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Ionic Polymers Act as Polyelectrolytes in Nonpolar Media

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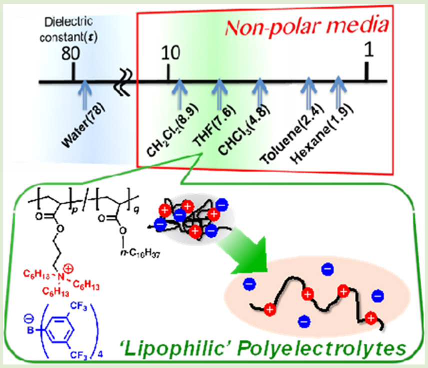
Supporting Information

ABSTRACT: Polyelectrolytes are ubiquitous materials, and their unique properties originate from dissociation of ionic groups to the small number of macromolecular ions and the large number of small counterions. They have been exploited only in water or high-dielectric media and scarcely in nonpolar ones ($\varepsilon < 10$). Herein, we demonstrate that poly(octadecyl acrylate) bearing tetraalkylammonium tetraarylborate as ionic groups behaves as a polyelectrolyte in the common nonpolar organic solvents such as chloroform, THF, and 1,2-dichloroethane. Conductivity measurement, DOSY NMR spectroscopy, and viscosity measurements clearly indicate that they form the extended conformation in them. This result emphasizes that the ionic polymers bearing suitable ion pairs ionizable in the given media act as polyelectrolytes. Various characteristic properties and processes of polyelectrolytes should be realized in nonpolar media by designing ion pairs and polymer chains in the ionic polymers. Moreover, our results imply that electrostatic interaction is readily available as a long-range repulsive force even in the nonpolar media.



Polyelectrolytes are defined as polymers with ionizable groups that can dissociate into leaving charges on polymer chains and release counterions into solutions. Charges fixed on polymers causes electrostatic repulsion among intra- and interpolymer chain, which lead to various specific solution behaviors, for example, high viscosity, efficient ion exchange, ion conductivity, osmotic pressure, and so on.[1] Due to their significant relevance in molecular biology[2,3] and their functions in polymer chemistry, the solution behaviors in water have been attracting considerable attention in the scientific community.[4,5] Indeed, common ionic polymers composed of either hydrophilic anions, such as halides, carboxylates, and sulfonates, or hydrophilic cations, such as alkali metal ions and ammonium ions, or both, are soluble and behave as polyelectrolytes in water and high-dielectric organic media, such as DMF and DMSO.[6−10] In low dielectric media, however, they are practically insoluble and do not behave as polyelectrolytes due to the formation of tightly bound ion pairs or higher aggregates via dipole−dipole interactions among the ion pairs. Moreover, the hydrophobic polymers bearing small amounts (less than 15 mol %) of these hydrophilic ionic groups, known as ionomers, are soluble, but do not act as classical polyelectrolytes but as thickners under semidiluted conditions.[11] This is attributed to good compatibility of the polymer chains and partial aggregation of the ionic groups to bridge the polymer chains in the intra- and interpolymer manners. Therefore, the requirements of chemical structures that act as a polyelectrolyte in the given media are both (1) the ionic groups can dissociate and (2) the polymer chain has high compatibility, which were summarized by Cooper et al.[12] More recently, the ionic polymers with more hydrophobic tetramethylammonium 1,1,2,3,3-pentacyanopropenide had been prepared as "hydrophobic polyelectrolytes". They were soluble and acted as polyelectrolytes in the organic solvents more polar than acetone ($\varepsilon \geq 20.6$), while the solution behaviors in cyclopentanone ($\varepsilon = 13.6$) and triethyl phosphate ($\varepsilon = 10.8$) indicated that they acted as typical nonionic polymers due to low polarity of these solvents.[13] Therefore, ionic polymers that work as polyelectrolytes in nonpolar media ($\varepsilon < 10$) have never been reported.

On the other hand, trials for designing dissociative and noncoordinating ion pairs in nonpolar media have attracted considerable interest with respect to the development of electrolytes and catalysis.[14] In particular, tetraphenylborates are known as hydrophobic anions, and conductive measurements revealed that their salts with hydrophobic tetraalkylammonium cations dissociate into free ions in THF and *o*-dichlorobenzene.[15−17] This prompted us to develop the ionic polymers that act as polyelectrolytes in nonpolar media by the incorporation of tetraalkyammonium tetraphenylborate salts into lipophilic and flexible poly(octadecyl acrylate), because they should have high compatibility of the polymer chains and high dissociation of the ionic groups. To the best of our knowledge, this is the first example of an ionic polymer that behaves as a polyelectrolyte in nonpolar media such as chloroform, THF, and dichloromethane.

The ionic polymer (**LP1** in Scheme 1) was prepared by the free-radical copolymerization of octadecyl acrylate and ionic

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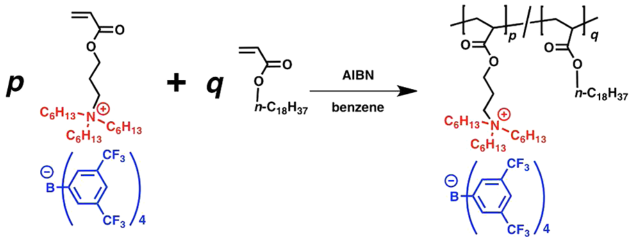
Scheme 1. Preparation of the Ionic Polymer (LP1)



monomer **1** initiated by AIBN in benzene at 70 °C. After isolation by reprecipitation from THF to methanol−THF mixture (=9/1 (v/v)), **LP1** was collected by filtration and dried in vacuo. The copolymerization ratio was determined according to the integration in ^{1}H NMR spectrum, and the average molecular weights were determined by GPC in chloroform with a polystyrene standard; **LP1**: M_n 1.5 × 10^5, M_w 4.5 × 10^5, 4.8 mol % of the ionic group. **LP1** was soluble in nonpolar solvents, such as toluene, chloroform, and THF, and practically insoluble in polar solvents, such as acetone, ethanol, methanol, DMF, DMSO and water. The poor compatibility of the octadecyl groups of **LP1** was mainly ascribed to partial crystallization of the octadecyl groups in them, although high-dielectric media should induce the dissociation of the ionic groups.

First of all, we measured the conductivity of tetra(*n*-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate (**TBA TFPB**), which is the same as the ionic group of **LP1**, in the target solvents to verify the dissociation of **TBA TFPB** in some nonpolar organic solvents. The concentration dependence on the conductivity in dichloromethane, THF, chloroform, and toluene is shown in Figure 1, and the limiting molar conductivity (Λ_0) and the equilibrium constant for ion-pair association (K_A) using the Fuoss−Kraus equation[18] are listed in Table 1. The lower the value of K_A, the greater the degree of dissociation of ion pairs. In toluene, the conductivity of **TBA TFPB** is undetectable (less than 0.02 μS/cm) by our equipment at a low concentration (<0.5 mM), suggesting that the **TBA TFPB** ion pair did not readily dissociate.[19] In the other three nonpolar solvents, dichloromethane, THF, and chloroform, the molar conductivity of **TBA TFPB** increased with the decreasing concentration, indicating that **TBA TFPB** acts as a weak electrolyte in their solvents. The association constants increased with their decreasing dielectric constants. Even in chloroform, the association constant has a magnitude of 10^5 and the ion pair should be able to partially dissociate into free mobile ions. The more polar dichloromethane and THF provided lower association constants, and the calculated degrees of dissociation at 0.2 mM were found to be about 70%. Therefore, the ionic groups in **LP1** should dissociate in them and should play a key role in their polyelectrolyte behaviors.

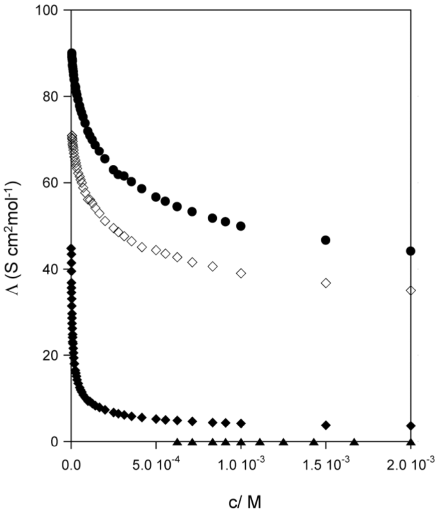


Figure 1. Molar conductivity of **TBA TFPB** at 25.0 °C in (▲) toluene, (◆) chloroform, (◇) THF, and (●) dichloromethane.

Table 1. Equilibrium Constants for Ion Pair Association (K_A), Limiting Molar Conductivity (Λ_0), and Dissociation Degree (α) at 0.2 mM of TBA TFPB in Nonpolar Solvents (Dielectric Constant ε) at 25.0 °C

solvent (ε at 25 °C)	K_A (M)	Λ_0 (S cm^2 mol^{-1})	α (%)
toluene (2.4)			
chloroform (4.8)	7.1 × 10^5	68.3	10.7
THF (7.6)	5.3 × 10^3	73.5	69.5
dichloromethane (8.9)	4.6 × 10^3	92.2	70.6

For more details of the ionic dissociation, we investigated the DOSY NMR of **LP1** in dichloromethane-d_2 and toluene-d_8, as shown in Figure 2. Because the ^{1}H NMR chemical shifts of the TFPB anion and the polymer chain were well separated, dissociation of the ion pair could be easily estimated from the difference in their diffusion coefficients. In dichloromethane-d_2, the estimated average diffusion coefficient from the phenyl proton of the TFPB anion was much higher than those of the other protons assigned to the polymer chain, such as the terminal methyl group and the methylene group adjacent to the ester oxygen atom, whereas all the diffusion coefficients were similar to each other in toluene-d_8. This result clearly indicates the dissociation of the TFPB anions from the cationic polymer chain of **LP1** in dichloromethane-d_2 and not in toluene-d_8.

We next performed classical viscosity measurements for **LP1** at 30.0 ± 0.1 °C in the concentration range of 4.1 × 10^{-4}−2.7 × 10^{-2} mol L^{-1} (0.015−1.0 g/dL^{-1}) in the following nonpolar solvents: 1,2-dichloroethane (ε = 10.4), dichloromethane (ε = 8.9), THF (ε = 7.6), chloroform (ε = 4.8), and toluene (ε = 2.4),[20] as shown in Figure 3. In toluene, the reduced viscosity was proportional to the **LP1** concentration, and intrinsic viscosity was found to be 8.41 L mol^{-1} (0.31 dL/g^{-1}). This behavior was typical for nonionic polymers, indicating **LP1** cannot behave as a polyelectrolyte under the condition in which the ionic group does not dissociate under diluted conditions. However, in the other solvents, the reduced viscosities increased with the decreasing concentrations, because dissociation of the ionic groups on **LP1** was enhanced by dilution and induced electrostatic repulsion among the charges. This solution behavior was typical for charged polymers and was the same as common polyelectrolytes in water,[21,22] which should be attributed to the electrostatic repulsion between the charges on the polymer chains. The effect of the electrolyte on solution viscosity of the **LP1** was then investigated. In the 5 mM 1,2-dichloroethane solution of **TBA TFPB**, the reduced viscosity of **LP1** was proportional to the concentration. This linear correlation illustrated that **LP1** behaved in a similar manner to nonionic polymers in the electrolyte solution, because **TBA TFPB** was dissociated into ions and the electrostatic repulsion was drastically screened. The solution behaviors of **LP1** in the nonpolar solvents, whose dielectric

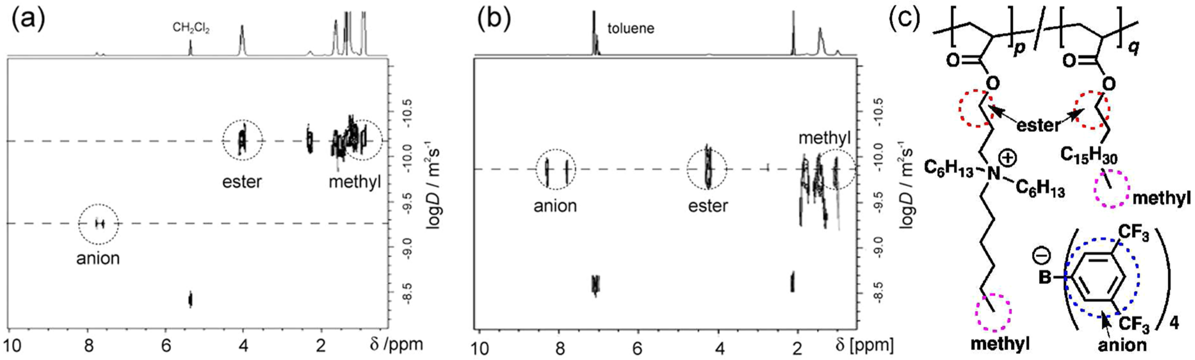


Figure 2. Diffusion-ordered ^{1}H NMR (DOSY) spectra of **LP1** (a) in dichloromethane-d_2 (polymer concentration: [**LP1**] = 1.8×10^{-2} mol L^{-1} (6.7 mg mL^{-1})) and (b) in toluene-d_8 (polymer concentration; [**LP1**] = 1.8×10^{-2} mol L^{-1} (6.7 mg mL^{-1})). (c) Corresponding proton to DOSY chart of **LP1**.

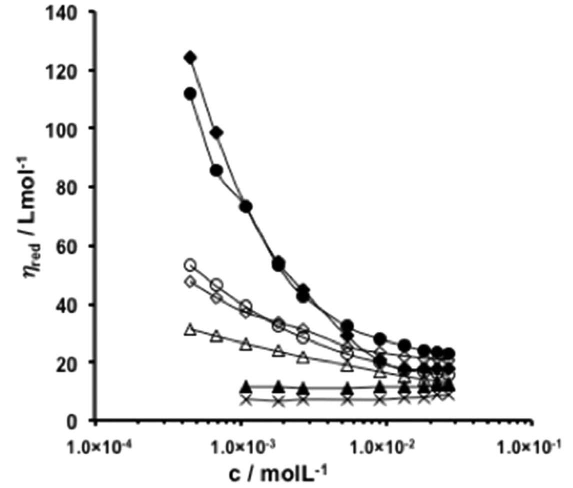


Figure 3. Concentration dependence on the reduced viscosities of **LP1** at 30.0 °C in (▲) toluene, (◆) chloroform, (◇) THF, (●) dichloromethane, (○) 1,2-dichloroethane, (△) 7/3 v/v of methanol and toluene, and (×) 5 mM **TBA TFPB** solution of 1,2-dichloroethane.

constants were in the range of 5−10, were quite similar to those of the common polyelectrolytes in aqueous media. Therefore, **LP1** behaved as polyelectrolytes in chloroform, THF, dichloromethane, 1,2-dichloroethane, and a methanol and toluene mixture.

Figure 4 shows the plots of reduced viscosities in the solution of **TBA TFPB** (1 μM − 5 mM) for revealing characteristics of **LP1** in 1,2-dichloroethane. In 10^{-5} M or more diluted solution of **TBA TFPB**, the reduced viscosity of **LP1** increased with decreasing the polymer concentration. On the other hand, no increase of η_{red} was observed above 10^{-5} M due to the strong screening of the electrostatic repulsion between the charges on the polymer chain of **LP1**. This critical concentration of the screening effect was one or two magnitude lower than the common polyelectrolytes in water (10^{-4} to 10^{-3} M),[23−32] that is, a much smaller amount of the electrolyte was required for diminishing of polyelectrolyte behaviors. The low content (4.8 mol %) of ionic groups in **LP1** should play a key role for this sensitive polyelectrolyte behavior by addition of the electrolyte. The longer-range repulsive force in nonpolar media might work for the polyelectrolyte behaviors including the chain extension of **LP1**.

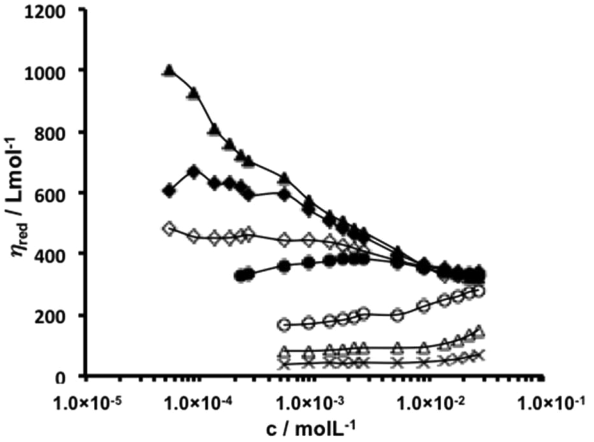


Figure 4. Salt concentration dependence on the reduced viscosities of **LP1** at 30.0 °C in **TBA TFPB** solution of 1,2-dichloroethane: (▲) 0, (◆) 1.0×10^{-6}, (◇) 5.0×10^{-6}, (●) 1.0×10^{-5}, (○) 1.0×10^{-4}, (△) 1.0×10^{-3}, and (×) 5.0×10^{-3} M.

In conclusion, we demonstrated the novel polyelectrolyte that dissociates into macromolecular ions and forms an extended chain conformation by electrostatic repulsion even in low-dielectric media ($5 < \varepsilon < 10$), such as chloroform, THF, and dichloromethane. To the best of our knowledge, this is the first example of a "lipophilic" polyelectrolyte active in nonpolar organic solvents, which breaks the limitation of the media that ionic polymers act as polyelectrolytes. The wide applications of polyelectrolytes that could be achieved in water, such as smart polymers,[33−39] polyelectrolyte brushes,[40,41] high water absorption resin,[42] and multilayers by layer-by-layer (LbL) deposition,[43] should be applicable in them. Indeed, extended polymer conformation in them provides the fundamental basis for the extraordinary high swelling abilities of the cross-linked lipophilic polyelectrolytes as organic solvent superabsorbent polymers.[44−47] Moreover, a "lipophilic" polycation and polyanion can be utilized to fabricate a LbL multilayer in nonaqueous media.[48] With respect to supramolecular chemistry and the design of smart polymers,[49−51] our result indicates that an electrostatic interaction acts as a long-range repulsive force, even in the nonpolar media, to expand the polymer conformation, and the smart polymers should be realized by competing with the electrostatic repulsion and various attractive intermolecular interactions that supramolecular chemistry have investigated, such as hydrogen bonding, π−π stacking, and alkyl chain packing. Exploration for dissociable ion pairs in a specific media should lead to designer's polyelectrolytes working in them, and a further theoretical calculation to argue the influence of the electrolyte quantitatively is currently under way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, instrumentation, experimental conditions, and the details of the syntheses and polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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