where λ_f is the length of the core in the reported experiment and N_f was the number of grid points needed to yield the correct amount of dispersion.

The foregoing formula has been enumerated for a relative resolution, $r = \Delta m/m_0$, of 0.25 for the two mass distributions and range of ν values that have been used. These are tabulated in Table IV. If the physical value of ν actually is 0.8, then it can be seen that this is encouraging for future experiments as core lengths of 0.65 m × 1.8 = 1.2 m should begin to give results that are open to chromatographic interpretation.

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Registry No. Xanthan gum, 11138-66-2.

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Notes

Poly(crown ether): A Potential Candidate for Solid-State Electrolytes

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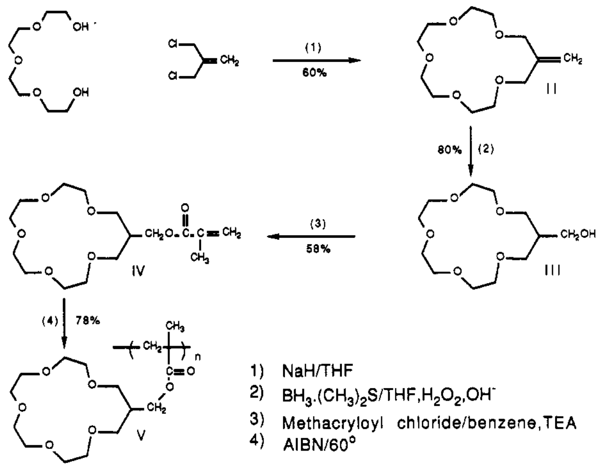
For the past few decades various classes of solid-state electrolytes have been extensively investigated. They include crystalline species such as β-alumina[1] and glasses such as $LiAlSiO_4$.[2] Recently the discovery of fast ionic conductivity in complexes such as poly(ethylene oxide) with lithium ion has kindled worldwide interest in similar systems and their ion-transport properties.[3-22] Applicability of polymers as solid electrolytes is based fundamentally on their ability to solvate metal ions, thereby isolating them effectively from their anions and thus avoiding the formation of immobile ion pairs. Clearly the energy of solvation of the salt by the polymer should be large enough to overcome the lattice energy of the salt. In addition to lattice energy considerations, a number of other factors seem to be crucial for the complexation process:[5,6,23-25] The solvation process is facilitated by the presence of a large concentration of polar groups; the polymer has to be flexible, as indicated by a low glass transition temperature, so that polymer molecules can be spatially reorganized during complexation to form the best local geometry for effective solvation.

On several occasions, solvation of metal ions in a polymer solid electrolyte has been shown to be analogous to that in macrocyclic crown ethers.[13,24,25] However, the ion conductive properties of a polymer with crown ether pendant groups incorporated into the backbone have not been previously reported. In this study poly((hydroxymethyl)-16-crown-5 methacrylate) was investigated as a possible candidate for an organic solid-state electrolyte in which a polymethacrylate backbone bears a pendant crown ether. Ionic conductivity of the model polymer–$LiClO_4$ complex was demonstrated by direct current measurement on a cell with platinum and/or lithium electrode.

Scheme I



1) NaH/THF
2) $BH_3.(CH_3)_2S/THF,H_2O_2,OH^-$
3) Methacryloyl chloride/benzene,TEA
4) AIBN/60°

Experimental Section

A. Materials. Solvents were dried either with Linde 4A molecular sieves or CaH_2. AIBN was recrystallized twice from methanol. Tetraethylene glycol was vacuum distilled over anhydrous $CuSO_4$. 3-Chloro-2-(chloromethyl)-1-propene was purified by distillation and stored over molecular sieves. Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride as described previously[26] (yield 80%).

B. Synthesis of the Monomer. The synthetic procedure leading to the target polymer is outlined in Scheme I. (Hydroxymethyl)-16-crown-5 (III) (80% yield) was prepared from methylene-16-crown-5 (II) (60% yield), in turn prepared according to the method of Tomoi et al.[27]

16-Crown-5 methylenemethacrylate (IV) was prepared by first dissolving 14.0 g (5.3 × 10^{-2} mol) of III in 150 mL of dry benzene. After 75 mL of benzene was distilled off, the solution was cooled to ice temperature, and 19 mL of triethylamine (TEA) (0.13 mol) was added. To this solution was added 6.2 mL (6.36 × 10^{-2} mol) of methacryloyl chloride dropwise and with vigorous stirring over a period of 30 min. The reaction mixture was stirred for 2 h at

0 °C and stirred overnight at room temperature. Suspended ammonium salt was removed by filtration, and the filtrate containing IV was first evaporated at the aspirator pump followed by heating at 40 °C for 3 h under high vacuum. The resulting oily residue was dissolved in chloroform and washed repeatedly with 0.5% aqueous NaOH saturated with NaCl, followed by deionized water. After the organic layer was dried with Na_2SO_4, removal of the solvent afforded crude IV product as a straw-colored oil. One-third of the product was chromatographed on a neutral alumina column (24-cm length, 2-cm diameter) with a mixture of acetone–chloroform–methanol (200:450:1). Fractions containing pure IV were combined, and the product was isolated as a thick oil by removal of the solvent. The latter was further dried under vacuum at room temperature to yield 3.4 g (58%), dec 245 °C. IR (neat NaCl disk) 1723 ($\nu_{C=O}$), 1635 ($\nu_{C=C}$), 1126 (ν_{C-O}) cm^{-1}; ^1H NMR ($CDCl_3$, TMS) δ 1.94 (s, 3 H, CH_3), 2.01 (m, 1 H, CH), 3.62 (s, 20 H, CH_2O), 4.21 (d, 2 H, $CH_2O(C{=}O)$, 5.54, 6.08 (s, 2 H, $=CH_2$). Anal. Calcd for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49; O, 33.69. Found: C, 57.79; H, 8.39; O (by diff), 38.82. (Note: Washing the crude methacrylate in chloroform with 0.5% NaOH leads to the formation of a thick emulsion. In this case, centrifuging is necessary to break the emulsion. Use of TEA in the preparation occasionally leads to gelation of the methacrylate ester, rendering it useless. The same procedure can be followed without TEA and without the danger of gelation, but the yield is substantially lower (~20%).)

C. Synthesis of the Polymer. Radical polymerization was carried out with 2,2′-azobis(isobutyronitrile) (AIBN). A solution of the monomer, 16-crown-5 methacrylate (IV), was placed in a glass ampule and degassed in 3 freeze–thaw cycles, sealed under vacuum, and polymerized for 70 h at 60 °C. The solution was concentrated under vacuum, and the polymer was precipitated in hexane. The polymer was purified by 3 dissolution–precipitation steps from chloroform–hexane. Yield (benzonitrile solvent) 76%; dec 250 °C; IR (film, NaCl disk) 1720 ($\nu_{C=O}$), 1121 (ν_{C-O}) cm^{-1}. Anal. Calcd for $C_{16}H_{28}O_7$: C, 57.81; H, 8.49; O, 33.69. Found: C, 57.76; H, 8.39; O (by diff), 33.85.

D. Preparation of Polymer Complexes. Weighed amounts of poly(methylene-16-crown-5 methacrylate) (IV) and vacuum-melted $LiClO_4$ were dissolved in dry acetone separately. The two solutions were mixed in appropriate proportions to obtain polymer–salt complexes of desired composition in solution.

E. Methods. Films were cast on glass plates to obtain samples for X-ray measurements. Similarly films were cast on NaCl plates for IR measurements. Films used for dc conductivity measurements were cast on a Teflon surface, peeled off, and cut to a circular shape. Standard inert atmosphere techniques were used during the preparation of complexes and casting of films. For differential scanning calorimetry (DSC) measurements, films of polymer–salt complexes were cast directly on DSC sample holders. Solutions of polymer–salt complexes in acetone were used to prepare Li NMR spectra. In this case, a capillary containing a solution of $LiClO_4$ in acetone-d_6 was used as the internal standard.

Films (1.3-cm diameter and 0.01-cm thickness) were used in dc conductivity measurements. Films were sandwiched between either platinum or lithium electrodes, and the sandwich was press-mounted between two copper terminals and placed in an aluminum microoven constructed in-house. Cell assembly was carried out under an inert atmosphere with a drybox. During measurements, the cell was kept in a fully evacuated glass chamber.

Average molecular weights were determined by a Waters GPC system containing a Model 6000A solvent delivery system coupled with a R-401 diffraction refractometer. IR measurements were carried out on a Beckmann FT-1100 spectrophotometer, and NMR measurements were done on a JEOL FX 90Q FT NMR with multinuclear capability. DSC measurements were performed on a Perkin-Elmer DSC-2 instrument. A scan speed of 20 °C/min was used. X-ray diffraction patterns were measured with a Philips X-ray spectrometer by using a Ni-filtered Cu Kα line. A Keithley 600B electrometer and Model LM261 Lambda voltage supply were used in dc conductivity measurements.

Results and Discussion

In an organic polymer-based solid-state electrolyte, interaction between lithium cations and the polymer is necessary to achieve dissociation of the incorporated salt. But too strong an interaction will make these solvated ions immobile, resulting in a low conductivity. The cavity radius of the macrocyclic crown pendant, 16-crown-5, can be approximated from its dibenzo analogue as 1.4 Å.[28] The radius of the lithium ion is 0.7 Å. The poor fit between Li^+ and the crown cavity results in a small enthalpy change associated with Li⋯O interactions. Since a small entropy loss is expected, the overall free-energy change associated with the complexation may be small, resulting in loosely bound lithium ions. Under these circumstances, provided the lattice energy of the salt is not too high, generation of ionic carriers through solvation should predominate over loss of ionic mobility resulting from interaction between metal ions and the host polymer, and the resulting complex should be ionically conductive.

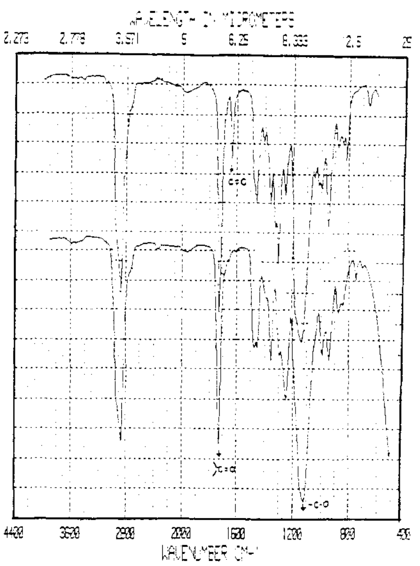


Figure 1. IR spectra of the monomer 16-crown-5 methylene-methacrylate (top spectrum) and the polymer poly(methylene-16-crown-5 methacrylate) (lower spectrum).

Table I
Physical Data on the Polymerization Process

solvent	conversion, %	$\bar{M}_w$
toluene	2	12000
tetrahydrofuran	25	47000
cyanobenzene	78	81000

Figures 1, 2, and 3 show IR, ^1H NMR, and ^{13}C NMR of compounds IV and V, respectively. Peak assignments are shown alongside each spectrum. Table I summarizes certain aspects of the polymerization process. Cyanobenzene was routinely used as the polymerization solvent. Polymer V is soluble in common organic solvents except CCl_4 and acetic acid.

Evidence related to complex formation between the polymer and $LiClO_4$ is provided in Figure 4. The ratio of salt per crown ether unit was varied systematically across a series of solutions in acetone. All solutions had the same concentration of the salt. In Figure 4, the position of the ^6Li resonance for each solution is expressed as a shift relative to that for $LiClO_4$ in acetone-d_6. The presence of a shift and its variation with salt/crown ratio suggest an interaction between lithium and crown ether units. Similar variations associated with the solvation of lithium ions in pure solvents[29] and lithium ion complexes with crown ethers[30] have been explained in terms of the equilibrium between separated ion pairs and contact ion pairs. A similar explanation may be valid for the variation of the position of the Li resonance shown in Figure 4. The

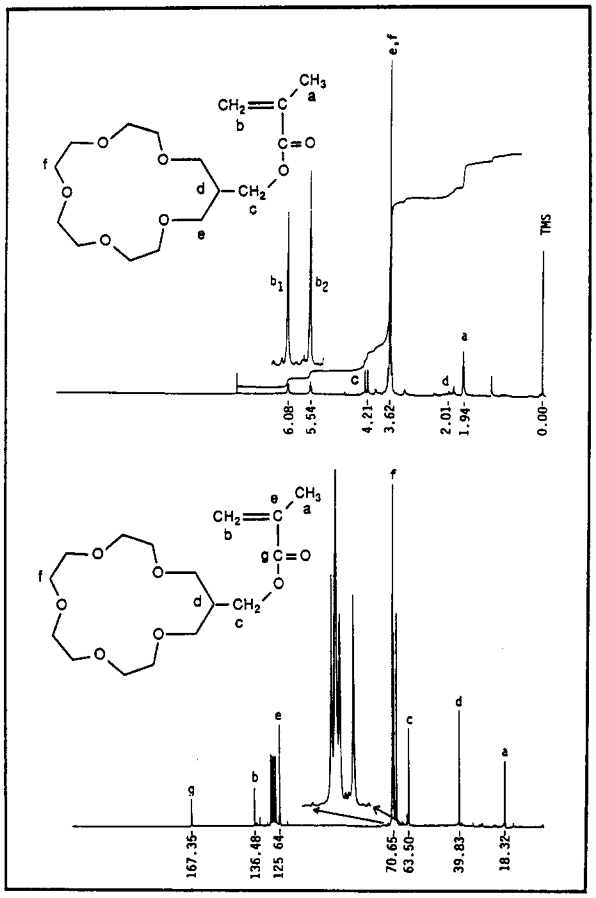


Figure 2. ^1H NMR spectrum of the monomer 16-crown-5 methylenemethacrylate in $CDCl_3$ (top spectrum) and the corresponding ^{13}C NMR spectrum in C_6D_6 (lower spectrum).

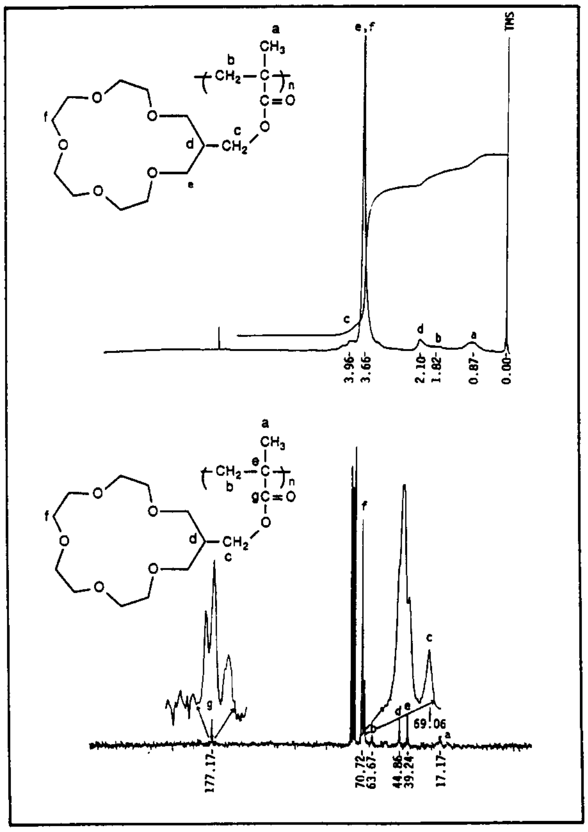


Figure 3. ^1H NMR spectrum of the polymer poly(methylene-16-crown-5 methacrylate) in $CDCl_3$ (top spectrum) and the corresponding ^{13}C NMR spectrum (lower spectrum).

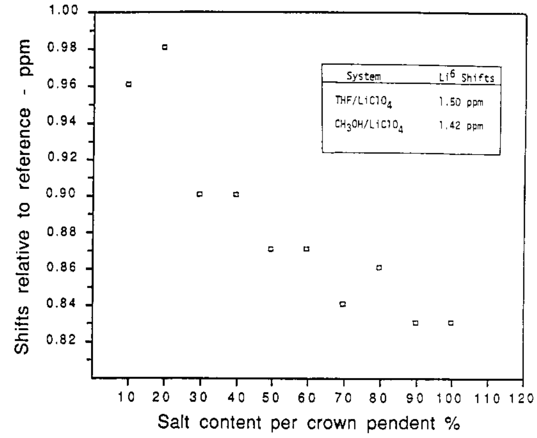


Figure 4. Position of ^6Li resonance for each test solution, expressed as a shift relative to that for $LiClO_4$ in $(CD_3)_2C{=}O$, as a function of the salt content per crown pendant. Inset shows the shift for $LiClO_4$ in two different solvents.

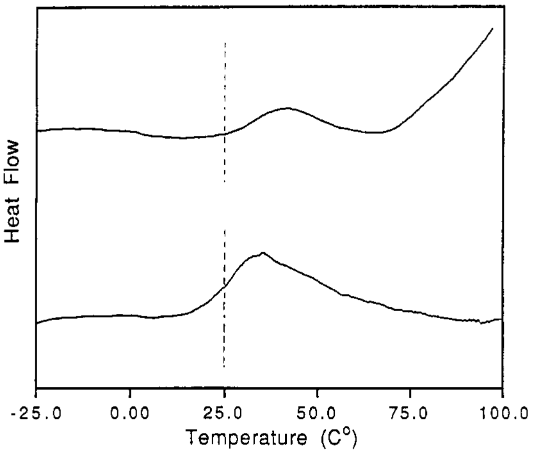


Figure 5. Profiles of differential scanning calorimetry curves for the uncomplexed polymer poly(methylene-16-crown-5 methacrylate) (lower curve) and the polymer–$LiClO_4$ complex. [salt]/[crown] = 0.1 (top curve).

Table II
IR Observations for Polymer–Salt Complexes

salt content, %	C=O stretch	C—O stretch
00	1728	1121
20	1728	1100
60	1728	1093
80	1725	1095

exceptionally narrow lithium resonance line makes it possible to measure lithium chemical shifts with considerable accuracy.

Table II illustrates further evidence for complex formation between the lithium ion and crown ether unit. The position of the C–O stretch was found to be sensitive to the salt/crown ratio for each complex. Shifts observed at low concentrations were significant despite the fact that the IR instrument used in this study had only 4-cm^{-1} resolution. At higher concentrations, the position of the C–O stretch seems to become insensitive to the salt content. As shown in Table II, the position of the ester carbonyl stretch is practically invariant with the salt content. These observations are consistent with the fact that lithium mainly associates with the crown ether side group and not with the polar backbone of the polymer.

DSC traces for the pristine polymer and a polymer–salt complex ([salt]/[crown] = 0.1) are shown in Figure 5. The peak shown in the figure was the only response observed within the temperature span ranging from −50 to 260 °C

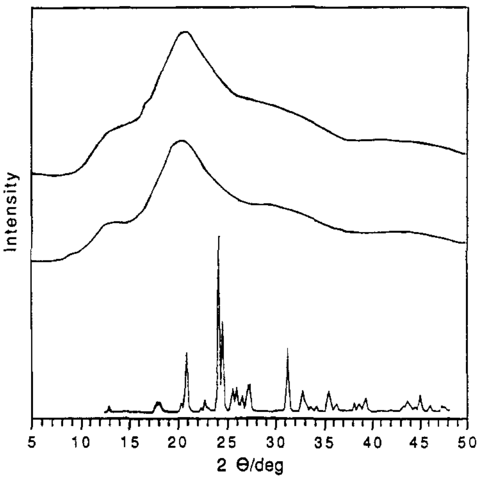


Figure 6. X-ray diffraction profiles for $LiClO_4$ (lower curve), poly(methylene-16-crown-5 methacrylate) (middle curve), and the polymer–$LiClO_4$ complex. [salt]/[crown] = 0.08 (upper curve).

and was attributed to the glass transition. Absence of a melting endotherm indicates the amorphous nature of the polymer and the complex. The polymer has a glass transition around 25 °C, which is higher than the glass transition temperature for any other polymer that has been found suitable for a solid-state electrolyte. But it is significantly low compared to higher glass transition temperatures usually associated with other methacrylic-type polymers.[31] When a polymer–salt complex is formed, the interaction between lithium cations and the polymer results in lower mobility for polymer chain segments, leading to a higher glass transition temperature, T_g. The DSC curve for the polymer–salt complex with 10% salt loading indicates a T_g value that is about 12 °C higher than that for the polymer.

Shown in Figure 6 are X-ray diffraction patterns for $LiClO_4$, polymer, and a typical complex. The absence of sharp features in the spectrum of the polymer indicates its amorphous character. This observation is consistent with the absence of a melting endotherm in the corresponding DSC curve. The X-ray spectrum of the polymer–salt complex shown in Figure 6 does not show any peak characteristic of crystalline $LiClO_4$, indicating that the lithium salt is intimately dispersed in the amorphous polymer and has lost its crystallinity completely. The spectra shown in Figure 6 have a "step"-like profile, indicating the possible existence of short-range order.

Figure 7 shows the time evolution of apparent dc conductivity at 60 and 105 °C estimated from the change in current with time under an applied voltage of 2.0 V. When the complex is sandwiched between Li electrodes, the apparent dc conductivity attains a steady state and shows only a slow decline thereafter. The steady-state conductivity corresponds to 1.6×10^{-7} $(\Omega\ \mathrm{cm})^{-1}$ at 60 °C. Direct current conductivity of the cell with Pt electrodes showed a sharp decrease in the dc conductivity of the cell with time, and in about 20 min the conductivity reached a value that was nearly 2 orders of magnitude less than the corresponding value for the cell with lithium electrodes. Although these results are not conclusive, they suggest that lithium ion is the main charge carrier. In the cell with lithium electrodes, Li^+ ions transfer freely at the Li–complex interface and migrate through the polymer, maintaining a steady current. Since the Pt electrode acts as a blocking electrode, ions accumulate at the interface to create an electric field that is opposite to the applied potential. Thus, the conductivity appears to decrease with time. Therefore, dc conductivity measurements with Pt and lithium electrodes are consistent with the ion conductive nature of the polymer–salt complex. Some insight into the mobility of ions can be obtained by application of a dc voltage in one direction for a few hours and then reversing the polarity of the applied voltage. The *I*–*t* curve after the reversal is shown in Figure 7. The curve apparently has a current maximum at about 4 min. After an application of voltage, mobile ions drift and accumulate as a sheet without discharging at the electrode of opposite polarity. After the polarity is reversed, these ions become mobile again. The bump observed at 4 min corresponds to the time when the effective mobile ion density in the bulk attains its highest value. The carrier mobility was determined from eq 1,[32] where μ is the carrier mobility,

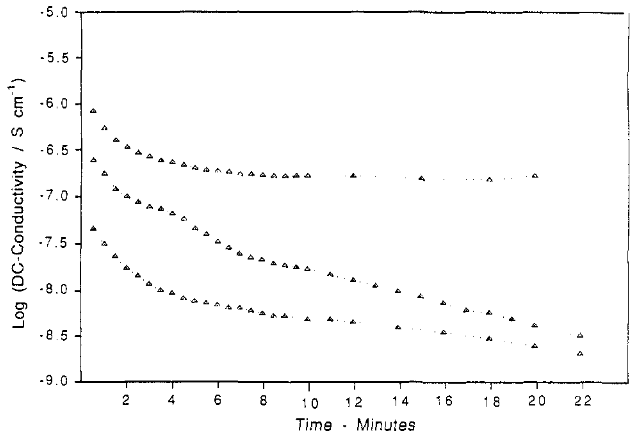


Figure 7. Time dependence of apparent dc conductivity of poly(methylene-16-crown-5 methacrylate)–$LiClO_4$ complexes. At 60 °C, under an applied potential of 2.0 V, with Pt electrodes (lower curve). Under the same conditions but with Li electrodes (top curve). At 105 °C, with Pt electrodes, after reversal of the applied voltage (middle curve).

$$\mu = \frac{d^2}{V\tau} \tag{1}$$

d is the film thickness, *V* is the applied voltage, and τ is the time at maximum current. Since the thickness of the sample, *d*, was 0.01 cm and $V = 2$ V, the mobility can be calculated as 2.1×10^{-7} cm^2 V^{-1} s^{-1}, which is of the same order as the mobilities reported for lithium ion in complexes consisting of a lithium salt and a straight-chain polymer host.[15,33] Obviously no direct comparison of ionic mobilities is possible since mobility is strongly dependent on temperature. Since we have not yet determined the main charge carrier species in the complex, we only assume that the mobility value obtained above corresponds to that of the lithium ion.

Conclusions

A polymer consisting of a methacrylate backbone with a 16-crown-5 ether pendant group was synthesized and fully characterized. The polymer forms complexes with $LiClO_4$. X-ray measurements reveal that the polymer and the complex are amorphous. Direct current conductivity measurements show that the polymer–salt complex behaves as expected for an ionic conductor. Conductivity of the complex is of the order 2×10^{-7} $(\Omega\ \mathrm{cm})^{-1}$, while the mobility of the main carrier is of the order 2×10^{-7} (cm^2 V^{-1} s^{-1}).

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Registry No. III, 69496-25-9; IV, 119071-30-6; IV (homopolymer), 119071-35-1; metacryloyl chloride, 920-46-7.

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Microphase Separation in Diblock-Copolymer Melts: Ordering of Micelles

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Introduction

Microphase-separated block–copolymer systems attract considerable attention from polymer scientists. One of the particular systems of that kind is a melt of diblock–copolymers A–B, incompatibility of A and B blocks being responsible for separation effects. It is well established that polymer melts are weakly fluctuating systems, so a mean-field approach (in a general sense) can be applied to the melts. The specific mean-field theories of block–copolymer melts were proposed by Helfand and Wasserman[1] for the case of narrow interphase width and by Leibler[2] for the opposite case. The final results of these papers[1] were obtained after some numerical work. More recent approaches[3,4] enable one to obtain essentially the same results in a purely analytical way. Moreover, a number of new analytical results were obtained in ref 3 and 4. In particular, it was shown that the interaction energy of two spherical domains (micelles) depends on the distance between them in a nonmonotonic manner. It was assumed that this prediction implied some special features of micelles formation and ordering. The aim of the present paper is to study quantitatively some equilibrium aspects of the process of formation and ordering of micelles.[5]

Let us consider a melt of block–copolymers A–B, A being the minor component: $f = N_A/N \ll 1$ ($N = N_A + N_B \gg 1$ is the number of links in a polymer chain). The radii of gyration of the blocks in a homogeneous melt are

$$R_A = N_A^{1/2}a_A; \qquad R_B = N_B^{1/2}a_B \tag{1}$$

where a_A and a_B are the characteristic sizes of A and B links. Let us consider the simplest symmetric case: $a_A = a_B = a$ and $v_A = v_B = v$, where v_A and v_B are the volumes per link in undiluted homopolymers A and B, respectively.

The excess free energy of mixing can be written as[7]

$$F_{\text{int}} = \chi T \int \varphi_A(r)\, \varphi_B(r)\, d^3r/v \tag{2}$$

where $\varphi_A(r)$ and $\varphi_B(r)$ are volume concentrations of A and B components relative to the pure polymers (an incompressibility condition, $\varphi_A(r) + \varphi_B(r) = 1$ is assumed), and χ is the (dimensionless) parameter of incompatibility.

Interaction of Micelles

If χ were sufficiently small, the melt would be homogeneous:

$$\varphi_A(r) = f; \qquad \varphi_B(r) = 1 - f$$

As χ increases, an effective repulsion of A and B blocks gives rise to aggregation of copolymer chains into spherical domains (micelles). The structure of a micelle was considered in ref 3 in detail: it includes a core filled by A blocks and a "coat" of B blocks "grafted" to the surface of the core (Figure 1). The size of the "coat" is of the order R_B; the radius of the core is[3]

$$R = 2.18(\chi N_A)^{1/6}R_A, \qquad R_A \ll R \ll R_B \tag{3}$$

It was also shown[3] that the free energy of an isolated micelle is

$$F_o = -TQN_A(\chi - \chi_c) \quad \text{if} \quad |\chi/\chi_c - 1| \ll 1 \tag{4}$$

where

$$Q = 4\pi R^3/3vN_A \gg 1 \tag{5}$$

is the number of polymer chains per micelle and

$$\chi_c \simeq N_A^{-1}\{\ln(1/f) + 2.06[\ln(1/f)]^{1/3}\} \tag{6}$$

Let $\mathcal{N}$ be the number of micelles in the system. If the concentration of micelles, $c = \mathcal{N}/V$, is small enough, an interaction between them can be neglected. Therefore, the free energy of the "gas" of micelles can be written as

$$\mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{N}F_o$$

where

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