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Fabrication of Soft Materials Utilizing the Control of Ionic Dissociation in Organic Media

Kazuya ISEDA

2014

Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan
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Chapter 1

General Introduction

1-1. Purpose of This Thesis

With the development of supramolecular chemistry in recent years, a number of functional soft materials using various supramolecular interactions such as hydrogen bonding, charge-transfer interactions, and coordinate bond have been developed. Especially, polyelectrolyte gels are one of the typical functional soft materials currently actively studied due to the unique swelling property. Starting with discovery of the volume phase transition of a polymer gel by Tanaka et al.[1], various functional soft materials using the polyelectrolyte gels have been exploited. They can drastically change their volume in response to various external stimuli such as pH[2], temperature[3], light[4], and electric field.[5] They have been of much interest due to various applications such as sensors[6], actuators[7], and drug delivery systems[8]. Although they are useful for the design of various stimuli-responsive materials due to their various applications, they collapse in most organic solvents because of the aggregation of the ionic groups and incompatibility of the polar polymer network to the media.[9] Limitation of the applicable media has restricted the broad applications of the polyelectrolyte gels. With that in mind, the author’s group demonstrated that poly(octadecyl acrylate) gels bearing a tetraalkylammonium tetraphenylborate derivative as a lipophilic ionic group acted as polyelectrolyte gels even in non-polar solvents such as tetrahydrofuran and chloroform.[10] This achievement showed that polyelectrolyte gels were applicable in various organic solvents. Moreover, this result strongly indicated that electrostatic interactions were available as strong intermolecular repulsive forces, whereas it has been generally considered as intermolecular attractive forces in organic solvents. Here, the main issue of this thesis is to clarify the utility of the electrostatic interaction in organic media as intermolecular repulsive force, and develop functional soft materials by controlling the electrostatic repulsive force.
1-2. Intermolecular Interactions for Construction of Soft Materials

Soft material is a general term that includes polymers, gels, colloids, micelles, liquid crystals, and biomacromolecules such as proteins and DNA, and their properties are controlled by weak intermolecular interactions through molecular assemblies. These intermolecular interactions include hydrogen bonding, \( \pi-\pi \) stacking interactions, electrostatic interactions, charge-transfer interactions, and van der Waals interactions. They have different features in many respects such as strength, distance, directionality, and attraction or repulsion. For example, nucleic acids and proteins spontaneously self-assemble into well-defined ternary or quaternary structures using these intermolecular interactions. Various functional soft materials have been purposefully created and provided new important findings by controlling the intermolecular interactions. In the next section, the construction of soft materials using intermolecular interactions and the relationships between the kind of weak interactions and function of them are reviewed.

1-2-1. Soft Materials Using Intermolecular Attractive Forces

The quantification of intermolecular interactions is of paramount importance for the design of new soft materials. Noncovalent bond energies range from coordinative bonds with a strength of several hundreds of \( \text{kJmol}^{-1} \) to weak van der Waals interactions of only a few \( \text{kJmol}^{-1} \). Among the intermolecular interactions, there are two intermolecular repulsions, exchange repulsions and electrostatic repulsive forces. And for intermolecular attractive forces, hydrogen bonds, van der Waals interactions, charge transfer interactions, and coordination bonds are known. Most of soft materials are organized by utilizing these intermolecular interactions.

Hydrogen bonding: Hydrogen bonding is pivotal in biochemistry and is also greatly employed in artificial supramolecules. It is much stronger interaction than others and has the clear directionality, which allows to control the geometry of the complexes, to design precisely complementary hosts for a given guest, and to prepare linear supramolecular polymers. E. W. Meijer et al. described the strong dimerization of 2-ureido-4[H]-pyrimidones by quadruple hydrogen bonding, and demonstrated the formation of the supramolecular polymer using the telechelic polymers with the quadruple hydrogen bonding (Figure 1-1a). J. Rebek, Jr. et al. demonstrated the reversibly formed polymeric capsules
formed from two calix[4]arene tetraureas covalently connected at their lower rims (Figure 1-1b).\cite{14} The polymerization and depolymerization of the polycaps were controllable by the addition of guest monomer and an excess of a simple dimeric capsule, respectively. More recently, many exciting examples of programmed structure formation of polymeric architectures such as nanorods, nanotubes, and three-dimensional network, which are called supramolecular gels have been reported.\cite{15}

![Image](image.png)

**Figure 1-1.** (a) Supramolecular polymers with quadruple hydrogen-bonded ureidopyrimidone units and the photograph of poly(ethylene/butylene) functionalized with the hydrogen-bonded units. (b) The basic unit of a polycap involves covalent connection of two calixarenes subunits through a spacer unit, and schematic illustration of polycap formation by encapsulation of guests (G).

Charge-transfer interactions: Charge-transfer (CT) interactions are intermolecular interactions between a \(\pi\)-electron-rich compound, a donor, and a \(\pi\)-electron-deficient compound, an acceptor. The high specificity and directionality of CT interactions enables the alternative arrangement between them to be controlled. The electron transfer from HOMO of the donor into LUMO of the acceptor provides distinct charge transfer bands in the visible region. These traits led to construct various supramolecular complexes such as organic crystalline materials\cite{16}, low-molecular-weight organic gelators\cite{17}, and supramolecular polymers\cite{18}. Sessler et al. reported a class of structurally characterized heterocomplementary, self-assembled materials obtained from the pairing of electron-rich tetrathiafulvalene-calix[4]-pyrroles (TTF-C4Ps) and electron-poor cis/trans-bis-
(dinitrophenyl)-calix[4]pyrroles (DNP-C4Ps) as shown in Figure 1-2. These self-assembled materials acted as intelligent chemoresponsive materials, displaying distinctive changes in structure, color, electro-chemical and spectroscopic features in exposure to the appropriate guests such as tetraethylammonium chloride (TEACl) and trinitrobenzene (TNB).

Coordinate bonds: A coordinate bond is a bond between metal ions and a ligand that is produced when one atom shares a pair of electrons with another atom lacking such a pair. Coordinate bonds have moderate to high energies, well-defined geometries, and restricted coordination numbers. Therefore, the structure of self-assembly using coordinate bonds is highly sensitive to the kind of metals and ligands, and the geometry of the ligands. Fujita et al. have utilized these reversible interactions to design and fabricate well-defined self-assembled nano structures such as $M_{12}L_{24}$ and $M_{24}L_{48}$ polyhedral coordination spheres from square planar Pd$^{2+}$ ions and bent dipyridylfuran ligand (3) and dipirydilthiophene ligand (1), respectively (Figure 1-3a).\textsuperscript{[19]} The characteristic nanometer-sized cavity of the $M_{12}L_{24}$ spherical complex even enables the encapsulation of large molecules such as ubiquitin.\textsuperscript{[20]} Shionoya et al. demonstrated a programmable and discrete metal array inside DNA\textsuperscript{[21]}, isostructural coordination capsules\textsuperscript{[22]}, hierarchical metal array\textsuperscript{[23]}, and a molecular ball bearing using two different disk-shaped ligands and metal ions (Figure 1-3b).\textsuperscript{[24]} Metal organic frameworks (MOFs) are a kind of coordination polymers, which are constructed from organic ligands as
linkers and metal ions as nodes, and are a new development on the interface between molecular coordination chemistry and material science. The robust frameworks have enabled us to design the sizes and shapes of the nanosize pores by replacement of the organic linkers and metal ions, and various functional porous materials for gas storage\cite{25}, catalyst\cite{26}, and sensor\cite{27}, have been exploited owing to their isoreticular frameworks.

![Diagram](image)

**Figure 1-3.** (a) Self-assembly of $\text{M}_{24}\text{L}_{48}$ spheres and $\text{M}_{12}\text{L}_{24}$ sphere and encapsulation of ubiquitin in an $\text{M}_{12}\text{L}_{24}$ spherical framework reported by Fujita et al. (b) Schematic representation of Cu$^{2+}$ mediated duplex formation between two artificial DNA strands, the formation of isostructural coordination capsules formed from eight disk-shaped tris-monodentate ligands 1 and six divalent d$^{8}$-d$^{10}$ transition-metal ions, and a trinuclear molecular ball bearing and a nonanuclear rotor-transmitter-rotor.
1-2-2. Soft Materials Using Intermolecular Repulsive Forces

As mentioned above, intermolecular repulsive forces are limited to exchange repulsion and electrostatic repulsion. The former arises between neighboring molecules when they are close enough that their electron clouds overlap. This intermolecular repulsion affects greatly the reactivity and regioselectivity in various organic reactions. On the other hand, although the importance of the exchange repulsion are known in the colloidal science\textsuperscript{[28]}, there is few example which utilize this force for the design of functional materials. Thus, for study of soft materials, electrostatic repulsion play a key role for repulsive interactions; photonic crystals\textsuperscript{[29]} (Figure 1-4a), solubilization of insoluble polymers\textsuperscript{[30]} (Figure 1-4b), polyelectrolyte brushes\textsuperscript{[31]} (Figure 1-4c), and superabsorbent polymer gels (Figure 1-4d).\textsuperscript{[32]} In particular, various functional soft materials using polyelectrolyte gels have been demonstrated after the discovery of the volume phase transitions of the polyacrylamide gels discovered by Tanaka \textit{et al.}\textsuperscript{[1]} The volume change of polyelectrolyte gels were induced by a disruption of the balance

\begin{figure}[h]
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\caption{Examples of soft materials utilizing electrostatic repulsion: (a) Schematic illustrations showing the creation of negative charges on the surface of superparamagnetic colloids in non-polar solvents by introducing charge control agent (left), and the assembly of such charged particles into tunable photonic structures upon application of an external magnetic field (right). (b) Photographs of aqueous suspension of pristine carbon nanotubes (CNTs) and suspension of CNTs with polyoxygenometalates. (c) The change of contact angles (CAs) of the surfaces, which were prepared by fabricating a poly(N-isopropyl acrylamide-co-acrylic acid) copolymer thin film on silicon substrate, by the change of pH and temperature. (d) Superabsorbent polymer gel for water.}
\end{figure}
between intermolecular repulsion such as electric repulsion and intermolecular attractive force such as van der Waals forces\textsuperscript{[1]}, hydrogen bonds\textsuperscript{[31]}, and hydrophobic interactions\textsuperscript{[34]}. These intermolecular interactions could be controlled by various stimuli such as pH\textsuperscript{[2]}, temperature\textsuperscript{[3b]}, solvent composition\textsuperscript{[35]}, and supply of electric field.\textsuperscript{[5]} Because of these features, many kinds of stimuli-responsive gels, capsules, and films that respond to the change in their surroundings have been developed (Figure 1-5)\textsuperscript{[6a, 36]}. For example, Sukhishvili et al. demonstrated the fabrication of hydrogel capsules based on poly(methacrylic acid) that showed reversible swelling in response to changes in solution pH and ionic strength (Figure 1-5b). The capsules encapsulated macromolecule such as 500 kDa FITC-dextran by locking

Figure 1-5. Examples of application using stimuli-responsive gels: (a) an energetic walking device driven by a humidity-responsive bilayer actuator comprising an action layer of cross-linked poly(acrylic acid)/poly(allylamine hydrochloride) films and a supporting layer of UV-cured adhesive reported by Sun et al., and (b) The induced color changes of photonic anion or cation-sensitive polyelectrolyte films upon soaking in diverse anion or cation solutions. (c) Conformational changes of polyelectrolytes in response to various stimuli.
the capsule wall with electrostatically associating polycations at high pH. The release of the encapsulated FITC-dextran was easily achieved under high salt concentrations where PMAA/polycation complexation was inhibited.

As mentioned in this section, controlling the intermolecular interactions is requisite for preparation of functional soft materials. Although there are a lot of examples of such soft materials utilizing intermolecular attractive forces such as hydrogen bonds, charge-transfer interactions, and coordinate bonds, examples of functional soft materials utilizing intermolecular repulsive forces are relatively rare. This is because the most of intermolecular interactions work as attractive forces, and the repulsive forces are limited to exchange repulsions and electrostatic repulsion. In addition, electrostatic interactions can work as attractive forces rather than as repulsive forces in organic solvents. If the electrostatic repulsion can be used even in various organic solvents, it is expected that it becomes a novel molecular design for preparation and functionalization of various soft materials. In the next section, the molecular design to generate electrostatic repulsive forces in organic solvents from a viewpoint of chemical structures and the utility of the repulsive forces for functional soft materials are summarized.

1-3. Ionic Dissociation in Organic Solvents

1-3-1. Bjerrum Theory\(^{[37]}\)

Bjerrum theory describes the basic estimation of the ionic dissociation from the balance between electrostatic attractive energy and thermodynamic energy of ions. Bjerrum length \(q\) is defined as the distance that both energy balance out: dissociative when \(r > q\), and undissociative when \(a < r < q\), where \(a\) is the distance of closest approach of ion-pairs. Therefore, undissociative state includes the free state less than \(q\) as well as contact ion-pair. The association constant \(K_A\) of ion-pairs is derived from the distance between cation and anion and the ratio of the distribution of existence probability.

\[
q = \frac{|\varepsilon_r\varepsilon_0|Ne^2}{2\varepsilon,RT}
\]  

(1)

\[
K_A = 4 \times 10^{-24} \pi Na^3b^3Q(b)
\]  

(2)

where \(\varepsilon_r\) is the dielectric constant of the media. \(b\) and \(Q(b)\) represent following:
In the case of monovalent ion, the relationship among the distance of closest approach $a$, dielectric constant $\varepsilon$, and association constant $K_A$ is represented as shown in Figure 1-6. The most important fact shown in this figure that large $a$ is necessary to achieve low $K_A$ in lower polar media. In other words, keeping the distance between the charge center away by surrounding with hydrophobic and bulky substituent groups enables dissociation in lower-polar media. When the sum of ionic radius of cation and anion, i.e. closest approach distance $a$, is a few angstrom such as sodium chloride, $K_A$ is over $10^8$ in non-polar media ($\varepsilon < 10$). In the case of $a = 1$ nm, on the other hand, the ion-pairs are able to dissociate to some extent even in non-polar solvent except $\varepsilon < 3$. The larger ions $a = 3$ nm are expected to achieve the dissociation in extremely low polar media ($\varepsilon < 3$). In fact, the synthesis of such cations and anions has been reported as described next.

![Figure 1-6](image-url)

**Figure 1-6.** The relationship among closest approach distance of ionic units $a$, dielectric constant $\varepsilon$, and association constant $K_A$ of ion-pair.
1-3-2. Lipophilic Electrolytes Soluble and Dissociable in Non-Polar Media

To increase the size and bulkiness is a major task for the preparation of ionic monomers that are soluble and dissociable in non-polar organic solvents.\textsuperscript{[38]} In fact, as described in 1-3-1, a lot of hydrophobic ion-pair have been reported based on this strategy.\textsuperscript{[39]} These ions are well known as weakly coordinating anions (WCAs)\textsuperscript{[40]} (Figure 1-7a) and weakly coordinating cations (WCCs)\textsuperscript{[41]} (Figure 1-7b), which have attracted remarkable interest because of their importance in catalyst\textsuperscript{[42]}, polymerization\textsuperscript{[43]}, electrochemistry\textsuperscript{[44]}, ionic liquids\textsuperscript{[45]}, and organic reaction.\textsuperscript{[46]} For example, in the organic transformation such as the 1,4-conjugate addition reactions catalyzed by Li\textsuperscript{+} ion, the WCAs provides access to almost naked Li\textsuperscript{+} ions, which are soluble and catalytically active even in non-polar solvents such as toluene.\textsuperscript{[46a]} WCAs were also useful for new stable electrolytes for lithium-ion batteries\textsuperscript{[47]} and supporting electrolytes\textsuperscript{[48]} used in electrochemistry due to their high solubility and conductivities. More recently, there is a growing understanding of the importance of WCAs and WCCs as polymer materials such as an anionic microporous polymer network\textsuperscript{[48]} and amphiphilic block copolymers.\textsuperscript{[49]} Thus, control of the intermolecular interactions between cations and anions in organic solvents are useful for various applications.

Although a lot of lipophilic electrolytes such as WCAs and WCCs dissociable in organic solvents have been reported in recent times, there was little example of functional soft

![Figure 1-7](image)

Figure 1-7. Some examples of the chemical structures of (a) weakly coordinating anions (WCAs) and (b) cations (WCCs).
materials that the electrolytes were utilized as a building block to generate electrostatic repulsion until Sada et al. reported the lipophilic polyelectrolyte gels working even in non-polar organic solvents.\textsuperscript{[10]} This is because the lipophilic electrolytes have attracted attention only in the functions and properties of the ion own such as their high solubility and catalytic activity. More recently, an application of lipophilic electrolytes for functional soft materials by polymerization of WCAs or WCCs has been reported as follows.

1-4. Soft Materials Using Electrostatic Repulsion of Lipophilic Electrolytes

Sada et al. demonstrated the first example of lipophilic polyelectrolyte gels as superabsorbent polymers that swell with a high degree in less-polar or non-polar media (3 < $\epsilon$ < 10, where $\epsilon$ represents dielectric constant) due to electrostatic repulsion and osmotic pressure (Figure 1-8a-c).\textsuperscript{[10]} They also demonstrated that linear poly(octadecyl acrylate) bearing lipophilic ionic groups without cross-linker behaved as a polyelectrolyte in non-polar media such as dichloromethane, THF, and chloroform by viscosity measurement and DOSY NMR spectroscopy.\textsuperscript{[50]} These results emphasized that the ionic polymers and polymer gels bearing suitable ion pairs ionizable in the given media act as polyelectrolyte. Moreover, discontinuous volume changes of the lipophilic polyelectrolyte gels were demonstrated by control of the attractive force of long alkyl chains and the repulsive force of the ionic groups in the polymer network.\textsuperscript{[51]} These results implied that the electrostatic interaction was readily available as a long-range repulsive force even in the non-polar media for functional soft materials. More recently, the utility of lipophilic electrolyte as strong intermolecular repulsive force in organic solvents has become recognized more and more as seen in the example of lipophilic polyelectrolyte gels reported by Straub et al.\textsuperscript{[52]}, and charged polymer particles in non-polar media reported by Bartlett et al.\textsuperscript{[53]}
Figure 1-8. (a) Chemical structure of lipophilic polyelectrolyte gel reported by Sada et al., and photographic images of (b) dried gel and (c) swollen gel in THF. (d) Chemical structure of lipophilic polyelectrolyte gel comprising aluminate anion reported by Straub et al., and photographic images of (e) dried gel and (f) swollen gel in 1,2-dichloroethane.
1-5. Survey of This Thesis

As reviewed in the previous sections, the lipophilic polyelectrolyte working even in non-polar media are realized by utilizing hydrophobic polymer and ion pair such as WCAs, and these polyelectrolytes are useful for various soft materials using electrostatic repulsive forces in non-polar organic solvents. Although a lot of intermolecular forces such as van der Waals interactions, hydrogen bonds, charge-transfer interactions, coordination bonds, and electrostatic interactions are available as attractive forces, the intermolecular repulsive force is limited to exchange repulsion so far. However, as mentioned above, electrostatic interactions are expected to be available as strong and long-range intermolecular repulsive forces even in non-polar organic solvents. If electrostatic interactions can use as intermolecular repulsive forces in various organic media, the molecular design for various soft materials like supramolecular materials would be extremely extended. Therefore, the main issue of this thesis is to verify the utility of the electrostatic repulsion in organic solvents, and to develop functional soft materials utilizing the force.

This thesis is composed of 5 chapters in total including general introduction and concluding remarks.

In Chapter 1, the purpose and the composition of this thesis were described from the background of functional soft materials utilizing electrostatic interactions.

In Chapter 2, I attempted the construction of superabsorbent polymer gels based on polystyrene with WCA that exhibit high swelling abilities at low temperature. Swelling properties of polymer gels at low temperature below 0 °C have been scarcely investigated, because polymer-polymer interactions should be much stronger than at room temperature and suppress swelling abilities in any media. I focused on the utility of lipophilic ionic groups as a strong repulsive force against polymer-polymer interactions at low temperature. As a result, the polyelectrolyte gel bearing a small amount of lipophilic ionic groups showed a large swelling ability at low temperature (-80 °C) in some organic solvents.
Chapter 3 demonstrated the control of ionic dissociation of chloride anion by complexation with a hydrophobic anion receptor in non-polar organic solvents such as THF and ethyl acetate. The molar conductance of tetrabutylammonium chloride (TBACl) solution was clearly enhanced by the complexation with meso-octamethylcalix[4]pyrrole (CP) due to the increase of the concentration of ionic species. Furthermore, I demonstrated that the ionic association constant ($K_{ip}$) of the complex (TBA(CP-Cl)) was much smaller than that of TBACl in THF.

Chapter 4 demonstrated the preparation of stimuli-responsive polymer gels based on polystyrene with chloride anion. Control of the ionic dissociation of the ionic groups in a polymer network is key point to construct a stimuli-responsive material based on an ionic polymer gel. In this respect, I focused on the utilizing a complexation between a hydrophobic anion receptor and a chloride anion in the polymer gel to control the ionic dissociation of chloride anion. As a result, the complexation enhanced the swelling abilities of the ionic polymer gels in various organic solvents.

In Chapter 5, the knowledge revealed in this thesis, the signification, and prospect for the future were mentioned.
1-6. References


Chapter 2

High Swelling Ability of Polystyrene-Based Polyelectrolyte Gels at Low Temperature

Abstract: Molecular design of polymer gels that exhibit high swelling abilities at low temperature was demonstrated with the aid of repulsive interaction among the polymer chains in the ionic polymer gels and the utility of organic solvents with relative low melting points. A small amount of tetraalkylammonium fluorinated tetraphenylborate as lipophilic ionic groups was incorporate into cross-linked polystyrene to yield novel ionic polymer gels (EG-TFPB). The ionic polymer gel showed larger swelling abilities than those of non-ionic polymer gels in various organic solvents (6 < ε < 40). Moreover, they swelled and absorbed some organic solvents such as THF and dichloromethane at low temperature (~80 °C), and showed similar swelling ability compared to that at room temperature. Although the swelling degrees of ionic polymer gels with chloride (Cl), hexafluorophosphate (PF₆), bis(trifluoromethanesulfonyl)imide (TFSI), and tetraphenylborate (TPhB) as counter anion at low temperature were much smaller than that at room temperature, that of EG-TFPB was similar to that at room temperature. These results indicated that the ionic groups in the EG-TFPB induced repulsive force among the polymer chains against the attractive force at low temperature because of the high dissociation ability in these solvents.
2-1. Introduction

The most characteristic property of polymer gels as functional materials is swelling, the drastic increase of their 3D network in volume or weight due to absorption of solvent molecules. The swelling properties of the polymer gels are generally evaluated by the volume or weight ratios before and after soaking in them and should be governed mainly by interaction of the polymer chains to the media and rubber elasticity due to crosslinking of the polymer chains. Good compatibility of the polymer chains to the media expands the network and poor one collapses. Densely cross-linked polymer gels should be tough and their swelling abilities should be low, while sparsely cross-linked ones should be soft and high. In addition to these two factors, in the cases of ionic polymer gels, osmotic pressure and electrostatic repulsion generated by dissociation of the ionic moieties in the polymer chains largely expands their networks, and association of the ions and ionpairs collapses them. Therefore, investigation of swelling abilities under the similar cross-linking densities should be a good indicator for both compatibility of the polymer chain to the media and ionization of the ionic groups in the media.[1] The swelling abilities of the polymer gels have been mostly studied under ambient conditions. The polymer gels based on poly(acrylic acid sodium salts), polyNIPAM, polystyrene and poly(dimethylsiloxane) were investigated at room temperature for superabsorbent polymers[2], thermal stimuli-sensitive polymers,[3] polymer supports[4] and microfluidic devices,[5] respectively. However, the swelling abilities under other extreme conditions such as higher or lower temperature are still infant for the following reason. As mentioned above, the most characteristic property of polymer gels as functional materials are swelling, thus, the solvents are requisite to be liquid for swelling. In the case of the hydrogels, the range of applied temperature is limited from 0 °C to 100 °C. In the case of organogels, the range of applied temperature depends on the solvents, however, the available temperature is

![Figure 2-1. Equilibrium swelling ratio of a poly(benzyl methacrylate) (PBzMA) gel particle as a function of temperature.](image)
limited below 100 °C because the boiling point of common organic solvents are below 100 °C. Watanabe et al. investigated the swelling abilities and LCST behaviors of poly(benzyl methacrylate) gels above 100 °C by using non-volatile ionic liquids, as a pioneer work at higher temperature (>100 °C) (Figure 2-1).[6] On the other hand, swelling properties of polymer gels at lower temperature below 0 °C have been scarcely investigated, because polymer-polymer interactions should be much stronger than at room temperature[7] and suppress swelling abilities in any media.

As molecular design for the high swelling polymer gels at low temperature, I focused on the utility of ionic groups. It is because ion dissociation of electrolytes is generally insensitive to temperatures of the media at low temperature,[8] and dielectric constants of less polar organic solvents increase with decreasing temperature.[9] Molinou et al. reported that the ion association constant ($K_A$) of n-tetradecylammonium tetraphenylborate (TBATPhB) in 3-pentanone decreased with the decrease of the temperature (Figure 2-2).[10] Safanova et al. also reported the temperature dependence of $K_A$ of various ionic compounds in DMF, and the $K_A$ of all salts decreased with decrease of the temperature, following the increase of the dielectric constant of the solvent.[11] These features strongly suggest that dissociation of ionic groups in ionic polymer gels is useful even at low temperature for large expansion of the network against strong polymer-polymer interactions. Moreover, most of the known ionic polymer gels are highly hydrophilic and their swelling abilities have been investigated mainly in water, and the swelling properties at low temperature below 0 °C have never been investigated. Recently, Sada et al. reported a new class of poly(alkyl acrylate) gels with tetraalkylammonium tetraphenylborate as a lipophilic ionic group, and they exhibited high swelling abilities in various non- or less-polar organic solvents due to ion dissociation. Moreover, they confirmed that the gels acted as polyelectrolyte gels in them.[12] This result prompted us to explore the ionic polymer gels that exhibit high swelling abilities at relative low temperature (= -20 °C, -80 °C) by similarly designed polyelectrolyte gels and organic
solvents with low melting points as summarized in Table 2-1\textsuperscript{[13]}, such as THF, acetone and dichloromethane. In this chapter, I demonstrated preparation of polystyrene-based polyelectrolyte gels bearing a small amount of tetraalkylammonium fluorinated tetraphenylborate as dissociable ionic groups and swelling abilities at room temperature and low temperature in various organic solvents.

### 2-2. Results and Discussion

#### 2-2-1. Preparation of Polyelectrolyte Gels Based on Poly(styrene) (EG-X)

**Scheme 2-1.** Synthetic route for ionic monomers 1 - 5.

![Scheme 2-1](image)

**Scheme 2-2.** Preparation of the polyelectrolyte gels EG-X (X = Cl, PF\textsubscript{6}, TFSI, TPhB, TFPB).

![Scheme 2-2](image)

**Table 2-1.** The melting point (m.p.) and boiling point (b.p.) of common organic solvents.

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<tr>
<th>Solvents</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>18.5</td>
<td>189</td>
</tr>
<tr>
<td>DMF</td>
<td>-60.4</td>
<td>153</td>
</tr>
<tr>
<td>MeOH</td>
<td>-97.7</td>
<td>64.5</td>
</tr>
<tr>
<td>Acetone</td>
<td>-94.7</td>
<td>56.1</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>-35.7</td>
<td>83.5</td>
</tr>
<tr>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>-94.9</td>
<td>39.6</td>
</tr>
<tr>
<td>THF</td>
<td>-108.4</td>
<td>66.0</td>
</tr>
<tr>
<td>AcOEt</td>
<td>-83.6</td>
<td>76.8</td>
</tr>
<tr>
<td>CHCl\textsubscript{3}</td>
<td>-63.5</td>
<td>61.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>-95.0</td>
<td>111</td>
</tr>
</tbody>
</table>
The ionic monomers were prepared according to Scheme 2-1. A quaternary alkylammonium salt with a styrene group was prepared from alkylation of tri(n-hexyl)amine by 4-(chloromethyl)styrene. The resulting quaternary alkyl-ammonium chloride (1) was treated with corresponding sodium salt to yield 2, 3, 4, and 5. Polyelectrolyte gels (EG-X) were prepared by radical polymerization initiated by AIBN in the presence of ionic monomer (1, 2, 3, 4, or 5), divinylbenzene (DVB) as a crosslinker, and styrene as comonomer, as shown in Scheme 2-2. As a reference, nonionic gels (NG) were prepared by the same procedure in the absence of an ionic monomer. The conditions for copolymerization were shown in Table 2-2. The feed ratios were adjusted to ionic monomer: styrene: DVB = a: 100-a: 1 for EG-X, and 0: 100: 1 for NG, respectively. In all cases, polymer gels were formed and the gels were washed by soaking in THF for 24 hours, and air-dried at room temperature, and then the samples were dried in vacuo at 40 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ionic monomer (mol / L)</th>
<th>Styrene (mol / L)</th>
<th>DVB  (mol / L)</th>
<th>AIBN  (mol / L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-Cl</td>
<td>1(0.25)</td>
<td>4.75</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>EG-PF₆</td>
<td>5(0.25)</td>
<td>4.75</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>EG-TFSI</td>
<td>4(0.25)</td>
<td>4.75</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>EG-TPhB</td>
<td>3(0.25)</td>
<td>4.75</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>EG-TFPB</td>
<td>2(0.25)</td>
<td>4.75</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>EG-TFPB(3%)</td>
<td>2(0.15)</td>
<td>4.85</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>NG</td>
<td>0</td>
<td>5.00</td>
<td>0.050</td>
<td>0.050</td>
</tr>
</tbody>
</table>

2-2-2. Swelling Abilities of EG-TFPB(3%) in Various Organic Solvents at Room Temperature

The swelling abilities of polyelectrolyte gels EG-TFPB(3%) and nonionic gels NG in organic solvents with various polarities from toluene (ε = 2.4) to dimethylsulfoxide (DMSO; ε = 47) were investigated at room temperature (23 °C). The swelling degrees (Q) of EG-TFPB(3%) and NG were calculated as the following equation, and summarized in Figure 2-3.

\[ Q = \frac{W_{\text{wet}}-W_{\text{dry}}}{W_{\text{dry}} (\text{wt / wt})}. \]

In extremely nonpolar solvents (ε < 5), the swelling degrees of EG-TFPB(3%) were smaller than those of NG. For example, the swelling degrees of EG-TFPB(3%) in toluene and in
chloroform were 5 and 30, respectively, whereas those of NG were 27 and 45, respectively. In these solvents, dissociation of the ionic groups was completely suppressed owing to low polarity, and they would act as tightly-bound ion pairs or highly aggregated species. As a result, collapse of the polymer network was observed for EG-TFPB(3%), and the swelling degrees were much lower than NG. On the other hand, in more polar solvents with dielectric constants $6 < \varepsilon < 40$, except for a series of aliphatic alcohols, the swelling degrees of EG-TFPB(3%) were larger than those of NG. In these solvents, the polystyrene backbone had enough good miscibility to expand the polymer chains, and the higher polarity promoted dissociation of the ion-pairs, which enhanced significantly the swelling degrees. For example, the swelling degrees for EG-TFPB(3%) in THF, dichloromethane and 1, 2-dichloroethane were 68, 109 and 113, and those of NG were 23, 35 and 32, respectively. The former were several times as large as the latter. Moreover, it is noteworthy that EG-TFPB(3%) swelled in some ketones, such as 2-octanone ($Q = 75$) and acetone ($Q = 92$), and in more polar solvents such as DMF, EG-TFPB(3%) took the largest swelling degree ($Q = 166$), whereas NG didn’t at all 2-octanone ($Q = 9$), acetone ($Q = 1$). The enhancement effect on the swelling degrees for EG-TFPB(3%) tended to increase with increasing solvent polarity owing to increase of
the number of dissociated ionic groups. These results clearly indicated that EG-TFPB(3\%) should act as the superabsorbent polymer for organic solvents.


I investigated the swelling behavior of EG-TFPB(3\%) at low temperature. Figure 2-4 shows the swelling degrees of EG-TFPB(3\%) and NG at various low temperatures in THF. The swelling degrees of EG-TFPB(3\%) in THF at room temperature (23 °C), 2 °C, -16 °C, -30 °C after 48 hours were 71, 82, 67 and 74 respectively. They were similar to each other. At -80 °C, swelling degree was about half. However, prolong incubation for 96 hours at -80 °C increased the swelling degree similar to that at room temperature. They were nearly constant against temperature. The rate of swelling became much slower because of the slower kinetics of expansion of the polymer network. Therefore, the swelling degrees of EG-TFPB(3\%) kept high even at low temperatures and were independent of the incubation temperatures. Comparison of the swelling degrees between EG-TFPB(3\%) and NG provided fruitful information for understanding the role of the ionic groups for swelling. After the same incubation time, the swelling degrees of NG at 23 °C, 2 °C, -16 °C, -30 °C and -80 °C, were 23, 29, 27, 30 and 14, respectively. They were all of a similar magnitude except for at -80 °C, and were about one-third as large as those of EG-TFPB(3\%). This decrease in the swelling degrees was attributed simply to the absence of electrostatic repulsion and osmotic pressure originated from the dissociated ionic groups in the polymer chain. Even at -80 °C, ion dissociation of EG-TFPB(3\%) played a key role for the enhancement of the swelling ability. Moreover, this result supported that the polystyrene polymer chains had enough compatibility to THF in this range of temperatures, due to the absence of attractive force among them.

Subsequently, swelling behaviors of EG-TFPB(3\%) in the other solvents such as dichloromethane and acetone were investigated. The swelling degrees are summarized in Figure 2-5. In dichloromethane, the swelling degree at -80 °C was similar at room temperature (23 °C) like in THF. In acetone, however the swelling degree at -80 °C was much lower than at room temperature. In the latter solvent, although the ionic groups could dissociate into free ions due to much higher dielectric constant, compatibility of the polymer chains to the media became much poorer, and the polymer-polymer interaction should be much stronger at -80 °C, which significantly suppressed the swelling ability.
Figure 2-4. (left) Swelling degrees of **EG-TFPB(3%)** (gray bar) and **NG** (open bar) in THF at various temperature after 48 hours and -80 °C after 96 hours incubation. (right) Photographic images of wet **EG-TFPB(3%)** in THF at -80 °C.

Figure 2-5. Swelling degrees of **EG-TFPB(3%)** at -80 °C (gray bar) and at room temperature (23 °C) (open bar) after 96 h incubation in THF, 48 h incubation in CH₂Cl₂ and acetone. In parentheses, their dielectric constants are shown.
2-2-4. Counter Anion Effect on the Swelling Abilities of EG-X in Various Organic Solvents at Room Temperature

In order to evaluate the counter anion effects on the swelling behaviors of EG-X, we calculated normalized swelling ratios ($Q' = Q/Q_0$, where $Q_0$ is the swelling degree of NG in each solvent). The swelling degrees of EG-X are summarized in Figure 2-6. In extremely non-polar solvents whose dielectric constants were less than five ($\epsilon < 5$) such as toluene ($\epsilon = 2.4$) and CHCl$_3$ ($\epsilon = 4.8$), no counter anion specificity was observed and the swelling degrees of the all EG-X were less than 1 ($Q' < 1$). These results indicated that the dissociation of the ionic groups of EG-X was completely suppressed owing to the low polarity, and no counter anion effect was observed in these media. On the other hand, in non-polar media whose dielectric constants ranged from five to eight ($5 < \epsilon < 8$) such as ethyl acetate ($\epsilon = 6.0$) and

![Diagram showing normalized swelling degrees of EG-X in various solvents.](image)

**Figure 2-6.** Normalized swelling degrees ($Q' = Q/Q_0$, $Q_0$ is the swelling degree of NG) of EG-Cl, EG-PF$_6$, EG-TFSI, EG-TPhB, and EG-TFPB in various organic solvents that possess different dielectric constants, increasing from left to right. Dielectric constants of these solvents are shown in the parentheses.
THF ($\varepsilon = 7.6$), only in the case of EG-TFPB, the $Q'$ values were larger than 1 ($1 < Q'$). In these media, the swelling degrees of EG-TFPB increased with increasing the solvent polarity: 1.5 in ethyl acetate, 2.7 in THF, whereas the $Q'$ of EG-TPhB, EG-TFSI, EG-PF$_6$, and EG-Cl were less than 1 or around 1 regardless of the change in polarity. These results indicated that the molecular structure of counter anion clearly affected the swelling abilities of EG-X. It is well known that the dissociation abilities of ion-pairs were closely related to the molecular structure of them, because increase of the bulkiness around counter anions reduced Coulomb interactions between the oppositely charged ions and promoted dissociation of the ion-pairs.$^{[14]}$ The ion association constants ($K_{ip}$) of tetrabutylammonium (TBA) salts of various anions (Cl, PF$_6$, TFSI, TPhB, and TFPB) are listed in Table 2-3.$^{[15]}$ According to these data, TFPB salt of TBA has the largest ability to dissociate in THF. These results strongly suggested that ionic groups in the EG-TFPB had enough abilities to dissociate in these media ($\varepsilon < 8$), and dissociation of the ion-pairs contributed to the large swelling abilities in these organic solvents. In non-polar solvents whose dielectric constants ranged from nine to fourteen ($9 < \varepsilon < 14$), the $Q'$ values of EG-TFPB were similar to those of EG-TPhB, and they were much higher than those of EG-TFSI, EG-PF$_6$, and EG-Cl. This indicated that TFPB and TPhB acted as dissociated counter anions compared to TFSI, PF$_6$, and Cl in these media. For more polar solvents with the dielectric constant ranging above 20, the $Q'$ values of all EG-X were obviously larger than 1 ($1 \ll Q'$), and the counter anion effect was observed; Cl $<$ PF$_6$ $<$ TFSI $<$ TPhB $\ll$ TFPB.

Table 2-3. Limiting molar conductivity ($\Lambda_0$) and ion association constant ($K_{ip}$) in THF

<table>
<thead>
<tr>
<th>salt</th>
<th>solvent</th>
<th>$\Lambda_0$ / Scm$^2$mol$^{-1}$</th>
<th>$K_{ip}$ / M$^{-1}$</th>
<th>T / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NBu$_4$][Cl]</td>
<td>THF</td>
<td>109</td>
<td>$3.90 \times 10^7$</td>
<td>25.0</td>
</tr>
<tr>
<td>[NBu$_4$][PF$_6$]</td>
<td>THF</td>
<td>121</td>
<td>$3.73 \times 10^5$</td>
<td>23.6</td>
</tr>
<tr>
<td>[NBu$_4$][TFSI]</td>
<td>THF</td>
<td>114</td>
<td>$1.80 \times 10^5$</td>
<td>25.0</td>
</tr>
<tr>
<td>[NBu$_4$][TPhB]</td>
<td>THF</td>
<td>85</td>
<td>$2.30 \times 10^4$</td>
<td>25.0</td>
</tr>
<tr>
<td>[NBu$_4$][TFPB]</td>
<td>THF</td>
<td>74</td>
<td>$5.30 \times 10^3$</td>
<td>25.0</td>
</tr>
</tbody>
</table>
Counter anion effect on the swelling abilities of EG-X in THF at low temperature was investigated. The swelling degrees of EG-X at -80 °C and those of at room temperature were shown in Figure 2-7. In the case of EG-TFPB, the swelling degree at -80 °C was similar to that at room temperature (23 °C), however, in the case of the other EG-X (X = Cl, PF₆, TFSI, and TPhB), the swelling degrees were much smaller than those at room temperature. These results indicated that the ionic groups in the EG-TFPB induced repulsive forces among the polymer chains even at low temperature because of the high dissociation ability of the ionic groups in THF. On the other hand, in the case of the other EG-X (X = Cl, PF₆, TFSI, and TPhB), the ionic groups in the polymer gels would act as tightly bound ion pairs or highly aggregated species, which significantly suppressed the swelling ability at low temperature. In spite of the similar molecular structures of TFPB and TPhB except for the fluorine substitution, the swelling behavior of EG-TFPB and EG-TPhB were obviously different especially in non-polar media whose dielectric constants are smaller than 8 (ε < 8). This result clearly indicated that fluorine substitution at the anion core promoted the dissociation of ionic groups especially in non-polar media (ε < 8) even at low temperature.

![Figure 2-7. Swelling degrees of EG-X at -80 °C (gray bar) and at room temperature (23 °C, open bar) after 96 h incubation in THF.](image-url)
2-3. Conclusion

In conclusion, I demonstrated a new class of polyelectrolyte gels that exhibit high swelling abilities in organic media on the basis of polystyrene as a polymer backbone bearing a small amount of tetraalkylammonium fluorinated tetraphenylborate as lipophilic ionic groups. This gel swelled and absorbed various organic solvents from low dielectric media ($\varepsilon = 6$) to highly polar ones ($\varepsilon = 40$). High swelling degrees were attributed to ionic dissociation of tetraalkylammonium fluorinated tetraphenylborate. Moreover, this polyelectrolyte gel could swell largely at low temperature (−80 °C) in some organic solvents. To the best of my knowledge, this is the first example of superabsorbent polymers working at low temperature, and this material should be the first step for development of absorbent materials or actuators\cite{16} under extreme conditions. Furthermore, high swelling abilities in THF at −80 °C should provide a potent solid support for chemical reactions.\cite{17} Finally, this electrostatic repulsion by ionic dissociation of polyelectrolytes should be a powerful tool to generate a repulsive force among the polymer chains at low temperature as well as at room temperature, although the other intermolecular interactions such as hydrogen bonds, and $\pi$-$\pi$ interaction should act as an attractive force at low temperature. Combining these repulsive and attractive groups in the polymer gels should enable us to develop various stimuli-sensitive polymer gels working at low temperature.
2-4. Experimental Section

2-4-1. Materials
Tri-(n-hexyl)amine, 4-(chloromethyl)styrene, azobisisobutyronitrile (AIBN), styrene and divinylbenzene were purchased from Tokyo Chemical Ind. Co. Styrene was purified by distillation before used. All solvents were purchased from some commercial suppliers and were used without further purification. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (NaTFPB) was synthesized according to the reported methods.[18]

2-4-2. Measurements

$^1$H NMR spectra were recorded on a Bruker AV300 and a JEOL JNM-AL300 apparatus. MALDI-TOF spectra were recorded on a Perspective Voyager RP. Conductivity measurements were performed using TOA DKK CM-30G. The method of measurements of swelling degree was as follows: A sliced gel was placed in the following typical organic solvents with various polarities at room temperature $^{[13]}$: toluene (dielectric constant $\varepsilon = 2.4$), chloroform ($\varepsilon = 4.8$), ethyl acetate ($\varepsilon = 6.0$), tetrahydrofuran (THF) ($\varepsilon = 7.6$), dichloromethane ($\varepsilon = 8.9$), 1,2-dichloroethane ($\varepsilon = 10.4$), cyclopentanone ($\varepsilon = 13.6$), acetone ($\varepsilon = 20.6$), dimethylformamide (DMF) ($\varepsilon = 36.7$), and dimethylsulfoxide (DMSO) ($\varepsilon = 46.5$). After immersion for 48 hours, we measured the swelling degrees ($Q$) of the gels defined as the following equation:

$$Q = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}} (\text{wt} / \text{wt})}$$

where $W_{\text{dry}}$ and $W_{\text{wet}}$ are weights of the dried gel and wet gel, respectively. The $Q$ indicates the weight ratio of the amount of the solvent entrapped in the gel over that of the dried gel.

Normalized swelling ratios were defined by the following equation: $Q' = Q/Q_0$, where $Q_0$ is the swelling degree of NG in each solvent. If $Q'$ is approximate to 1 ($Q' \approx 1$), dissociation of the ionic groups is not enough to enhance the swelling degrees, and the swelling behaviors are attributed to good compatibility between the media and the polymer chains. However, if $Q'$ is larger than one ($Q' \gg 1$), ionic dissociation plays a key role in enhancement of the swelling degrees due to the expansion of the polymer network. On the other hand, if $Q'$ is less than one ($Q' \ll 1$), dissociation of the ionic groups is completely suppressed and should lead to aggregation of ions and ion-pairs.
2-4-3. Syntheses of the Ionic Monomers

2-4-3-1. Synthesis of 4-vinylbenzyl-\(N, N, N\)-tri(\(n\)-hexyl)ammonium chloride (1)

A mixture of tri-(\(n\)-hexyl)amine (5.40 g, 20.0 mmol) and 4-(chloromethyl)styrene (9.16 g, 60.0 mmol) and DMF (40 ml) was stirred at 60 °C for 48 h under Ar atmosphere. The solvent was removed by a rotary evaporator, and the viscous liquid was purified by reprecipitation into excess amount of hexane to yield 5 as a white powder (7.6 g, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS standard, r.t.), \(\delta = 0.89\) (t, \(J = 6.3\) Hz, 9H NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.28 (m, 18H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.77 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 3.32 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 4.99 (s, 2H, NCH\(_2\)C\(_6\)H\(_4\)CHCH\(_2\)), 5.35 (d, \(J = 10.8\), 1H, alkeneH), 5.82 (d, \(J = 17.7\), 1H, alkeneH), 6.71 (dd, \(J = 10.8, 1H\), alkeneH) 7.49 (d, \(J = 8.1\), 2H, PhH) 7.52 (d, \(J = 7.8, 2H\), PhH). MS (MALDI-TOF): m/z calcd for C\(_{27}\)H\(_{48}\)N\(^+\): 386.68; found: 386.67.

2-4-3-2. Synthesis of 4-vinylbenzyl-\(N, N, N\)-tri(\(n\)-hexyl)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2)

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (10.6 g, 12.0 mmol) and 1 (5.07 g, 12.0 mmol) was dissolved in methanol (20 mL). Water was added dropwise to the stirring solution, and white solid gradually precipitated. The resulting mixture was stirred for more 3 hours. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO\(_2\), dichloromethane) to yield 1 as a white solid. (12.1 g, 80%). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS standard, r.t.) \(\delta = 0.88\) (t, \(J = 6.9\) Hz, 9H NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.32 (m, 18H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.72 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.96 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 4.16 (s, 2H, NCH\(_2\)C\(_6\)H\(_4\)CHCH\(_2\)), 5.43 (d, \(J = 10.8\), 1H, alkeneH), 5.85 (d, \(J = 17.7\), 1H, alkeneH), 6.70 (dd, \(J = 10.8, 1H\), alkeneH), 7.18 (d, \(J = 8.1\), 2H, PhH), 7.52 (m, 6H, PhH), 7.69 (s, 8H, PhH). MS (MALDI-TOF): calcd for C\(_{27}\)H\(_{48}\)N\(^+\): 386.68; found: 386.67, C\(_{32}\)H\(_{12}\)BF\(_4\)^- 863.21; found 862.53.; elemental analysis : calcd(%) for C\(_{59}\)H\(_{10}\)BF\(_{25}\)N: C 56.70, H 4.84, N 1.12; found: C 56.75, H 4.84, N 1.19.
2-4-3-3. Synthesis of 4-vinylbenzyl-\( N, N, N \)-tri(\( n \)-hexyl)ammonium tetraphenylborate (3) 

Sodium tetraphenylborate (1.71 g, 5.00 mmol) and 1 (2.11 g, 5.00 mmol) was dissolved in methanol (10 mL). After 2 hours, distilled water was added dropwise to the stirring solution, and white solid gradually precipitated. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO\(_2\), hexane / acetone = 1 / 1 (v/v)) to obtain 2 as a white solid (3.00 g, 85%). \(^1\)H NMR (500 MHz, CDCl\(_3\), TMS standard, r.t.) \( \delta \) = 0.93 (t, \( J \) = 6.9 Hz, 9H NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.14-1.35 (m, 24H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.22 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 2.98 (s, 2H, NCH\(_2\)C\(_6\)H\(_4\)CHCH\(_2\)), 5.42 (d, \( J \) = 10.9, 1H, alkeneH), 5.86 (d, \( J \) = 17.6, 1H, alkeneH), 6.75 (dd, \( J \) = 10.9, 17.6, 1H, alkeneH), 7.28 (m, 8H, p-H in B-Ar), 7.44 (d, \( J \) = 8.1, 2H, o-H in vinyl-C\(_6\)H\(_4\) and m, p-H in B-Ar).

2-4-3-4. Synthesis of 4-vinylbenzyl-\( N, N, N \)-tri(\( n \)-hexyl)ammonium bis(trifluoromethanesulfonyl)imide (4) 

Potassium bis(trifluoromethanesulfonyl) imide (3.19 g, 10.0 mmol) and 1 (3.38 g, 8.00 mmol) was dissolved in methanol (20 mL). After 2 hours, distilled water was added dropwise to the stirring solution, and white solid gradually precipitated. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO\(_2\), dichloromethane) to obtain 3 as a white solid (3.95 g, 74%). \(^1\)H NMR (300 MHz, CDCl\(_3\), TMS standard, r.t.) \( \delta \) = 0.90 (t, \( J \) = 6.3 Hz, 9H NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.25 (m, 18H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.70 (br, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 3.03 (m, 6H, NCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 4.38 (s, 2H, NCH\(_2\)C\(_6\)H\(_4\)CHCH\(_2\)), 5.29 (d, \( J \) = 11.1, 1H, alkeneH), 5.75 (d, \( J \) = 17.4, 1H, alkeneH), 6.63 (dd, \( J \) = 11.1, 1H, alkeneH) 7.20 (d, \( J \) = 8.7, 2H, PhH) 7.44 (d, \( J \) = 8.7, 2H, PhH). elemental analysis: calcd(%) for C\(_{29}\)H\(_{48}\)F\(_6\)N\(_2\)O\(_4\)S\(_2\): C 52.23, H 7.26 N 4.20; found: C 52.43, H 7.26, N 4.25
2-4-3-5. Synthesis of 4-vinylbenzyl- N, N, N-tri(n-hexyl)ammonium hexafluorophosphate (5)

Sodium hexafluorophosphate (1.68 g, 10.0 mmol) and 1 (3.38 g, 8.00 mmol) was dissolved in methanol (20 mL). After 2 hours, distilled water was added dropwise to the stirring solution, and white solid gradually precipitated. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO₂, hexane / acetone = 1 / 1 (v/v)) to obtain 4 as a white solid (3.00 g, 70%). ¹H NMR (300 MHz, CDCl₃, TMS standard, r.t.) δ = 0.89 (t, J = 7.0 Hz, 9H NCH₂CH₂CH₂CH₂CH₂CH₃), 1.31 (m, 18H, NCH₂CH₂CH₂CH₂CH₂CH₃), 1.73 (br, 6H, NCH₂CH₂CH₂CH₂CH₂CH₃), 3.05 (m, 6H, NCH₂CH₂CH₂CH₂CH₂CH₃), 4.36 (s, 2H, NCH₂C₆H₄CHCH₂), 5.38 (d, J = 11.1, 1H, alkeneH), 5.82 (d, J = 17.4, 1H, alkeneH), 6.70 (dd, J = 11.1, 1H, alkeneH) 7.28 (d, J = 8.2, 2H, PhH) 7.45 (d, J = 8.2, 2H, PhH). elemental analysis: calcd(%) for C₂₇H₄₈F₆NP: C 61.00, H 9.10 N 2.63; found: C 60.92, H 9.09, N 2.62

2-4-4. Preparation of Polymer Gels (EG-X and NG)

A typical protocol is as follows; 312 mg (0.25 mmol) of 2, 495 mg (4.75 mmol) of styrene (St), 6.50 mg (50.0 μmol) of divinylbenzene (DVB), and 8.21 mg (50.0 μmol) of AIBN were placed in glass tube and dissolved in DMF 500 μl. The solution was degassed by three freeze-thaw cycles and polymerized by heating at 65 °C for 24 hours. The feed ratio was adjusted to ionic monomer: St: DVB = 5: 95: 1 and the obtained gels denoted as EG-TPFB. Another ionic polystyrene gels (EG-X: X = Cl, PF₆, TFSI, TPhB) were prepared under the same copolymerization condition using corresponding ionic monomers. As a reference, non-ionic polystyrene gel (NG) was prepared under the same copolymerization condition (St: DVB = 100: 1) without ionic monomer. The formed gels were washed by soaked in THF for 24 hours, and air-dried at room temperature, and then the samples were dried in vacuo at 40 °C.
2-5. References


Chapter 3

Control of the Ionic Dissociation of Alkylammonium Chloride via Complexation with Hydrophobic Anion Receptor

Abstract: The conductivity of tetrabutylammonium chloride (TBACl) increased in the presence of meso-octamethylcalix[4]pyrrole (CP) in non-polar solvents such as tetrahydrofuran and ethyl acetate. This increase of the conductivity indicated that the ionic dissociation of ion-paired TBACl was enhanced by the complexation between chloride anion and CP. Thus, CP could recognize chloride anion not only as free ion but also as ion-paired salt, that is, CP can act as an ion-pair receptor in such media. Moreover, the ionic association constant ($K_{ip}$) of the complex (TBA(CP-Cl)) was much smaller than that of TBACl in THF. These results show that the complexation between hydrophobic anion receptor and anion is promising approach to developing functional soft materials using electrostatic repulsion in non-polar organic solvents.

Switching from Ion-Pair to Free Ion via Complexation with Anion Receptors
3-1. Introduction

Ionic species have played a dominant role in modern supramolecular chemistry, and the design and synthesis of molecular receptors for recognizing and sensing ions selectively have been thoroughly investigated over the last three decades. In particular, anion recognition processes by hydrogen bonding have been of considerable interest due to their importance in biological, medical, environmental, and chemical sciences. Many efforts in anion receptors and their molecular recognitions are currently being directed towards the implementation of functional materials, resulting in smart or intelligent soft materials, such as supramolecular organogels and hydrogels, chemosensors, molecular capsules, liquid crystals, and artificial ion channels as shown in Figure 3-1.[1] To tune their potential applications, there is a strong demand to predict and control the weak interactions between an anion and a receptor on the basis of supramolecular chemistry. As a result, a number of experimental methods have been reported to measure association constants, including calorimetry and various spectroscopic measurements. Many of these techniques basically employ equation (1)

$$R + X^- \rightleftharpoons RX^-$$

(1)

However, the biological models and eq. 1 are intended for use with aqueous solutions, whereas many synthetic complexes are studied in low dielectric constant organic media in order to avoid hydrogen-bonding competition. In such low dielectric media, the reported binding constants of an anion (or a cation) receptor have been found to vary significantly depending on receptor concentration, the specificity of the ionic guest, their counterion concentrations.[2] As a result, the interactions between the receptors and the guests are often complicated. The reason for such effects is that ion binding in apolar solvents is affected by
ion-pairing\textsuperscript{[3]} as a competitive reaction. In spite of all this, in most cases, this ion-pairing effect has often been ignored in host/guest studies of the salts as guest molecules in low dielectric constant media except the case of ditopic receptors that recognized them as ion-pairs.\textsuperscript{[4]} Although neglecting the ion-pairing effect can be an acceptable approximation for singly charged ions in water, it is not a realistic assumption in non-polar organic media.\textsuperscript{[5]} For all of these reasons, it is very important to understand and clarify the ion-pairing effect in organic media because many complicated supramolecular systems contain more than two ionic species.\textsuperscript{[6]} Some trials for estimation of the ion-pairing effect have been attempted. Recently, mathematical treatment for the equilibria involved in the complexation between dibenzylammonium\textsuperscript{[2a]} and paraquat\textsuperscript{[2b]} salts and crown ether ligand in non-polar solvents, which explicitly considers both ion-pairing processes have been reported by Gibson and co-workers.\textsuperscript{[2, 7]} They demonstrated that concentration-dependent fluctuations in the apparent binding constant were caused by ion-pairing and that it was necessary to take into account ion-pairing equilibria to evaluate the binding constants. Although these approaches have yield

![Figure 3-2. Chemical structure of tripod al ureidic receptor.](image)

**Table 3-1.** Cumulative formation constants ($\beta$) for complexes of ureidic receptor (R) with tetramethylammonium chloride (QX).

<table>
<thead>
<tr>
<th>Species</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RQX</td>
<td>$(1.32\pm0.02) \times 10^6$ M$^{-2}$</td>
</tr>
<tr>
<td>RX</td>
<td>$(8.83\pm0.02) \times 10^2$ M$^{-1}$</td>
</tr>
<tr>
<td>R$_2$</td>
<td>$(6.06\pm0.06) \times 10^0$ M$^{-1}$</td>
</tr>
<tr>
<td>R$_2$X</td>
<td>$(3.25\pm0.11) \times 10^4$ M$^{-2}$</td>
</tr>
<tr>
<td>QX</td>
<td>$(1.23\pm0.01) \times 10^4$ M$^{-1}$</td>
</tr>
</tbody>
</table>

![Figure 3-3.](image) Plot of complexation-induced chemical shift versus the receptor’s total concentration in the titration of 0.13 mM (solid line) and 1.06 mM (dotted line) tetramethylammonium chloride (TMAC) with receptor in CDCl$_3$/CD$_3$CN (80:20). a) Me (TMA), b) NH-1, and c) NH-2.
insights into ion-pair receptors[8] and template-directed syntheses for supramolecular architectures[9], the developed treatment was a graphical approximation and not including ion-pairing equilibria of the resulting complex. As a result, only qualitative treatments of ion-pairing have prevailed so far, and this was pointed out by Roelens[10] in recent years. Roelens et al. demonstrated a non-approximated approach for estimation of ion-pairing and ion-pair equilibria in multi-equilibrium systems using a tripodal ureidic receptor (Figure 3-2). They used the nonlinear least-squares fitting of chemical shift data from $^1$H NMR titrations[11] without resorting to graphical approximations, to yield the cumulative formation constants as shown in Figure 3-3 and Table 3-1. Their results indicated that the ureidic anion receptor recognized a chloride anion as an ion-paired salt and that the ionic dissociation of the ion-paired salt was enhanced by the complexation with the anion receptor.

Calix[4]pyrroles are a well known class of neutral receptors for selective anion-binding[12]. This macrocycle have attracted much interest in recent years due to their wide range of applications such as sensors[13], ion mediated electron transfer system[14], extractants[15], solid support for the HPLC separation[16]. Recently, Sessler and Gale et al. found that calix[4]pyrroles acts as a ditopic receptor for certain salts in the solid state[17]. In this system,

![Figure 3-4](image)

**Figure 3-4.** Schematic representations of the conformational change of calix[4]pyrrole in non-polar solvents upon chloride binding and subsequent ion-paired complex formation.
anion binding fixes the conformation of the calix[4]pyrrole scaffold in the cone shape in which the pyrrolic NHs were directed to rim and hydrogen bonded to the anion on one face of the macrocycle as shown in Figure 3-4. In this conformation, the calix[4]pyrrole unit displays a bowl-shaped cavity opposite to the bound anion, and this electron-rich aromatic cavity begs for the inclusion of electropositive guests.\textsuperscript{12d, 18} Furthermore, they also reported that the complexation of calix[4]pyrrole with chloride salts in various organic solvents is highly dependent on the choice of solvents and the counter cations. In dichloromethane, association constants of calix[4]pyrrole on the order of $10^4$ M$^{-1}$ and $10^2$ M$^{-1}$ were observed, for tetraethylammonium chloride (TEACl) and tetra(\textit{n}-butyl)ammonium chloride (TBACl), respectively.\textsuperscript{19} These results strongly suggested that the ion-pairing effect should be taken into account to understand the binding mechanism in organic solvents. Although a plethora of research efforts in anion receptor chemistry including calix[4]pyrrole have focused on the solving this problem,\textsuperscript{12d, 20} the exact mechanism of these ion-pairing effect still remains unclear. While $^1$H NMR spectroscopy is a powerful and the most-widely used tool to detect the interaction between host and guest in various organic media, the method has inherently limitation to estimate binding in non-infinitely diluted solutions, and the ionic guest should be partially or fully ion-paired under such conditions especially in non-polar media.\textsuperscript{21} The chemical shifts observed by means of $^1$H NMR are therefore averaged over associated and non-associated ionic species. Within this context, conductance measurement is a powerful tool to clarify the ion-pairing effect in non-polar organic media because it has no limitation on the concentrations of the salts, and dissociation of the ion-paired salts can be easily detected as the change of the conductivity. This feature enables us to detect complex formation between a chloride anion and the receptor even under highly diluted conditions, which are suitable for investigation of the change of ionic dissociation of chloride anion. I therefore describes herein the effect of complexation on the change of the dissociation of ion-pairs by complexation with the anion receptor in organic media by means of conductance measurement, and confirm that the complexation enhance ionic dissociation of the ion-paired salts.
In organic solvents especially in non-polar solvents, it is necessary to take into account the following four equilibria occurring in solution, which are shown in Scheme 3-1, in which **CP** = *meso*-octamethylcalix[4]pyrrole. In most cases, differences of the ion-pairing equilibria between the presence and the absence of **CP** (**K**<sub>ip1</sub> and **K**<sub>ip2</sub>) are ignored for the complexation of an anion with **CP** despite that the ion-pairing equilibria should affect in non-polar media as mentioned above.[3] In general, guest salts such as **TBACl** are presented as ion-paired salts in non-polar solvents (**ε** < 10) due to the low polarity of the media especially under high concentration conditions that are used for ¹H NMR measurement. On the other hand, the ion association constant between TBA cation and **CP-Cl** anion complex (**K**<sub>ip2</sub>) is expected to be smaller than **TBACl** (**K**<sub>ip1</sub>) on account of the larger size of the **CP-Cl** anion from Fuoss’ law[3]. Supposing this hypothesis is correct, the complexation of **TBACl** with **CP** should increase the molar conductivity of the **TBACl** due to the conversion of the ion-pair into the free ion, which induced the increase of ionic species in the solution[22], and this change can be detected easily by change of conductance. It is noteworthy that an increase of the conductivity of **TBACl** solution could be occurred only in the case that **CP** recognize the chloride anion as ion-paired salt, because if **CP** recognize the chloride anion as free ion, the molar conductivity of the salt should be decreased by complexation due to the conversion of the free anion into complex, where the size of the latter is larger than that of the former and therefore the mobility decreases. That is, if the increase of the conductivity was observed by the complexation in organic solvents, the increase means that the ionic guest switched from ion-pair to free ion by the complexation. Although there is no direct way to determine the concentration either the free ion and ion paired by the other methods, in conductance measurements, the change of concentrations of free ion in the solution can be detected as change of the conductivity.
Scheme 3-1. Four binding equilibria occurring in organic media: eq. 2 is equilibrium for complexation between CP and ion-paired TBACl, eq. 3 is equilibrium for complexation between CP and free chloride anion, eq. 4 is equilibrium for ion-pairing between TBA cation and Cl anion, and eq. 4 is equilibrium for ion-pairing of TBA cation and CP-Cl anion complex.
3-2. Results and Discussion

3-2-1. Conductivity Titrations of TBACl with CP in THF

Conductometric titrations at different concentrations (10^{-3} mM - 1 mM) were carried out in tetrahydrofuran (THF) (\(\varepsilon = 7.6\)) at 298.15 K. The plots of molar conductivity (\(\Lambda_m\)) against the ligand:anion (CP/Cl-) molar ratio are shown in Figure 3-5. The molar conductivity increased with increase of the molar ratio of CP. In all cases, the molar conductivity curves were saturated at the 1:1 stoichiometry which suggest the formation of relatively strong complexes in THF. It is well known that the conductivity of a solution depends on the concentration of the charged species due to dissociation of electrolytes and their mobility.\[23\] Increasing the size of the charged species by complexation decrease the mobility of the anion, which causes the decrease of molar conductivity.\[24\] In light of this point, the observed increase of the molar conductivity upon the addition of CP in THF clearly indicated that the complexation between chloride anion and CP promoted dissociation of the ion-pairs.\[22\] In order to reveal the mobility of the charged species, I measured diffusion NMR spectroscopy to determine diffusion coefficient of TBACl by the complexation with CP in THF. As expected, the diffusion coefficient (\(D\)) of TBACl in the presence of CP was much smaller than that of TBACl and CP alone as shown in Table 3-2. Under this condition, the ion-pair of TBACl was dissociated to free ion induced by complexation with CP. Additionally, these results demonstrated that CP recognized the chloride anion not only as free ion but also as ion-paired salt. Moreover, it is noteworthy that the complexation between CP and chloride anion in THF could be detected even in highly diluted condition (10^{-7} M), which cannot be applied to other methods.
**Figure 3-5.** Conductometric curves for the titration of tetrabutylammonium chloride with CP in THF at 298.15 K.

**Table 3-2.** Diffusion coefficients ($D$) observed from DOSY NMR in THF.

<table>
<thead>
<tr>
<th></th>
<th>$D$ (×10$^{-10}$ m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBACl + 1.0 equiv CP</td>
<td>3.35</td>
</tr>
<tr>
<td>TBACl</td>
<td>6.97</td>
</tr>
<tr>
<td>CP</td>
<td>6.45</td>
</tr>
</tbody>
</table>
3-2-2. Solvent Dependence on the Change of Conductivity upon the Addition of CP

Subsequently, the molar conductivity of 0.1 mM TBACl solution upon the addition of CP was investigated in various organic solvents as shown in Figure 3-6. In acetone ($\varepsilon = 20.6$) as a relatively polar solvent, the molar conductivity decreased with increase of the amount of CP. TBACl is predominantly dissociated in acetone, and thus, the concentration of ionic species in the solution was not changed by complexation with CP. As a result, molar conductivity decreased by addition of CP due to the larger size of the complex relative to the free chloride anion.$^{[25]}$ In 1,2-dichloroethane (1,2-DCE) ($\varepsilon = 10.4$) $\Lambda_m$ were slightly decreased upon the addition of CP. The binding constants ($K_a$) of CP for chloride anion as TBA salt is $1.5 \times 10^4$ M$^{-1}$ in 1,2-DCE$^{[19]}$, therefore CP formed a complex with chloride anion in this solvent. The observed slightly change of conductivity in 1,2-DCE can be explained as follows: The conductivity change by complexation with CP was governed by the balance of the decrease of the mobility due to the larger size of the complex and the increase of the dissociation of the ion-pair. The degrees of ionic dissociation of TBACl in acetone and 1,2-DCE are about 97%, 50% at 0.1 mM, respectively.$^{[26]}$ As mentioned above, the enhancement of the dissociation of the ion-paired TBACl by addition of CP was not so large in acetone due to their high dissociation degree. On the other hand, it is thought that the complexation with CP affected the change of both of the mobility and dissociation of the anion in 1,2-DCE due to the moderate degree of dissociation of TBACl in this solvent (50%). As a result, a slight variation of the conductivity was observed compared to the result in acetone. In much lower polarity solvents such as o-dichlorobenzene ($\varepsilon = 9.9$), trifluoromethylbenzene ($\varepsilon = 9.0$), CH$_2$Cl$_2$ ($\varepsilon = 8.0$), THF ($\varepsilon = 7.6$), 2-methyltetrahydrofuran ($\varepsilon = 7.0$), methyl acetate ($\varepsilon = 6.7$), ethyl acetate ($\varepsilon = 6.0$), tetrahydropyran ($\varepsilon = 5.6$), chlorobenzene ($\varepsilon = 5.6$), and butyl acetate ($\varepsilon = 5.0$), the conductivity of TBACl solution increased upon the addition of CP. In these solvents, TBACl is dominantly associated to tightly-bound ion pair owing to their low polarity, and thus, the enhancement of the dissociation of ion-paired TBACl by complexation was observed as increase of the conductivity. On the other hand, the conductivity was almost unchanged by the addition of CP in chloroform (CHCl$_3$) ($\varepsilon = 4.8$) despite the fact that CP should act as an anion receptor for chloride anion in this solvent.$^{[27]}$ These results indicated that dissociation of TBACl was completely suppressed owing to the low polarity.
acetone ($\varepsilon = 20.6$)

1,2-dichloroethane ($\varepsilon = 10.4$)

o-dichlorobenzene ($\varepsilon = 9.9$)

trifluoromethylbenzene ($\varepsilon = 9.0$)

dichloromethane ($\varepsilon = 8.9$)

THF ($\varepsilon = 7.6$)

2-methyltetrahydrofuran ($\varepsilon = 7.0$)

methyl acetate ($\varepsilon = 6.7$)
**Figure 3-6.** Conductometric curves for the titration of TBACl with CP in various organic solvents at 298.15 K.
3-2-3. Relationships between the Change of Conductivity and the Dielectric Constants

To clarify the mechanism of the conductivity change by complexation, dielectric constants dependence on the conductivity change was demonstrated by using mixed solvents. The dielectric constants of binary mixed solvents are provided by the following equation:

\[ \varepsilon = \phi_A \varepsilon_A + \phi_B \varepsilon_B \]

where \( \phi_n \) and \( \varepsilon_n \) are volume fraction and dielectric constant of each solvent, respectively. The conductivity of TBACl solution upon the addition of CP in the binary mixtures of acetone-ethyl acetate (0.11/0.89 (v/v)) was measured. The calculated dielectric constant of the binary mixed solvent was adjusted to be 7.6, which is the same as THF (\( \varepsilon = 7.6 \)). In the mixture of acetone/AcOEt, the conductivity clearly increased by the addition of CP as shown in Figure 3-7. Moreover, the conductivity change was quite similar to that in THF. It is thought that the slight difference in the maximum molar conductivity attributed to the difference of the viscosity of the solvents. These results clearly indicated that the change of the conductivity of TBACl solution strongly depended on the dielectric constant of the solvent.

![Figure 3-7](image)

**Figure 3-7.** Comparison of the results of conductivity change of TBACl upon the addition of CP in THF and mixed solvents; in THF (square) and acetone/ethyl acetate (0.11/0.89) (diamond).
3-2-4. Dependence of Anions on the Change of Conductivity by the Complexation with CP in THF

The conductometric titrations of various TBAX salts (X = Cl, Br, and I) upon the addition of CP in THF solutions were shown in Figure 3-8a. In the case of TBACl, the conductivities abruptly increased and the molar conductivity showed saturation at the 1:1 stoichiometry, suggesting the formation of a 1:1 complex. The initial slope of the curvature was lower in the titration of bromide with CP, suggesting the complex between CP and bromide was weaker than the case of chloride. In the case of TBAI, the conductometric curve showed complicated behavior with minimum value around 0.5 equiv. of CP, and then showed a slight increase. These results of conductometric titrations in THF differed from those in acetonitrile (MeCN) as shown in Figure 3-8b. In MeCN, the conductivities of TBAX (X = F, Cl, and Br) were decreased upon the addition of CP. Moreover, the change of the molar conductivity of TBABr solution in the presence of CP in MeCN was obviously smaller than in THF. It is thought that these differences caused by the difference of acceptor number of the media (18.9 for MeCN and 8.0 for THF) which affect the solvation of anions.

Figure 3-8. Conductometric curves for the titration of tetrabutylammonium halide with CP (a) in THF and (b) in MeCN at 298.15 K
To determine the ionic association constant \( (K_{ip}) \) of \( \text{TBA(} \text{CP-Cl}) \) in THF, I performed conductance measurements at different anion salt concentrations. In all cases, the molar conductivity increased drastically with the decreasing concentration of \( \text{TBACl} \), indicating that \( \text{TBACl} \) and \( \text{TBA(} \text{CP-Cl}) \) complex acted as a weak electrolyte in THF. The molar conductivities of \( \text{TBACl} \) clearly increased with increase of amounts of \( \text{CP} \) in the whole range of concentrations as shown in Figure 3-9. These results clearly indicated that the ionic dissociation of ion-paired \( \text{TBACl} \) was enhanced by the complexation with \( \text{CP} \) in THF. The limiting molar conductivity \( (\Lambda_0) \) and the equilibrium constant for ion-pair association \( (K_{ip}) \) of \( \text{TBACl} \) in the absence and presence of \( \text{CP} \) calculated from the Fuoss-Kraus equation are listed in Table 3-3. I calculated these values on the assumption that the \( \text{TBACl} \) completely formed the complex with \( \text{CP} \) in the whole concentration range. As expected, the value of \( \Lambda_0 \) in the presence of \( \text{CP} \) was smaller than that in the absence of \( \text{CP} \) (only \( \text{TBACl} \)) due to the larger size of the complex. The lower the value of \( K_{ip} \), the greater the degree of dissociation of ion-pairs, and the value of \( K_{ip} \) in the presence of \( \text{CP} \) was much smaller than that of \( \text{TBACl} \), indicating that the \( \text{TBA(} \text{CP-Cl}) \) complex have much larger ability to dissociate of the ion-pair than that of \( \text{TBACl} \). Moreover, the value of \( K_{ip} \) of the complex is much smaller than that of TBA salts with TFSI and PF\(_6\), and comparable with TPhB (the structures are shown in Figure 3-10) as counter anions as shown in Table 3-4. These anions are well known as hydrophobic anions, which are commonly used as a supporting electrolyte in non-polar organic solvents, or counter anions of ionic liquids.\(^{[29]}\) These results clearly indicated that the complexation with \( \text{CP} \) enhanced the ionic dissociation of ion-paired \( \text{TBACl} \), and resulting complex (\( \text{TBA(} \text{CP-Cl}) \)) had a relatively large ability to dissociate in non-polar organic solvents.
Figure 3-9. Molar conductivity (\(\Lambda\)) plots of TBACl in the presence of various amount of CP in THF.

Table 3-3. Limiting molar conductivity (\(\Lambda_0\)) and equilibrium constants for ion pair association (\(K_p\)) of TBACl in the absence and presence of CP in THF at 298.15 K.

<table>
<thead>
<tr>
<th></th>
<th>(\Lambda_0)</th>
<th>(K_p) (M(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBACl</td>
<td>109</td>
<td>3.9 \times 10^7</td>
</tr>
<tr>
<td>TBACl + CP (1 eq.)</td>
<td>58</td>
<td>1.8 \times 10^4</td>
</tr>
</tbody>
</table>

Figure 3-10. The chemical structures of TPhB, TFSI, and PF\(_6\) anion.

Table 3-4. Ionic association constants (\(K_p\)) of TBAX in THF.

<table>
<thead>
<tr>
<th>TBAX</th>
<th>(K_p) (M(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = PF(_6)</td>
<td>3.73 \times 10^5</td>
</tr>
<tr>
<td>X = TFSI</td>
<td>1.80 \times 10^5</td>
</tr>
<tr>
<td>X = TPhB</td>
<td>2.30 \times 10^4</td>
</tr>
</tbody>
</table>
3-2-6. Determination of the Ionic Association Constants ($K_{ip1}$ and $K_{ip2}$) and the Binding Constants ($K_{a1}$ and $K_{a2}$) in THF

Finally, I attempted to determine the ionic association constants ($K_{ip1}$ and $K_{ip2}$) and the binding constants ($K_{a1}$ and $K_{a2}$) in THF. The ionic association constant of TBACl ($K_{ip1}$) was calculated from the conductivity measurement of only TBACl in THF, and $K_{ip1}$ was $3.9 \times 10^7$ M$^{-1}$. For the determination of the ionic association constant of TBA(CP-Cl) ($K_{ip2}$) in THF, I performed conductance measurements of TBACl in the presence of excess amount of CP in THF as shown in Figure 3-11. The molar conductivity in the presence of excess amount of CP (TBACl:CP = 1:2) were almost identical to that in the presence of one-equivalent of CP (TBACl:CP = 1:1), and the ionic association constants calculated from these plots were comparable as shown in Table 3-5. These results indicated that the CP formed the complex (TBA(CP-Cl)) in the whole range of concentration. Therefore, I hypothesized the ionic association constant of TBA(CP-Cl) complex ($K_{ip2}$) was nearly identical to that of TBACl in the presence of excess amount of CP ($K_{ip} = 1.95 \times 10^4$ M$^{-1}$). The association constant ($K_a$) of CP for chloride anion in THF was determined by $^1$H NMR titration under the concentration of TBACl was 5.0 mM. A significant upfield shift of the pyrrole $\beta$-proton was observed upon the addition TBACl, consistent with the formation of CP-chloride hydrogen bonds as shown in Figure 3-12. The binding constant of CP in THF-$d_8$ was calculated from the observed chemical shift and the value was $3.40 \times 10^3$ M$^{-1}$. In this condition ([TBACl] = 5.0 mM), TBACl was completely present as ion-paired salt (degree of dissociation $\alpha < 0.001\%$) according to the $K_{ip1}$ ($= 3.9 \times 10^7$ M$^{-1}$) in THF. Therefore, the calculated binding constant was assumed to be nearly equal to that of CP for ion-paired TBACl ($K_{a1}$). The binding constant of CP for free chloride anion ($K_{a2}$) was calculated from the following relational expression, $K_{a2} = (K_{a1} \times K_{ip1})/K_{ip2}$, and $K_{a2}$ was $6.80 \times 10^6$ M$^{-1}$. These binding constants and ionic association constants are summarized in Table 3-6. These results demonstrated that CP had larger binding ability for free chloride anion than ion-paired TBACl ($K_{a1} < K_{a2}$), and the complex (TBA(CP-Cl)) had larger dissociative ability than TBACl in THF.
**Figure 3-11.** Molar conductivity ($\Lambda_m$) plots of TBACl in the presence of one-equivalent (square) and two-equivalent (diamond) of CP in THF.

**Figure 3-12.** The chemical shift of the $\beta$-CH of CP upon the addition of TBACl in THF.

**Table 3-5.** The ionic association constants ($K_{ip}$) of TBACl in the presence of CP in THF.

<table>
<thead>
<tr>
<th>[TBACl]:[CP]</th>
<th>$K_{ip}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>$1.8 \times 10^4$</td>
</tr>
<tr>
<td>1:2</td>
<td>$1.95 \times 10^4$</td>
</tr>
</tbody>
</table>

**Table 3-6.** Binding constants of CP for ion-paired TBACl and free chloride anion ($K_{a1}$ and $K_{a2}$) and ionic association constant of TBACl and TBA(CP-Cl) ($K_{ip1}$ and $K_{ip2}$) in THF.

<table>
<thead>
<tr>
<th>$K_{a1}$ (M$^{-1}$)</th>
<th>$K_{a2}$ (M$^{-1}$)</th>
<th>$K_{ip1}$ (M$^{-1}$)</th>
<th>$K_{ip2}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.40 \times 10^3$</td>
<td>$6.80 \times 10^6$</td>
<td>$3.90 \times 10^7$</td>
<td>$1.95 \times 10^4$</td>
</tr>
</tbody>
</table>
3-3. Conclusion

In conclusion, I demonstrated the conductivity change of TBACl by complexation with CP in various organic solvents to reveal the ion-pairing effect on the binding of CP with chloride anion. In non-polar solvents such as THF, the molar conductivity was clearly enhanced by the complexation with CP due to the increase of the concentration of charged species. These results showed that CP could recognize the chloride anion not only as free ion but also ion-paired one in organic solvents. Furthermore, CP had larger binding affinity for free ion than for ion-paired salt ($K_{a1} < K_{a2}$), and the resulting complex TBA(CP-Cl) had a large dissociative ability in non-polar organic solvents compared to TBACl on account of the larger size. In recent years, Kokubo et al. reported that the encapsulation of lithium cation by [60]fullerene enhanced the conductivity of the lithium salt as hexafluorophosphate salt. These findings including my results show that the complexation and encapsulation between hydrophobic and bulky ion receptor and ionic species is applicable for novel molecular design of functional soft materials utilizing electrostatic repulsive forces in non-polar organic solvents.
3-4. Experimental Section

3-4-1. Materials
Tetrabutylammonium chloride, sodium hexafluorophosphate, lithium bis(trifluoromethanesulfonyl)imide, were purchased from Tokyo Chemical Industry, and meso-octamethylcalix[4]pyrrole (CP) was purchased from Wako Chemical Ind. Co. All solvents and inorganic reagents including anhydrous grades were purchased from some commercial suppliers and used without further purification.

3-4-2. Measurements
$^1$H NMR spectra were performed at 25 °C using a JEOL JNM-ECP300 with a proton resonance frequency of 300 MHz. Elemental analysis and mass spectrometry were conducted by Instrumental Analysis Division, Equipment Management Center, Creative Research Institution of Hokkaido University. Conductivity measurements were performed using TOA DKK CM-30G. For the conductance titrations, the cell was filled with the solution of TBACl and left in a thermostatic bath at 298.15 K. After thermal equilibrium was reached, the ligand solution was added in steps.

3-4-3. Preparations of the Ionic Monomers for Conductivity Measurement

3-4-3-1. Synthesis of tetrabutylammonium hexafluorophosphate (TBAPF$_6$)
Tetrabutylammonium chloride (3.00 g, 10.8 mmol) and sodium hexafluorophosphate (1.81 g, 10.8 mmol) was dissolved in methanol (5 mL). After the mixture was stirred for 3 h, water was added dropwise to the stirring solution, and white solid gradually precipitated. The solid was extracted with dichloromethane and evaporated to dryness. The residue was recrystallized from ethanol-water to afford TBAPF$_6$ (3.81 g, 91%). $^1$H NMR (300 MHz, CDCl$_3$, TMS standard, r.t.) $\delta = 0.99$ (t, $J = 7.4$ Hz, 12H NCH$_2$CH$_2$CH$_2$CH$_3$), 1.40 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.59 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 3.15 (t, $J = 8.5$ Hz, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$).
3-4-3-2. Synthesis of tetrabutylammonium bis(trifluoromethanesulfonylimide (TBATFSI)

Tetrabutylammonium chloride (3.00 g, 10.8 mmol) and lithium bis(trifluoromethane-
sulfonylimide (3.10 g, 10.8 mmol) was dissolved in methanol/water (5 mL / 2 mL). After
the mixture was stirred for 3 h, water was added dropwise to the stirring solution, and white solid
gradually precipitated. The solid was extracted with dichloromethane and evaporated to
dryness. The residue was recrystallized from ethanol-water to afford TBATFSI (4.97 g, 88%).

$^1$H NMR (300 MHz, CDCl$_3$, TMS standard, r.t.) $\delta = 0.94$ (t, $J = 7.4$ Hz, 12H
NCH$_2$CH$_2$CH$_2$CH$_3$), 1.36 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.60 (m, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$), 3.13
(t, $J = 8.5$ Hz, 8H, NCH$_2$CH$_2$CH$_2$CH$_3$).

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[26] The degrees of dissociation of TBACl in 1,2-dichloroethane calculated using the value of limiting molar conducivity. The limiting molar conductivities in this solvent was calculated from the Walden product.


Chapter 4

Preparation of Stimuli-Responsive Polymer Gels by Control of the Ion Dissociation via Complexation between Anions and Anion Receptors

Abstract: Stimuli-responsive polymer gels that can change their volumes drastically in response to various external physical and chemical stimuli have been of much interest due to their various applications. Ionomer gels are a kind of ionic polymer gels and have covalently-crosslinked hydrophobic polymer chain attached with free counter ions. Generally, in non or less polar media, they collapse because the ionic groups would act as tightly bound ion-pairs clusters or highly aggregated species. In this chapter, novel stimuli-responsive gels were achieved through the complexation between anion receptors and the chloride anion of polystyrene based ionomer gels in aprotic organic solvents. The volume expansions induced by the addition of the receptors originated from breaking the aggregation of ionic groups and enhancing the dissociation of the ion-pairs, accompanied by their color changes.
4-1. Introduction

The design and synthesis of molecular receptors for the selective recognition and sensing have been well investigated during the last three decades.\(^1\) In particular, anion recognition processes by hydrogen bonding have been found in many proteins and have been of considerable interest due to importance in biological, medical, environmental and chemical sciences.\(^2\) Many efforts in anion receptors and their molecular recognitions are currently being directed towards implementation of functional materials, resulting in smart or intelligent soft materials, such as supramolecular organogels\(^3\) and supramolecular hydrogels,\(^4\) chemosensors,\(^5\) molecular capsules,\(^6\) liquid crystals,\(^7\) and artificial ion channels.\(^8\) However, utility of anion binding properties as essential construction principles for stimuli-responsive materials have remained the great challenge.\(^9\)

Stimuli-responsive polymer gels can produce large and reversible volume changes triggered by external stimuli such as temperature\(^{10}\), pH\(^{11}\), light\(^{12}\), chemical substances\(^{9,13}\) and are of great interest with respect to many applications for actuators\(^{14}\), drug release\(^{15}\) and microfluidics.\(^{16}\) The macroscopic volume changes of the polymer gels, especially swelling in a solvent arise with the solvation of the polymer chains, electrostatic repulsion between the charges on the polymer chains, and the osmotic imbalance between the interior and exterior of the gels. On the other hand, deswelling of the gels induced by the association between the polymer chains, electrostatic attractive force, and disappearance of the osmotic pressure due to aggregation of the ionic groups. When the repulsive force, usually from electrostatic repulsion in nature, overcomes the attractive force such as hydrogen bonding or the hydrophobic interaction between the polymer chains, the volumes of the gels should increase.

![Figure 4-1](image)

**Figure 4-1.** Schematic illustration of a stimuli-responsive gel induced by a complexation between an anion receptor and a chloride anion.
discontinuously in some cases and continuously in others. The variables triggering this transition influence these intermolecular forces and thereby the balanced state of the attractive and repulsive forces.\textsuperscript{[17]} In the case of ionomer gels which have covalently-crosslinked hydrophobic polymer chain attached with small amount (less than 10 mol\%) of ionic groups with free counter ions, they collapse in non or less polar media because the ionic groups would act as tightly bound ion-pairs clusters or highly aggregated species, although the main part of the polymer chain has a good compatibility to the media.\textsuperscript{[18]} Thus, the control of the ionic dissociation in the polymer network and that of intermolecular attractive force play a key role to realize stimuli-responsivity. In this respect, I focused on the utilizing the complexation between hydrophobic anion receptors and some anions in the polymer gels. The complexation of the counter ions along the polymer chain with the hydrophobic anion receptors should break the clusters of the ionic groups and increase osmotic pressure by promotion of dissociation of the ion-pairs, which should trigger the transition between swollen and collapsed state in the ionomer gels as schematically shown in Figure 4-1. In this chapter, I demonstrated that anion receptors triggered macroscopic volume and color changes of ionomer gels having chloride anion. The molecular design for new stimuli-responsive gels lays on the anion receptors (\textbf{CP}\textsuperscript{[19]}, \textbf{R2}\textsuperscript{[20]} and \textbf{R3}\textsuperscript{[21]}) for chloride anion and the polystyrene-based ionomer gel with quaternary alkylammonium chloride as ionic groups (\textbf{EG-Cl}) as shown in Figure 4-2.

![Figure 4-2.](image)

\begin{verbatim}
(a) EG-Cl (X = Cl); p: q: r = 10: 90: 1
EG-TFPB (X = TFPB); p: q: r = 10: 90: 1
NG; p: q: r = 0: 100: 1

(b) CP
R2
R3
\end{verbatim}
4-2. Results and Discussion

4-2-1. Preparations of Polymer Gels (**EG-Cl**, **EG-TFPB** and **NG**)

I prepared ionic polymer gels (**EG-Cl**, **EG-TFPB**) by radical polymerization using azobisisobutyronitrile (AIBN) as the initiator in the presence of ionic monomer, divinylbenzene (DVB) as a crosslinker, and styrene as shown in Scheme 4-1. The content of the ionic groups in the polymer chains was suppressed to less than 10%, because incorporation of too much ionic groups would cause physical crosslinking by higher aggregation of the ionic groups and consequently collapse of the gels.\cite{18b,22} As a reference, non ionic gel (**NG**) was prepared under the same copolymerization condition (styrene: DVB = 100: 1) without the ionic monomers. The resulting network products denoted as **EG-X** and **NG** were insoluble in most common organic solvents and swelled in some organic solvents.

---

**Scheme 4-1.** Preparation of ionic monomers (1 and 2) and polymer gels (**EG-Cl**, **EG-TFPB**, and **NG**).

\[
\begin{align*}
\text{Cl} & \quad \text{DMF} & \quad (n-C_6H_{13})_2N & \quad (n-C_6H_{13})_2N \\
\text{DMF} & \quad \text{MeOH/H}_2\text{O} & \quad \text{NaTFPB} & \quad \text{TFPB} \\
1 & \quad p & \quad q & \quad r \\
\text{Cl} & \quad \text{(X)} & \quad \text{(X)} & \quad \text{(X)} \\
1: & \quad X = \text{Cl} & \quad 2: & \quad X = \text{TFPB} \\
\text{EG-Cl} (X = \text{Cl}); & \quad p:q:r = 10:90:1 & \quad \text{EG-TFPB} (X = \text{TFPB}); & \quad p:q:r = 10:90:1 \\
\text{NG}; & \quad p:q:r = 0:100:1 & \quad \text{NG} & \quad \text{NG} 
\end{align*}
\]
4-2-2. Color Change of EG-Cl upon the Addition of Anion Receptors in Acetone

I investigated the color changes of EG-Cl and NG upon the addition of anion receptors (R2 and R3) in acetone. The gels were soaked in acetone for 6 hours at room temperature for equilibrium swelling and transferred into the solutions of R2 and R3 (1 mM) and kept in a similar way. The colorless wet gels turned to orange and deep green after immersion for 6 hours in the receptor solution as shown in Figure 4-3. After sufficient washing with acetone, EG-Cl was still stained with R2 and R3, whereas NG was completely decolorized. This result indicated that the complexations between the anion receptors and the chloride anions in the polymer gels occurred in the ionomer gels of EG-Cl.

Figure 4-3. Photographic images of (a, b) EG-Cl and (c, d) NG under different conditions: 1) Dried gel, 2) swollen gel in acetone, 3) swollen gel in acetone in the presence of anion receptor (R2 or R3), and 4) swollen gel after sufficient washing with acetone.
4-2-3. Change of Swelling Abilities of **EG-Cl** upon the Addition of Anion Receptors in Acetone

The swelling behaviors of **NG** and **EG-Cl** in the presence or absence of the anion receptor in acetone were investigated as shown in Figure 4-4. Firstly, **NG** hardly absorbed acetone ($Q = 1.16$), indicating the poor compatibility of the polystyrene polymer backbone in acetone. The addition of the anion receptors had little or no effect on the degrees of swelling: $Q = 1.15, 1.19$ and $1.18$ for **CP**, **R2**, and **R3**, respectively. The anion receptors should have no ability to improve compatibility and osmotic pressure of the polymer gels in acetone, when the polymer gel did not have chloride anion. For **EG-Cl**, the degree of swelling increased to 1.80 in acetone compared to that of **NG** ($Q = 1.16$). The enhanced degree of swelling should be attributed to generation of osmotic pressure and electrostatic repulsion due to dissociation of quaternary tetraalkylammonium chloride in the polymer gel. In the case of **EG-Cl**, addition of the anion receptors clearly affected the swelling abilities. The degrees of swelling of **EG-Cl** rose to 2.28, 2.31, and 2.40 in the acetone solution of **CP**, **R2**, and **R3**, respectively. This is a good contrast to no effect of these receptors for the degrees of swelling of **NG** (**NG**, **NG+CP**, **NG+R2**, and **NG+R3** as shown in Figure 4-4). Therefore, these results clearly indicated that the swelling ability of **EG-Cl** was enhanced by **CP**, **R2**, and **R3**. Then, I further investigated

![Figure 4-4](attachment:image.png)

**Figure 4-4.** Degrees of swelling ($Q$) of **NG** and **EG-Cl** in the absence and presence of **CP**, **R2** and **R3** in acetone.
anion receptor concentration dependence of the degrees of swelling, and enhancement of the swelling abilities was estimated by 
\[ \Delta L / \Delta L_{\text{max}} \] (\( \Delta L = L_{\text{add}} - L_{\text{dry}}, \Delta L_{\text{max}} = L_{\text{max}} - L_{\text{dry}} \)) as shown in Figure 4-5. The degrees of swelling ratios (\( \Delta L / \Delta L_{\text{max}} \)) increased with increasing anion receptor concentration in each case. In the case of CP, the relative degree of swelling abruptly increased at 5.0 \( \times \) \( 10^{-5} \) M, and saturated above 1.0 \( \times \) \( 10^{-3} \) M. The similar concentration dependence was observed for R2 and R3, but \( \Delta L / \Delta L_{\text{max}} \) was sharply increased at 2.5 \( \times \) \( 10^{-5} \) M and 1.0 \( \times \) \( 10^{-5} \) M for R2 and R3, and saturated above 1.0 \( \times \) \( 10^{-3} \) M and 5.0 \( \times \) \( 10^{-5} \) M for R2 and R3, respectively. Therefore, all of the anion receptors provided the similar concentration dependence of \( \Delta L / \Delta L_{\text{max}} \), and R3 affected the swelling abilities at much smaller concentration than CP and R2. Thus, R3 was more capable to stimulate volume change of the ionomer gel. This should be attributed to the difference of their anion binding abilities.

![Figure 4-5. The log plot of anion receptor concentrations to the change ratio of degrees of swelling of EG-Cl in acetone; CP (black), R2 (red), and R3 (green).](image)

![Figure 4-6. Partial ¹H NMR spectra of solution of CP (left) and the chemical shift of the β-CH of CP upon the addition of TBACl in acetone-\( d_6 \) (right).](image)
As the model system, anion-binding properties of CP, R2 and R3 toward chloride anion in acetone were evaluated by $^1$H NMR titrations for CP, and by UV/vis absorption spectral changes upon the addition of tetra(n-butyl)ammonium chloride (TBACl) for R2 and R3. In the $^1$H NMR titrations for CP in acetone-$d_6$, a significant upfield shift of the $\beta$-CH proton was observed upon the addition of TBACl, consistent with the formation of CP-chloride hydrogen bonds as shown in Figure 4-6. In the UV/vis titrations, the absorption maximum at 513 nm was decreased gradually for R2, and the absorption maximum at 446 nm was shifted and enhanced for R3 as shown in

| Table 4-1. Binding constants ($K_a$) of CP, R2 and R3 for chloride in acetone and CH$_2$Cl$_2$. |
|---|---|---|
| receptor | in acetone | in CH$_2$Cl$_2$ |
| CP       | $4.80 \times 10^3$ | $4.30 \times 10^2$ |
| R2       | $2.26 \times 10^5$ | $3.60 \times 10^5$ |
| R3       | $1.42 \times 10^6$ | $2.20 \times 10^6$ |

Figure 4-7. UV/vis absorption spectral changes (top) and corresponding titration plots (down) of (a) R2 ($5.0 \times 10^{-6}$ M), and (b) R3 ($1.0 \times 10^{-6}$ M) upon the addition of chloride as tetrabutylammonium salts in acetone.
Figure 4-7. According to the reported procedure, binding constants of R2 and R3 toward chloride anion were estimated as 226,000 and 1,420,000 M$^{-1}$, respectively, which are comparable with those in CH$_2$Cl$_2$. The resulting binding constants ($K_a$) of CP, R2, and R3 in acetone are summarized in Table 4-1. These results of $^1$H NMR and UV/vis titrations indicated that all of the anion receptors have enough binding constants for chloride anion in acetone, and the complexation should promote dissociation of quaternary ammonium chloride or breaking the aggregation of ionic groups to enhance the swelling abilities.

In order to clarify the role of complexation, I tried removal of the anion receptor from the swollen gels in acetone by soaking them in a 10 mM acetone solution of TBACl. After immersion in TBACl solution for 6 hours at room temperature, the swollen gels collapsed as shown in Figure 4-8. Especially in the case of R2 and R3, after immersion for 6 hours at room temperature, the colored gels collapsed and turned to be nearly colorless. Further cycles of immersion in the solution of CP or R2 or R3, TBACl and fresh acetone provided cyclic swelling behaviors as shown in Figure 4-9. This result clearly indicated that the volumes of

Figure 4-8. Photographic images of EG$^-\text{Cl}$ upon the addition of a) CP in acetone, b) R2 in acetone, c) R3 in acetone: 1) in 1 mM anion receptor solution, 2) in 10 mM TBACl solution, 3) in acetone, and 4) in 1 mM anion receptor solution.
EG-Cl were controlled by addition of the anion receptors, and they should be regarded as a stimuli-responsive material on the basis of anion recognition.

4-2-4. Counter Anion Effect on the Swelling Behaviors upon the Addition of Anion Receptors in Acetone and Dichloromethane

To demonstrate importance of the complexation for the enhancement of the swelling abilities, I compared the swelling behaviors of EG-TFPB with EG-Cl in acetone and CH$_2$Cl$_2$ upon the addition of anion receptors. As shown in Figure 4-10, the relative degrees of swelling ($Q'$) of EG-TFPB didn’t change by addition all of CP, R2, and R3, and the values in acetone and CH$_2$Cl$_2$ were 1.01 and 1.00 for CP, 1.01 and 1.00 for R2, and 1.00 and 0.99 for R3, respectively, which are comparable with those of NG. This result clearly indicated that the degrees of swelling of EG-Cl were enhanced by the complexation between chloride anions in the ionomer gel and anion receptors.

![Figure 4-9](image)

**Figure 4-9.** Change of the relative degrees of swelling ($Q'$) of EG-Cl upon the addition of anion receptors and TBACl in acetone. $Q' = Q/Q_0$, where $Q$ and $Q_0$ are degrees of swelling in the presence and absence of anion receptors, respectively.

![Figure 4-10](image)

**Figure 4-10.** The relative degree of swelling ($Q'$) of EG-Cl, EG-TFPB, and NG in the presence of CP, R2, and R3 in acetone and CH$_2$Cl$_2$. 

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4-2-5. Solvent Dependence of the Swelling Behaviors of \textbf{EG-Cl} upon the Addition of Anion Receptors

For evaluation of the solvent dependence of swelling behaviours of \textbf{EG-Cl}, the degrees of swelling ($Q$) in the absence and presence of \textbf{CP} in various organic solvents were investigated as shown in Figure 4-11. Starting from the non-polar solvents, the degrees of swelling were almost unchanged by the addition of \textbf{CP} in toluene ($\varepsilon = 2.4$, $Q' (=Q/Q_0) = 1.00$) and chloroform ($\varepsilon = 4.8$, $Q' = 1.00$). In the aprotic non-polar media, anion binding of the anion receptor should have high affinity to chloride anion but didn’t affect the swelling ability. Thus, even in the presence of the anion receptor, dissociation of quaternary alkylammonium chloride in \textbf{EG-Cl} was completely suppressed owing to their low polarity, and the ionic groups in the polymer gels would be tightly bound ion-pairs. The receptor should recognize chloride anion as the ion-pairs. On the other hand, the degrees of swelling increased with increasing polarity, i.e., dielectric constants, and the maximum $Q'$ was observed in acetone. This increase was explained simply by promotion of ionic dissociation due to increasing polarity of the media. Finally, in the highly polar solvents such as DMF ($\varepsilon = 36.7$) and DMSO

![Figure 4-11](image.png)

**Figure 4-11.** The degree of swelling ($Q$) of \textbf{EG-Cl} in the absence (open bar) and presence (black bar) of \textbf{CP} in various organic solvents. The inserted figure shows the relationship between the degree of swelling ($Q$) and dielectric constant ($\varepsilon$).
(ε = 46.5), the relative degrees of swelling decreased to 1.0 (Q’ = 1.01 in DMF and 1.02 in DMSO, respectively), indicating that the receptor had no effect for increase of the degrees of swelling. It is mainly because the ionic groups of EG-CI might be dissociated fully in these media, and thus, the swelling abilities were not enhanced by the addition of the receptor, although the receptor had enough affinity to chloride anions. In addition, the degrees of swelling (Q) of EG-CI in the presence of CP were approximately proportional to the logarithm of dielectric constant of the media as shown in the insertion in Figure 4-11. This result suggested that the degrees of swelling of EG-CI in the presence of CP correlated with the degree of dissociation of the ionic groups. In order to clarify this hypothesis, I demonstrated the dielectric constant dependence of the degrees of swelling in the presence of CP. The degrees of swelling of EG-CI in the absence and presence of CP were measured by using mixtures composed of acetone (ε = 20.6) and 1,2-dichloroethane (ε = 10.6) as shown in Figure 4-12. The degrees of swelling in the presence of CP were larger than those in the absence of CP in the whole range of dielectric constant, and the former showed a positive correlation with the dielectric constant of the media, whereas the latter didn’t show such a relationship. In the absence of CP, the compatibility of the polymer chain to the media should be decreased with an increase in the amount of acetone due to the incompatibility of the polystyrene backbone with acetone. These results strongly supported the hypothesis mentioned above, and the degrees of swelling were controlled mainly by dissociation of ion-pairs induced by complexation of the hydrophobic anion receptor.

In order to clarify the effect of the enhancement of ionic dissociation by complexation on the swelling behaviors, the dissociation degrees of TBACl and TBA(CP-Cl) complex in THF, pyridine, and acetone were calculated as shown in Figure 4-13. In any these solvents, the dissociation degrees

![Figure 4-12. The degree of swelling (Q) of EG-CI in the absence (black circle) and presence (open circle) of CP versus dielectric constant of the media.](image-url)
degrees of TBA(CP-Cl) were larger than those of TBACl in the whole range of concentrations. And so, the relationship between the swelling degrees of EG-X (X = Cl, PF$_6$, TFSI, and CP-Cl) and $K_p$ in THF was investigated. The $K_p$ of TBA(CP-Cl) has the largest ability to dissociate in THF and the swelling degree of EG-(CP-Cl) was also larger than those of EG-X (X = Cl, PF$_6$, and TFSI) as shown in Figure 4-14. These results strongly indicated

<table>
<thead>
<tr>
<th>$K_p$ (M$^{-1}$)</th>
<th>THF</th>
<th>pyridine</th>
<th>acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBACl</td>
<td>3.9×10$^7$</td>
<td>3.5×10$^3$</td>
<td>4.1×10$^2$</td>
</tr>
<tr>
<td>TBACl + CP</td>
<td>1.8×10$^4$</td>
<td>9.8×10$^2$</td>
<td>1.7×10$^2$</td>
</tr>
</tbody>
</table>

Figure 4-13. The dissociation degrees of TBA(CP-Cl) complex and TBACl in THF ($\varepsilon = 7.6$), pyridine ($\varepsilon = 12.6$), and acetone ($\varepsilon = 20.6$).

<table>
<thead>
<tr>
<th>TBAX</th>
<th>$K_p$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = Cl</td>
<td>3.9 × 10$^7$</td>
</tr>
<tr>
<td>X = PF$_6$</td>
<td>3.9 × 10$^5$</td>
</tr>
<tr>
<td>X = TFSI</td>
<td>1.9 × 10$^5$</td>
</tr>
<tr>
<td>X = CP-Cl</td>
<td>1.8 × 10$^4$</td>
</tr>
</tbody>
</table>

Figure 4-14. Swelling degrees of EG-X (X = Cl, PF$_6$, TFSI, and CP-Cl)
that the change of the swelling degrees of \textbf{EG-Cl} upon the addition of \textbf{CP} in organic solvents caused by the enhancement of ionic dissociation of ionic groups in \textbf{EG-Cl} by complexation between chloride anion and \textbf{CP}.

Subsequently, I demonstrated the dependence of the molecular structure of the anion receptors on the swelling behavior. The relative degrees of swelling ($Q'$) of \textbf{EG-Cl} upon the addition of \textbf{CP}, \textbf{R2}, and \textbf{R3} in various organic solvents are shown in Figure 4-15. I used 1 mM solution of the anion receptors for this experiment because the changes of the swelling degree upon the addition of \textbf{CP} should be saturated in this condition as predicted by the experiment in the section 4-2-3. In highly polar solvent such as DMSO, the addition of anion receptors had no effect on the swelling abilities in all cases ($Q' = 1.00$ for \textbf{CP}, \textbf{R2}, and \textbf{R3}). As mentioned above, it is mainly because the ionic groups of \textbf{EG-Cl} should be dissociated fully in this solvent. In acetone ($\varepsilon = 20.6$), the addition of the anion receptors clearly enhanced swelling abilities of \textbf{EG-Cl}, however there was no structural dependence of the anion receptors on the degrees of swelling in acetone ($Q' = 1.32$ for \textbf{CP}, 1.34 for \textbf{R2}, and 1.33 for \textbf{R3}). On the other hand, in non-polar solvents such as \textbf{CH$_2$Cl$_2$} and \textbf{CHCl$_3$}, the swelling abilities were dependent on the molecular structures of anion receptor, and the relative degrees of swelling ($Q'$) of \textbf{EG-Cl} were 1.02 for \textbf{CP}, 1.09 for \textbf{R2}, and 1.18 for \textbf{R3} in \textbf{CH$_2$Cl$_2$}, and 1.00 for \textbf{CP}, 1.04 for \textbf{R2}, and 1.07 for \textbf{R3} in \textbf{CHCl$_3$}, respectively. In the both cases in

![Figure 4-15](image_url)

\textbf{Figure 4-15.} The relative degrees of swelling ($Q'$) of \textbf{EG-Cl} in the presence of \textbf{CP} (black bar), \textbf{R2} (gray bar), and \textbf{R3} (open bar) in various organic solvents.
non-polar media, the $Q'$ values were $\text{CP} < \text{R2} < \text{R3}$. It is well known that a fluorine substitution of an anion core serves to delocalize the negative charge, and promote a dissociation of ion-pair in organic solvents.\textsuperscript{[24]} Thus, it is thought that \textbf{R3} has more capable to enhance the dissociation of ionic groups in the polymer gels because of the presence of fluorine substitution. These results indicated that the structural features such as the size, lipophilicity, and the presence of electron-withdrawing substitutions strongly affects the ability to enhance the dissociation of ion-pairs. Therefore, a novel stimuli-responsive materials working in non-polar solvents such as toluene and hexane could be realized by a synthetic approach that utilizes even larger anion receptor and selective fluorination.

4-3. Conclusion

In conclusion, I demonstrated the macroscopic volume and color changes of the polystyrene-based ionomer gels bearing chloride anions triggered by the addition of anion receptors as stimuli. The swelling and deswelling of the gels should be induced by the result of the complexation and regarded as visualization of molecular recognition processes of the polymer chains.\textsuperscript{[17]} This should open new perspectives in the utilities of anion receptors in material science and should suggest new molecular design as chemomechanical systems.\textsuperscript{[25]} Reliable molecular recognitions that have been well documented in the field of supramolecular chemistry should provide various stimuli-responsive materials.
4-4. Experimental Section

4-4-1. Materials

Tri-(n-hexyl)amine, 4-(chloromethyl)styrene, azobisisobutyronitrile (AIBN), styrene and divinylbenzene were purchased from Tokyo Chemical Ind. Co. CP was purchased from Wako Chemical Ind. Co. Styrene was purified by distillation before being used. All solvents were purchased from commercial suppliers and were used without further purification. Compounds 1, 2 and sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (NaTFPB) were synthesized according to reported methods.[26] R2 was supplied from Prof. H. Maeda in Ritsumeikan University and R3 was supplied from Prof. H. Furuta in Kyushu University.

4-4-2. Measurements

1H NMR spectra were recorded on a Bruker AV300 and a JEOL JNM-AL300 apparatus using tetramethylsilane as an internal standard for compound characterization. Mass spectral data were obtained using a Perceptive Voyager RP MALDI TOF mass spectrometer and a Bruker Daltonics Autoflex III. UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer with a JASCO ETC-50ST temperature controller. NMR spectra for the titration experiments were recorded on a JEOL JNM-AL300 apparatus. The method of measurements of degree of swelling was as follows: A capillary gel with the diameter of ca. 0.6 mm and the length of ca. 2.5 mm was placed in the following typical organic solvents with various polarities; toluene (dielectric constant $\varepsilon = 2.4$), chloroform ($\varepsilon = 4.8$), tetrahydrofuran (THF) ($\varepsilon = 7.6$), dichloromethane ($\varepsilon = 8.9$), cyclopentanone ($\varepsilon = 13.6$), acetone ($\varepsilon = 20.6$), N,N-dimethylformamide (DMF) ($\varepsilon = 36.7$), and dimethylsulfoxide (DMSO) ($\varepsilon = 46.5$). After immersion for 6 hours, I measured lengths of the cylindrical gels to calculate degrees of swelling ($Q$) of the gels defined as the following equation;

$$Q = \frac{L_{\text{wet}}}{L_{\text{dry}}} \text{ (mm/mm)}$$

where $L_{\text{wet}}$ and $L_{\text{dry}}$ were lengths of wet gel and dry gel. The effect of the anion receptors for degrees of swelling was evaluated by relative degrees of swelling ($Q'$) as the following equations;

$$Q' = \frac{Q}{Q_0}$$

where $Q$ and $Q_0$ were degrees of swelling in the presence ($10^{-5} - 10^{-3}$ M) and absence of the anion receptors, respectively.
4-4.3. Synthesis of 4-vinylbenzyl-N, N, N-tri(n-hexyl)ammonium chloride (1)

A mixture of tri(n-hexyl)amine (5.40 g, 20.0 mmol) and 4-(chloromethyl)styrene (9.16 g, 60.0 mmol) and DMF (40 ml) was stirred at 60 °C for 48 h under Ar atmosphere. The solvent was removed by a rotary evaporator, and the viscous liquid was purified by reprecipitation into excess amount of hexane to yield 1 as a white powder (7.6 g, 90%). 1H NMR (300 MHz, CDCl₃, TMS standard, r.t.) δ = 0.89 (t, J = 6.3 Hz, 9H NCH₂CH₂CH₂CH₂CH₂CH₂), 1.28 (m, 18H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 1.77 (m, 6H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 3.32 (m, 6H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 4.99 (s, 2H, NCH₂C₆H₄CHCH₂), 5.35 (d, J = 10.8, 1H, alkeneH), 5.82 (d, J = 17.7, 1H, alkeneH), 6.71 (dd, J = 10.8, 1H, alkeneH) 7.49 (d, J = 8.1, 2H, PhH) 7.52 (d, J = 7.8, 2H, PhH). MS (MALDI-TOF): m/z calcd for C₂₇H₄₈N⁺: 386.68; found: 386.67

4-4.4. Synthesis of 4-vinylbenzyl-N, N, N-tri(n-hexyl)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2)

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate sodium salt (10.6 g, 12.0 mmol) and 1 (5.07 g, 12.0 mmol) was dissolved in methanol (20 mL). Water was added dropwise to the stirring solution, and white solid gradually precipitated. The resulting mixture was stirred for more 3 hours. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO₂, dichloromethane) to yield 2 as a white solid. (12.1 g, 80%). 1H NMR (300 MHz, CDCl₃, TMS standard, r.t.) δ = 0.88 (t, J = 6.9 Hz, 9H NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 1.32 (m, 18H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 1.72 (m, 6H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 2.96 (m, 6H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂), 4.16 (s, 2H, NCH₂C₆H₄CHCH₂), 5.43 (d, J = 10.8, 1H, alkeneH), 5.85 (d, J = 17.7, 1H, alkeneH), 6.70 (dd, J = 10.8, 1H, alkeneH), 7.18 (d, J = 8.1, 2H, PhH), 7.52 (m, 6H, PhH), 7.69 (s, 8H, PhH). MS (MALDI-TOF): calcd for C₂₇H₄₈N⁺: 386.68; found: 386.67, C₃₂H₁₂BF₄⁻ 863.21; found 862.53; elemental analysis: calcd(%) for C₅₉H₆₀BF₂₄N: C 56.70, H 4.84, N 1.12; found: C 56.75, H 4.84, N 1.19
4-4-5. Preparations of Polymer Gels (EG-Cl, EG-TFPB, and NG)

A typical protocol is as follows; 211 mg (0.50 mmol) of 1, 469 mg (4.50 mmol) of styrene, 6.50 mg (0.05 mmol) of divinylbenzene (DVB), and 8.21 mg (0.05 mmol) of AIBN were placed in a glass tube and dissolved in DMF 500 ml. The solution was degassed by three freeze-thaw cycles and polymerized by heating at 65°C for 24 hours. The feed ratio was adjusted to 1 (or 2): styrene: DVB = 10:90:1 and the obtained gels denoted as EG-Cl and EG-TFPB. The formed gels, EG-X (X = Cl or TFPB) and NG were washed by swelling in THF, and air-dried at room temperature, then the samples were dried in vacuo at 45 °C for 24 hours. The polymerization conditions are summarized in Table 4-3.

Table 4-3. Polymerization conditions of polymer gels (EG-Cl, EG-TFPB and NG)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ionic monomer (mol/L)</th>
<th>Styrene (mol/L)</th>
<th>DVB (mol/L)</th>
<th>AIBN (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-Cl</td>
<td>1 (1.00)</td>
<td>9.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>EG-TFPB</td>
<td>2 (1.00)</td>
<td>9.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>NG</td>
<td>0</td>
<td>10.0</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Reaction temperature = 65 °C. Reaction time = 24 h. Solvent = DMF.
4-5. References


Chapter 5

Concluding Remarks

With the rapid development of supramolecular chemistry, a wide variety of soft materials can be realized by control of weak intermolecular interactions such as hydrogen bonds, van der Waals interactions, and electrostatic interactions. The function of soft materials can be controlled by the balance of intermolecular attractive and repulsive forces. More recently, various stimuli-responsive soft materials that can change their macroscopic properties such as mechanical actions and swelling of gels in response to various external stimuli have been realized by utilizing a reversibility of the weak interactions. It may be said that understanding of existing weak intermolecular interactions has been deepen in recent years. For the future, it is expected that an attention will be paid to a construction of a more complex molecular assembly by simultaneous control of multi-intermolecular interactions, and to a development of an unprecedented functional soft material by utilizing an intermolecular interaction that has never been used so far.

In this thesis, I aimed to verify the utility of electrostatic repulsive force in organic solvents and to fabricate a functional soft material utilizing the repulsive force. As mentioned in Chapter 1, intermolecular repulsive forces in non-polar organic solvents are limited to exchange repulsions, however, I demonstrated that lipophilic electrolytes such as WCAs worked as a strong intermolecular repulsive force even in non-polar organic solvents and even at low temperature. Moreover, I demonstrated that a dissociation of a chloride anion as TBA salt was controllable by complexation with a hydrophobic anion receptor in organic solvents, and this control of ionic dissociation by supramolecular interactions was useful to construct a stimuli-responsive polymer gel based on ionic polymer gels. The results of this paper are summarized below.

In Chapter 2, molecular design of polyelectrolyte gels that exhibit high swelling abilities even at low temperature was demonstrated with the aid of electrostatic repulsive interaction among the polymer chains in the ionic polymer gels and the utility of organic solvents with relative low melting points. The polyelectrolyte gel with lipophilic electrolyte swelled and absorbed some organic solvents such as THF and dichloromethane at -80 °C, and the swelling
degrees were similar to those at room temperature. To the best of our knowledge, this is the first example of super-absorbent polymers working at low temperature, and this material should be the first step for development of absorbent materials or actuators under extreme conditions. As mentioned in the Chapter 1, intermolecular repulsive forces are limited to exchange repulsions in non-polar organic solvents, whereas there are a lot of intermolecular attractive forces such as hydrogen bonds, van der Waals interactions, \( \pi-\pi \) interactions, charge-transfer interactions, and coordinate bonds. The results observed in this chapter strongly indicate that electrostatic repulsive force should be a powerful tool to develop various functional soft materials such as supramolecular materials and stimuli-responsive gels.

In Chapter 3, the enhancement of conductivity of chloride anion as TBA salt by complexation with meso-octamethylcalix[4]-pyrrole (CP) in various organic solvents was demonstrated. I demonstrated that the binding affinities of CP for free chloride anion and ion-paired one were obviously different in non-polar solvent such a THF, whereas such ion-pairing effect has often been ignored in host/guest studies of ionic species as guest molecules in low dielectric constant media in most cases. Moreover, it is noteworthy that the ion association constants of the resulting complex (TBA(CP-Cl)) was much smaller than that of TBACl in THF. It is hoped that this control of the ionic dissociation of ion-paired salts based on non-covalent bonds are useful as molecular design for functional soft materials utilizing electrostatic repulsive forces in non-polar organic solvents.

In Chapter 4, molecular design of stimuli-responsive polymer gels based on ionic polymer gel bearing chloride anions with the aid of the complexation between chloride anions in the polymer gel and hydrophobic anion receptors was demonstrated. In general, hydrophilic and relatively small ionic groups such as sodium cation, and chloride anion in the ionic polymer gels act as an intermolecular attractive force because they form highly bound ion-pairs clusters or highly aggregated species. The complexation between hydrophobic anion receptors and chloride anions in the ionic polymer gels generated intermolecular repulsive forces such as an electrostatic repulsion and an osmotic pressure in various organic solvents, and the swelling abilities of the ionic polymer gel were clearly enhanced by the repulsive forces.
This thesis describes that the electrostatic interaction can work as a strong intermolecular repulsive force even in non-polar media and even at low temperature, and such repulsive forces are controllable by supramolecular approach such as complexation between anions and anion receptors. In the field of material science, electrostatic interactions have been mainly recognized and utilized as an attractive force especially in non-polar organic solvents so far. However, in practice, optimally-designed ionic compounds can act as an intermolecular repulsive force even in non-polar solvents, and the utility of the repulsive force in the field of supramolecular chemistry and material science became clear. Considering the fact that the intermolecular repulsive force utilizable in organic solvents was limited to exchange repulsions, it is expected that the electrostatic repulsion in organic solvents is useful for fabrication of novel supramolecular assembly, and such supramolecular assembly offers a new approach to the fabrication of various functional soft materials in the future. From a perspective of synthesis of highly dissociable ionic compounds in non-polar organic solvents, supramolecular approach should be a powerful tool to realize such ions. Under the present circumstances, a recent investigation reported a novel synthetic strategy toward a number of extremely large and rigid molecular ions. However, if the ionic compound is too large and bulky, its steric hindrances prevented the direct synthesis of much larger ions. On the other hand, self-assembly offers a route for assembling some components into larger, functional ensembles, therefore, self-assembly will be a solution to the problem of synthesizing structures larger than molecules. Such ionic compounds constructed by a supramolecular approach and functional soft materials utilizing such ions are expected.
Publication List

Chapter 2
High swelling ability of polystyrene-based polyelectrolyte gels at low temperature

Chapter 3
Switching from ion-pair to free ion of alkylammonium chloride via complexation with anion receptors
K. Iseda, K. Kokado, K. Sada, to be submitted.

Chapter 4
Visualization of the complexation between chloride and anion receptors using volume change of ionomer gels in organic solvents

Other publications not included in this thesis
Counter Anion Dependent Swelling Behaviour of Poly(octadecyl acrylate)-based Lipophilic Polyelectrolyte Gels as Superabsorbent Polymers for Organic Solvents

Design and function of smart polymer gels based on ion recognition
Postscript

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