperature. The friction force was measured by a strain gauge attached to the arm of the tester and was recorded as a function of time. The friction coefficient was given by the friction force divided by the normal load. Every friction test used a virgin surface area on the brush substrate to measure the friction coefficient for the first reciprocating scan of the sliding probe. The friction coefficients for at least five trials were measured and averaged. In the case of a bare silicon wafer, the friction coefficients of the fourth scan were stored to avoid the influence of the oxide layer on the silicon surface. The test piece substrate was pinned by a Teflon belt and screws in a Teflon trough filled with an ionic liquid. The Teflon trough was fixed on the moving stage. In the case of a non-modified silicon wafer under a normal load of 50 g (0.49 N), the theoretical contact area between the glass probe and substrate could be estimated to be $3.51 \times 10^{-9}$ m$^2$ by Hertz's contact mechanics theory$^{26}$ and the average pressure on the contact area was estimated to be 139 MPa. Although the actual contact area and pressure on the brush surface cannot be estimated by Hertz’s contact mechanics theory, the normal pressure would have been over $10^2$ MPa in our experiments.
5.3 Results and Discussion

5.3.1 Preparation of a Polymer brush with an Ionic Liquid Moiety

The SI-ATRP of MIS at 318 K from the silicon wafer with immobilized initiator proceeded slowly for 3 days to yield a PMIS brush with a thickness of 54 nm, as shown in Scheme 5.2. The formation of the PMIS brush was confirmed by XPS as shown in Figure 5.1. The peaks corresponding to C-C, C-O (C-N), C=O, and CF$_3$ bonds were appeared at 285.0, 286.5, 288.8, and 295.0 eV, respectively. The N$_{1s}$ spectrum exhibited two peaks at 399.2 and 401.8 eV attributed to the sulfonylimide and imidazorium units. The F$_{1s}$ and S$_{2p(3/2)}$ peaks of sulfonylimide anion were observed at 688.5 and 168.4 eV. The surface atomic concentrations of carbon, oxygen, fluorine, nitrogen, and sulfur measured by XPS revealed good agreement with the theoretical values calculated from the atomic composition of MIS monomer.

![Figure 5.1 XPS spectra of PMIS brush surface; (a) survey scan spectrum, high resolution spectra of (b) F$_{1s}$, (c) O$_{1s}$, (d) N$_{1s}$, (e) C$_{1s}$, (f) S$_{2p}$ peak region.](image)

As can be seen in Figure 5.2, the AFM observation revealed that a homogeneous polymer layer was formed on the substrate, and the surface roughness was less than 0.5
nm in vacuo in a 5 μm × 5 μm scan area. A 60-nm thick PHMA brush was also prepared by a similar SI-ATRP protocol. SI-ATRP in the presence of the unbound initiator simultaneously produced a polymer brush and an unbound polymer. The number-average molecular weight ($M_n$) value of unbound PMIS estimated by MALS-SEC was 316,000, and its polydispersity index ($M_w/M_n$) was 1.32.

![AFM image of PMIS brush on a silicon wafer.](image)

**Figure 5.2** AFM image of PMIS brush on a silicon wafer. The surface roughness was less than 0.5 nm in vacuo in a 5 μm × 5 μm scan area.

The $M_n$ of free PHMA and $M_w/M_n$ measured by SEC using THF as an eluent were 65,400 and 1.74, respectively. The $M_n$ of the surface-grafted polymer on the silicon wafer was not directly measured in the present study, but it is widely known that a polymer brush should have the same molecular weight as the corresponding free polymer. The unbound PMIS was a highly viscous polymer at room temperature because the glass transition temperature ($T_g$) obtained by DSC was 268.5 K, which is very close to the $T_g$ of PHMA (268.0 K). The unbound PMIS dissolved well in acetone, acetonitrile, methanol, and EMImTFSI, but was insoluble in water, diiodomethane, and toluene. As described in Introduction, the relationship between the solubility of PMIS and the frictional properties of the brush is important. The graft density, $\sigma$, of the PMIS brush was estimated to be 0.14 chains nm$^{-2}$ based on the relationship between the thickness $L$ (nm) and $M_n$, as follows:
\[ \sigma = d \times L \times N_A \times 10^{-21} / M_n, \]

where \( d \) and \( N_A \) are the assumed density of bulk polymer (g cm\(^{-3}\)) at 293 K and Avogadro’s number, respectively. This value is lower than the typical graft density of a PMMA brush (0.60–0.70 chains nm\(^{-2}\)) or a PHMA brush (0.56 chains nm\(^{-2}\)) prepared by the “grafting-from” method. The low value is attributed to bulky imidazolium group on the side chain of PMIS, which occupies a larger cross-sectional area on the surface compared to PMMA and PHMA.

Contact angles against water and diiodomethane were listed in Table 6.1. The surface free energy of PMIS brush calculated by Owens’ protocol\(^{29}\) was 30.1 mJ m\(^{-2}\). The contact angle of the EMImTFSI on PMIS brush surface was 10° within 1 min after the EMImTFSI was dropped. However, the ionic liquid spread continuously and permeated into the brush, and the contact angle reached nearly zero degree within 10 min as indicated in Figure 5.3. This result indicated the excellent affinity of PMIS brush towards EMImTFSI.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle (deg)</th>
<th>Surface free energy (mJ m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water(^a)</td>
<td>CH(_2)I(_2)(^a)</td>
</tr>
<tr>
<td>PMIS brush</td>
<td>79</td>
<td>68</td>
</tr>
<tr>
<td>PMIS spin cast film</td>
<td>84</td>
<td>71</td>
</tr>
<tr>
<td>PHMA brush</td>
<td>92</td>
<td>74</td>
</tr>
</tbody>
</table>

\(^{a}2.0 \mu L\)
5.3.2 Frictional Properties of the PMIS Brush

5.3.2.1 PMIS brush vs. Bare Silicon Wafer – Effect of Sliding Velocity

Figure 5.4 shows the effect of sliding velocity of a glass ball probe on friction coefficients against PMIS brush surface and non-modified silicon wafer surface in EMImTFSI, over a distance of 20 mm under a load of 0.49 N at 298 K. The friction coefficients at each sliding velocity were measured on a virgin surface area of the brush and silicon substrate. The friction coefficients of the PMIS brush were much lower than the bare silicon wafer surface in the sliding velocity range of $10^{-4}$–$10^{-1}$ m s$^{-1}$. These results indicated that the combination of PMIS brush and EMImTFSI showed an excellent friction reduction. One reason for reduction in the friction is that the PMIS brush has a particular affinity for EMImTFSI. Therefore, EMImTFSI easily permeated into the PMIS brush and the PMIS brush would be highly solvated with EMImTFSI to form an effective boundary layer. It is thought that the swollen brush layer retained EMImTFSI under friction condition and the swollen brush with an ionic liquid can support the normal load to reduce the interaction between the substrate and glass probe.

Figure 5.3 Contact angles of EMImTFSI droplet on (a) PHMA brush and (b) PMIS brush surface at 298 K.
Figure 5.4 Sliding velocity dependence of the friction coefficient of (a) glass ball probe with immobilized PMIS brush vs. PMIS brush and (b) bare glass ball probe vs. silicon wafer in EMImTFSI under a load of 0.49 N at 298 K.

The decrease in the friction coefficient with an increase in the sliding velocity was observed in both the brush-on-brush and glass-on-silicon friction systems. The friction coefficient of the silicon wafer gradually decreased from 0.28 to 0.08 when the sliding velocity increased from $10^{-4}$ to $3 \times 10^{-2}$ m s$^{-1}$ and increased with a further increase in sliding velocity after $3 \times 10^{-2}$ m s$^{-1}$. In contrast, the friction coefficient of the PMIS brush gradually and continuously decreased from 0.07 to 0.01 with an increase in the sliding velocity over a wide range of $10^{-4}$ to $10^{-1}$ m s$^{-1}$.

The drastic reduction in the friction coefficient at a certain velocity could be caused by transition in the friction regime. Making a comparison to the Stribeck curve, the decreasing friction with increasing sliding velocity suggests that this system is in the mixed lubrication regime. At low sliding velocity, the interaction between the polymer brushes and their interpenetration dominated the friction to give a large friction coefficient (boundary or interfacial friction). With an increase in the sliding velocity, a thicker liquid layer would be formed between the sliding surfaces by the hydrodynamic lubrication effect to reduce the effective contact area and the friction force (mixed
lubrication region). At higher sliding rates (or viscosities or lower pressure), the Striebeck curve will move to the elastohydrodynamic and hydrodynamic regimes, and an increase in the friction force with the sliding velocity is expected due to the shear resistance of the fluids. Hydrodynamic lubrication by poly(styrene) brush in a solvent has been already confirmed by microtribological test on an AFM, which was well described by the relationship between shear velocity and degree of swelling of a poly(styrene) brush.\textsuperscript{31}

5.3.2.2. PMIS Brush vs. PHMA Brush against Glass Ball –Effect of Solvent

Figure 5.5 shows the friction coefficients of the PMIS and PHMA brushes measured by sliding a glass ball probe over a distance of 20 mm at a sliding velocity of $1.5 \times 10^{-3}$ m s$^{-1}$ in a dry nitrogen atmosphere, water, methanol, toluene, and EMImTFSI under a normal load of 0.49 N at 298 K. A high friction coefficient was observed under the dry N$_2$ condition for both brushes, whereas lower friction coefficients were observed in the water and organic solvent due to fluid lubrication effect. The friction coefficient of the non-modified silicon wafer was larger than 0.2 in the dry N$_2$ atmosphere, although the corresponding value is not shown in Figure 5.5. It is notable that the friction coefficient appears to be dependent on the solvent quality. A remarkable reduction in the friction coefficient was observed for the PMIS brush in methanol and EMImTFSI, which are good solvents for PMIS, while a higher friction coefficient was observed in water and toluene which are poor solvents for PMIS. The effect of the solvent quality on the frictional properties of polymer brushes in various solvents has been previously reported. When the solvent was changed from a good solvent to a theta solvent, Kilbey et al. detected larger shear forces between sliding surfaces with immobilized PS brushes using SFA.\textsuperscript{32}
Figure 5.5 Friction coefficients of (a) PMIS and (b) PHMA brushes in dry N₂ atmosphere, water, methanol, toluene, and in EMImTFSI by sliding a glass ball over a distance of 20 mm at a sliding velocity of $1.5 \times 10^{-3}$ m s⁻¹ under a load of 0.49 N at 298 K.

Spencer and coworkers observed that the friction coefficient of a poly(ethylene glycol) (PEG) brush surface in water, measured by colloidal-probe lateral force microscopy, increased from 0.2 to 0.6 when the volume fraction of 2-propanol exceeded 85%.³³ They found that a hydrated PEG brush in water adopted an extended chain conformation to afford effective boundary lubricants, whereas an increase in the 2-propanol fraction resulted in the collapse of the brush-like structure to a more random-coil-like polymer conformation. High-density PMMA brushes in toluene and acetone exhibited lower friction coefficients than in hexane and cyclohexane when a stainless steel ball was used as the sliding probe.³⁴ Therefore, the magnitude of the polymer/solvent interaction must have played an important role in the solvent quality effect. In this study, EMImTFSI and methanol were regarded as good solvents whereas water and toluene were inferior in quality for PMIS. A PMIS brush would be highly solvated with EMImTFSI to form a swollen boundary layer. EMImTFSI would moderate the interaction between the brush surface and the glass ball probe to give a
lower friction coefficient. In contrast, the PMIS chains in water or toluene would be unwilling to be in contact with solvent molecules, but rather prefer to interact with the polymers or friction probe rather than solvent molecules, thus giving a higher friction coefficient. A similar trend was observed with the PHMA brush. PHMA brush showed a much lower friction coefficient in toluene, which is a good solvent for PHMA. On the other hand, water, methanol, and EMImTFSI are poor solvents for PHMA. Therefore, the friction coefficient of the PHMA brush was not reduced, even in EMImTFSI. These results indicated that the imidazolium moiety in the polymer brush contributed to the reduction in the friction coefficient, especially when combined with an ionic liquid.

When a glass ball probe with immobilized PMIS brush was used as the sliding probe, as shown in Figure 5.6, the friction coefficient of the PMIS brush was further reduced. For instance, the brush-vs.-brush friction coefficient in an ionic liquid was 0.048, which was lower than that of the brush-vs.-glass (0.078).

![Figure 5.6](image)

**Figure 5.6** Friction coefficient of PMIS brush in dry N₂ atmosphere, water, methanol, toluene, and in EMImTFSI by sliding a glass ball with immobilized PMIS brush over a distance of 20 mm at a sliding velocity of $1.5 \times 10^{-3}$ m s⁻¹ under a load of 0.49 N at 298 K.
We proposed that this reduction in the friction coefficient was caused by the presence of a thicker boundary film produced by the swollen brush and high osmotic pressure from densely-grafted polymer chains with the approach of brush bearing surfaces.

5.3.2.3. PMIS vs. PHMA Brush against Bare Glass – Effect of Friction Cycles

Fig. 5.7 shows the variations in the friction coefficients of the PMIS brush and PHMA brush in a dry nitrogen atmosphere with the number of friction cycles. The friction coefficient of the PHMA brush film began to increase in the early stage of the friction test, attaining a magnitude of 0.12 within 150 tracking cycles. This result indicates that the PHMA brush was abraded away by the sliding glass probe. In contrast, the relatively low friction coefficient of the high-density PMIS brush was continuously observed, as shown in Fig. 5.7 (a), implying a better wear resistance compared with the PHMA brush. Actually, the high-density PMIS brush maintained a friction coefficient of around 0.16 even after 800 friction cycles.

![Figure 5.7](image)

Figure 5.7 Evolution of the friction coefficient vs. the number of friction cycles \( N \) for the surface of (a) PMIS brush and (b) PHMA brush at a sliding velocity of \( 1.0 \times 10^{-2} \text{ m s}^{-1} \) under a load of 1.96 N in dry \( \text{N}_2 \) atmosphere.
5.3.3. Optical Microscopic Observation and XPS Surface Analyses of Wear Track

Fig. 5.8 displays an optical microscope image of the wear track after 400 friction cycles by the glass probe sliding at a sliding velocity of $1.0 \times 10^{-2} \text{ m s}^{-1}$ under a load of 1.96 N in a dry N$_2$ atmosphere at 298 K and high-resolution XPS spectra of C$_{1s}$ and Si$_{2p}$ regions for the virgin surface and the worn surface inside the wear track after 400 friction cycles. Even with the wear track formed on the brush surface by the friction test, the components of the brush would remain in the wear tracks. With an increase in the number of friction cycles from 0 to 400, the atomic ratio of carbon and silicon ($C_{1s}/\text{Si}_{2p}$) decreased from 31.8 to 10.3, probably due to the reduction of the brush thickness.

![Optical microscope image of the wear track and XPS spectra](image)

**Figure 5.8** Optical microscope image of the wear track of the PMIS brush surface after 400 friction cycles by glass ball probe sliding at a sliding velocity of $1.0 \times 10^{-2} \text{ m s}^{-1}$ under a load of 1.96 N in dry N$_2$ atmosphere at 298 K and high resolution XPS spectra of C$_{1s}$ and Si$_{2p}$ peak regions for (a) the original surface and (b) the worn surface inside the wear track after 400 friction cycles.
The C\textsubscript{1s} spectra of brush surfaces before and after the friction tests showed similar peak patterns, indicating that the chemical structure of PMIS still remained. We also confirmed that the atomic ratio of carbon and fluorine decreased drastically after 1000 friction cycles, whereas the sulfur component still remained on the worn surface. These results reveal that the chemical decomposition of the PMIS and counter anions took place after the brush layer peeled off.\textsuperscript{35}

As mentioned in the Introduction, the tribological properties of an ionic liquid largely depend on counter anions. Minami\textsuperscript{36} and Itoh et al.\textsuperscript{37} reported excellent tribological properties when using hydrophobic anions, such as trifluorotris(pentafluoroethyl) phosphate and perfluoroalkyl sulfate, probably because the low moisture content of ionic liquids retards unfavorable chemical reactions. In this work, only TFSI was investigated as a counter anion for an imidazolium-type poly(ionic liquid). Further improvement in the tribological properties of poly(ionic liquids) can be expected by optimizing the combination of organic anions and cations.

5.4. Conclusions

In the work described in this chapter, we have investigated the tribological properties of a poly(ionic liquid) brush, PMIS, and have compared this brush with a non-ionic PHMA brush. The PMIS brush showed a friction coefficient of around 0.16 even after 800 cycles of reciprocating sliding against a glass ball probe under a dry nitrogen atmosphere. On the other hand, under identical condition while the PHMA brush showed a friction coefficient much higher than 0.3 and completely worn out after 150 friction cycles. These results indicate that the poly(ionic liquid) brush contributed to the formation of a good lubricant layer. In addition, we showed that the combination of a poly(ionic liquid) brush and an ionic liquid showed a low friction coefficient.
The influences of solvent quality on the tribological properties have been well studied, and in general, a polymer brush immersed in a good solvent would afford extremely low friction coefficient. The affinity of the polymer brush for the solvent (or lubricant) plays an important role in controlling the interaction between the brush and the friction probe, as well as the frictional properties. XPS analysis of the wear tracks revealed that the PMIS brush layer was gradually abraded away by sliding the glass ball probe in a dry N\textsubscript{2} atmosphere under a load of 1.96 N, and the layer was peeled off after 1000 friction cycles, which resulted in a much higher friction coefficient.
References


(22) He, X.; Yang, W.; Pei, X. *Macromolecules* **2008**, *41*, 4615–4621.


(26) If a circle with radius $a$ (m) is regarded as the contact area between a glass ball and substrate under a normal load $P$ (0.49 N), Hertz's theory affords the following relationship using Young's modulus of glass and silicon wafer, $E_A$ ($7.16 \times 10^{10}$ Pa), $E_B$ ($1.30 \times 10^{11}$ Pa), and Poisson's ratio $\nu_A$ (0.23), $\nu_B$ (0.28), respectively;

$$2/E = (1 - \nu_A^2)/E_A + (1 - \nu_B^2)/E_B$$

$$a = (3/4 \times 2/E \times P \times R_A)^{1/3}$$

where $R_A$ is curvature radius ($5.00 \times 10^{-3}$ m) of glass ball. The contact area can be calculated by $\pi a^2$.


Chapter 6

Conclusion and Perspective
In this thesis, the methods for controlled radical polymerization of nonionic and ionic monomers in polar protic solvents have been first established, and then the chain dimensions and chain conformations of well-defined cationic polyelectrolytes and cationic polyelectrolyte brushes in aqueous NaCl solutions have been investigated. The main aim of this research was to obtain more detailed understanding of how the chain conformations of polyelectrolyte brushes are different from those of unbound polyelectrolyte chains in aqueous solutions and how the chain conformations of the polyelectrolyte brushes is related to their excellent surface properties.

In Chapter 2, the methods for controlling atom transfer radical polymerization (ATRP) in polar protic solvents have been demonstrated in order to synthesize well-defined polyelectrolytes and polyelectrolyte brushes directly from electrolyte monomers. Unfavorable side reactions often take place in protic solvents because of their polar character, however, electrolyte monomers are soluble only in polar protic solvents. The addition of organic chloride salts into ATRP system with protic solvents effectively suppresses the side reactions; moreover the halogen exchange occurs between added chloride salt and growing alkyl bromide chain ends, which largely improves control of ATRP.

In Chapter 3, chain dimensions and chain conformations of single cationic polyelectrolytes in aqueous NaCl have been investigated by dynamic light scattering and small-angle X-ray scattering (SAXS). Theoretical analysis using helical wormlike chain model revealed that not only excluded volume strength and chain stiffness but also the local chain conformation of cationic polyelectrolytes largely affected by the ionic strength of the solution. This fundamental research is essential for in-depth understanding in a characteristic chain conformation of polyelectrolytes brushes as discussed in Chapter 4.
In Chapter 4, well-defined high-density polyelectrolyte brushes on silica nanoparticles have been characterized by synchrotron radiation ultra-small-angle X-ray scattering and SAXS. The swollen brush thickness in aqueous NaCl solutions (0.05–0.5 M) was more than twice chain dimensions of corresponding single cationic polyelectrolyte chain, and as large as about 50% of the full contour length of the grafted chain. These results indicated a highly extended conformation of the grafted polyelectrolyte chains. The relationship between the brush thickness and molecular weight of the grafted chains was qualitatively explained by the modified Daoud–Cotton scaling theory. It was confirmed that the crossover from a high-density regime to an intermediate-density regime occurs with increasing concentration of the added salt.

In Chapter 5, novel high-density polyelectrolyte brushes bearing ionic liquid moieties were prepared in order to improve tribological properties. The polyelectrolyte brushes with ionic liquid moieties showed extremely low friction coefficient in an ionic liquid, and the brushes also showed better wear resistance than nonionic high-density polymer brushes. As ionic liquids have low volatility, low flammability, and high thermal stability, this lubrication system is expected to be used under extreme conditions such as high temperatures and aerospace.
Acknowledgements

I am indebted to my supervisor, Prof. Atsushi Takahara for his helpful advices, insightful comments, considerable encouragement, and wide-ranging discussions toward the completion of this thesis. I would like to thank Prof. Hideyuki Otsuka for his helpful comments and valuable advices. I am deeply grateful to Prof. Motoyasu Kobayashi and Dr. Moriya Kikuchi for their continuing supports, technical helps, and extensive discussions. Without their guidance and persistent help, this thesis would not have been completed. I received generous supports from Takahara Lab members in Institute for Materials Chemistry and Engineering and ERATO Takahara Soft Interfaces Project. The synchrotron radiation experiments were performed at beamline BL40B2 and BL19B2 at the SPring-8 facility with the technical help of Dr. Noboru Ohta. Prof. Keiji Tanaka and Prof. Satoru Kidoaki are greatly appreciated for their helps and advices to complete this thesis. This work was supported by Grant-in-Aid for JSPS fellows. I would like to thank JSPS for the grant that made it possible to complete study. Finally, I would like to express my gratitude to my family, Ichiro, Akiyo, Shinji, Chiaki, and Masumi for their moral supports and warm encouragements.