Synthesis and Properties of Styrene–Butadiene–Oxyethylene Multiblock Polymers

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SYNOPSIS

Multiblock copolymers of styrene, butadiene, and ethylene oxide were synthesized by coupling together telechelic dihydroxyl polystyrene, telechelic dihydroxyl polybutadiene, and poly(ethylene glycol), using 2,4-toluene diisocyanate as coupling agent. The copolymers were purified by extractions and characterized by infrared (IR), ^1H nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), transmission electron microscopy (TEM), membrane osmometry, and dynamic viscoelastometry. The multiblock copolymers are amphiphilic, exhibiting very good emulsifying properties. They possess a good phase transfer catalytic ability in Williamson reaction, and their $LiClO_4$ complexes exhibit a conductivity above 1×10^{-4} S/cm at 35°C. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Oxyethylene-containing block copolymers exhibit special properties, such as emulsifying properties, phase transfer catalytic properties in Williamson reaction, and conductive properties of their $LiClO_4$ complexes, due to the special structure of polyoxyethylene. This is why they have stimulated considerable interests in research and development. Most of the block copolymers studied were two-component block copolymers containing polyoxyethylene as one component and polystyrene,[1-3] polybutadiene,[4,5] polyoxypropylene,[6] or polyisoprene[7,8] as the other component. We have recently reported three-component block copolymers containing polyoxyethylene, polyoxypropylene, and polystyrene blocks linked together either with diisocyanate[9] or with methylene chloride.[10]

This article deals with the synthesis, characterization, and properties of three-component multiblock copolymers consisting of polystyrene, polybutadiene, and polyoxyethylene blocks, in order to utilize good mechanical properties of polystyrene, good film-forming and resilient properties of poly-butadiene, and the special properties of polyoxyethylene and to get a kind of block copolymers showing good emulsifying properties, phase transfer catalytic properties, as well as the ionic conducting properties of their $LiClO_4$ complexes.

EXPERIMENTAL

Materials

α,ω-Dihydroxyl[1] polystyrene (THPS) was synthesized according to literature.[11] The hydroxyl functionality was determined by the isocyanate method to be 2.0 ± 0.1, and the number average molecular weight (M_n) was determined by Knauer vapor pressure osmometry (VPO) to be 7110. α,ω-Dihydroxyl polybutadiene (THPB) was supplied by Liming Institute of Chemical Technology. M_n was determined to be 4530, and the functionality was 2.0. Poly(ethylene glycol) (PEG) with different M_n was imported from Japan and dried with azeotropic distillation with toluene. 2,4-Toluene diisocyanate (TDI) was distilled under reduced nitrogen pressure before use. All the solvents, phenol, n-butyl bromide, and dibutyl tin dilaurate (DBTDL) were chemically pure, whereas KOH and $LiClO_4 \cdot 3H_2O$ were analytical reagents. Toluene was dried with a 4A molecular sieve overnight. $LiClO_4 \cdot 3H_2O$ was dehy-

drated at 160°C in vacuum oven for 24 h. Potassium phenolate was synthesized from phenol and KOH according to the literature,[12] and its purity was determined by acid titration using methyl red as an indicator.

Synthesis of the (Styrene–Butadiene–Oxyethylene) Multiblock Copolymers

Certain amounts of the prepolymers (THPS, THPB, PEG) and DBTDL were added to dried toluene. The mixture was stirred at 60°C until dissolution of all the components. A certain amount of TDI was injected to the mixture, and the reaction mixture was stirred at 60°C for 12 h. Then the residual TDI was terminated with a small amount of methanol for 0.5 h, and a small amount of antioxidant 264 was added to the reaction mixture. The solvent was evaporated and the product was vacuum dried at 40°C until constant weight. The ln η_r/c of the copolymer was determined at 0.005 g/mL concentration with an Ubbelodhe viscosimeter using tetrahydrofuran as solvent at 35°C.

Purification of the Multiblock Copolymers

The crude product was cut into small chips and extracted with cyclohexane at 40°C for 24 h three times in order to remove the homopolymers of styrene or butadiene, followed by extraction with distilled water for 24 h three times to remove the homopolymer of ethylene oxide. The residue was vacuum dried at 40°C until constant weight.

Characterization of the Multiblock Copolymers

The IR spectra of the purified multiblock copolymers were recorded on a PE-580B spectrophotometer. The composition of the copolymer was calculated according to the ^{1}H NMR spectrum, using $CDCl_3$ as solvent and tetramethyl silane as internal standard. The GPC curve of the copolymer was obtained with an SN-01-type apparatus, using THF as eluent and surface-treated silica gel as filler in the column. M_n of THPS and THPB was determined by the Knauer VPO apparatus using $CHCl_3$ as solvent and sucrose octaacetate as standard. M_n of the copolymers was determined by a modified Bruss membrane osmometer using dimethylformamide as solvent and regenerated cellulose as membrane at concentrations of 0.005, 0.004, 0.003, 0.002, and 0.001 g/mL. Dynamic mechanical spectrum of the copolymer was measured by a DDV-II-EA Viscoelastometer with a frequency of 3.5 Hz and a heating rate of 3°C/min.

Morphology of the multiblock copolymer was examined by a Hitachi H-300 transmission electron microscope (TEM) after staining with OsO_4 vapor.

Water Absorbency of the Multiblock Copolymers

The samples were first hot pressed into 0.3-mm films, which were then cut to 1 cm^2 and weighed. The samples were immersed in water at room temperature for 48 h. After removing water with filter paper from the surface, the films were weighed. The water absorbency is given by

$$H_2O(\%) = (W_a - W_b)/W_b \times 100$$

where W_b is the weight of sample before water absorption and W_a is the weight of sample after water absorption.

Emulsifying Volume

Copolymer (0.2 g) was dissolved in 30 mL toluene, and then 60 mL water was added. The mixture was shaken thoroughly for 5 min and then poured into a measuring cylinder with a cover. The system separated overnight into two layers. The emulsifying volume was taken as the total volume of the toluene plus water minus the volume of the lower water layer after separation.

Phase Transfer Catalyst Properties in Williamson Reaction

Toluene (40 mL), n-butyl bromide (2 mL), and a certain amount of copolymer were added to a bottle containing potassium phenolate (1.0 g, accurately weighed). After purging with N_2, the system was heated at 90°C for 4.5 h with stirring. After reaction, 50 mL distilled water was added and toluene was evaporated. The precipitated copolymer was filtered and washed. The unreacted potassium phenolate in solution was titrated with standard HCl, using methyl red as indicator, to find the conversion of potassium phenolate into butyl phenolate.

Crystallinity of the Multiblock Copolymers

Crystallinity of the copolymers was also measured by wide-angle X-ray diffraction (WAXD) using a Rigaku 3015 apparatus with a scanning rate of 2°/min. Crystallinity was calculated according to a published method.[13]

Table I   Effect of Polymerization Conditions on ln η_r/c of the Products

NCO/OH (Molar Ratio)	Temperature (°C)	Prepolymers Concentration (g/mL)	ln η_r/c (mL/g)
1.00	60	0.20	89.0
1.05	60	0.20	94.9
1.10	60	0.20	96.9
1.15	60	0.20	105.3
1.20	60	0.20	gel
1.30	60	0.20	gel
1.15	40	0.40	46.2
1.15	50	0.20	63.3
1.15	60	0.20	105.3
1.15	70	0.20	gel
1.15	80	0.20	gel
1.15	60	0.14	79.8
1.15	60	0.17	92.5
1.15	60	0.20	105.3
1.15	60	0.25	gel
1.15	60	0.33	gel

Charging weight ratio of THPS/THPB/PEG = 20/50/30, 0.5% DBTDL, 12 h.

Preparation of LiClO₄ Complex of the Copolymer and Measurement of Its Conductivity

To a toluene solution of the copolymer was added a certain amount of ethanolic solution of $LiClO_4$ while stirring. Then the mixture was evaporated under infrared lamp and the complex formed was vacuum dried. The complex was hot pressed in a die into pellets (about 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminium disks at 80°C, and then kept in a vacuum desiccator with fresh P_2O_5 for 2 days.

The ac conductivity was measured with a DDS-11 conductometer using copper disk electrodes operated at a frequency of 1100–1200 Hz. Before measurement, the sample was equilibrated with P_2O_5 in the conductivity cell for 1 day. The determination was repeated once more, until reproducible results were obtained.

RESULTS AND DISCUSSION

Synthesis and Purification of the Multiblock Copolymers

Table I shows the effects of NCO/OH molar ratio, reaction temperature, and concentration of the prepolymers on the ln η_r/c of the product. With increasing NCO/OH molar ratio, ln η_r/c of the crude

product increases, but gel formation occurs when the NCO/OH molar ratio exceeds 1.2. The ln η_r/c of the product increases with polymerization temperature up to 70°C. Further increase of polymerization temperature also induces gelation. As the concentration of the total prepolymers increases, ln η_r/c of the product also increases. However, gel forms when the concentration is above 0.25 g/mL. The optimum synthesis conditions are NCO/OH molar ratio at 1.15, concentration of the prepolymers at 0.2 g/mL, concentration of DBTDL at 0.5%, reaction temperature of 60°C, and reaction time of 12 h.

After the crude product was extracted with warm cyclohexane at 40°C three times to remove THPS, THPB, and their homopolymers and extracted with water three times to remove PEG and its homopolymer, the GPC curve of the residue shows a single peak (Fig. 1), which indicates that the purification procedure is efficient and no prepolymer remained in the purified copolymer.

Characterization of the Multiblock Copolymers

The IR spectrum of the purified block copolymers (Fig. 2) indicated absorption peaks at 910, 960, and 1650 cm^{-1} for C $=$ C groups of the PB blocks; peaks at 1100 cm^{-1} for C $-$ O $-$ C groups of the PEO blocks; peaks at 1450, 1524, and 1600 cm^{-1} for benzene rings of the PS blocks; a peak at 1720 cm^{-1} for the C $=$ O group of urethane; and a peak at 3500 cm^{-1} for the NH group of urethane.

^{1}H NMR spectrum (Fig. 3) showed the presence of CH$_3$ and CH$_2$ protons at 1.4–2.1 ppm, alkyl protons next to oxygen at 3.6 ppm, protons next to double bonds at 5.1–5.4 ppm, and protons of benzene at 6.9 and 7.1 ppm. These data demonstrate that the purified product are urethane-linked block copolymers of oxyethylene, styrene, and butadiene. From the height of the integrals in the NMR spectrum, the proportions of these blocks were calculated. It is shown in Table II that the composition
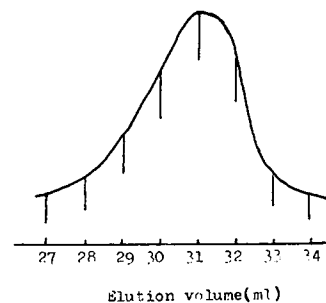

Figure 1   GPC curve of the purified multiblock copolymer.
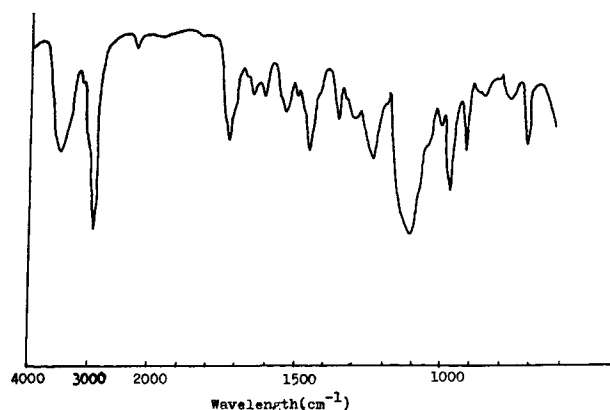
Figure 2   IR spectrum of the purified multiblock copolymer.

of the purified copolymer is somewhat different from the charging weight ratio of the prepolymers. Table I also shows the structure parameters of the block copolymers, which were calculated from the molecular weight of the copolymer, and the prepolymers determined by membrane osmometry and VPO, respectively. Thus it can be deduced that the block copolymers are really multiblock copolymers.

Figure 4 illustrates the dynamic mechanical spectrum of the multiblock copolymer. There appear four peaks in the tan δ vs. T plot—namely, $-127°C$, $-74°C$, $-52°C$, and about $85°C$, which correspond to the relaxation temperature of the copolymer due to the crank motion of the PB segments and the glass transition temperatures of PB, PEO, and PS blocks, respectively.

Figure 5 is the TEM microphotograph of the purified copolymer stained with OsO_4 vapor. Many dark, short rods of PB domains were distributed in the bright ground, which indicates the microphase separation in the copolymer.

Water Absorbency and Emulsifying Properties of the Multiblock Copolymers

Table III indicates that the water absorbency of the copolymer increases with its PEO content, since the PEO blocks are hydrophilic whereas the other two kinds of blocks are hydrophobic.

The emulsifying properties of amphiphilic copolymers can be expressed by their emulsifying volumes. The emulsifying volume of the multiblock copolymers reaches a maximum value at a PEO content of 46.5%. This result may be attributed to the fact that emulsifying properties are related to both the hydrophilic part and the hydrophobic part of the copolymer. This kind of multiblock copolymer

show much higher emulsifying volume than (styrene–oxypropylene–oxyethylene) multiblock copolymers.[9,10]

The molecular weight of the PEO blocks also shows an obvious effect on the water absorbency and emulsifying volume, as shown in Table III. At about $56 \pm 2\%$ PEO content, with increasing molecular weight of the PEG used in synthesis, the water absorbency increases, whereas the emulsifying volume decreases. It seems that the longer the PEO blocks, the more water they can combine via hydrogen bonds. However, the lower the molecular weight of PEO blocks, the larger the number of emulsifying sites formed, resulting in larger emulsifying volume. The multiblock copolymer containing 46% PEO blocks with molecular weight of 1000 is a very good nonionic emulsifier.

Phase Transfer Catalyst Properties of the Multiblock Copolymers

Phase transfer catalyst properties of the copolymer in a Williamson reaction can be represented by the increased conversion of potassium phenolate. It can be seen from Figure 6 that conversion of potassium phenolate increases with the amount of copolymer added in the Williamson reaction up to 20 wt % of copolymer/potassium phenolate. This result indicates that the multiblock copolymer can complex the potassium ions of the phenolate and transfer them from solid to organic solution, thus enhancing the reaction between potassium phenolate and n-butyl bromide. Figure 6 also indicates that the conversion of potassium phenolate increases with reaction temperature and reaches more than 95% at 120°C for 4.5 h, when 10 wt % of the block copolymer based on potassium phenolate is used as phase transfer catalyst. Figure 7 shows the effect of PEO content of the copolymer on the conversion of potassium phenolate. The copolymer
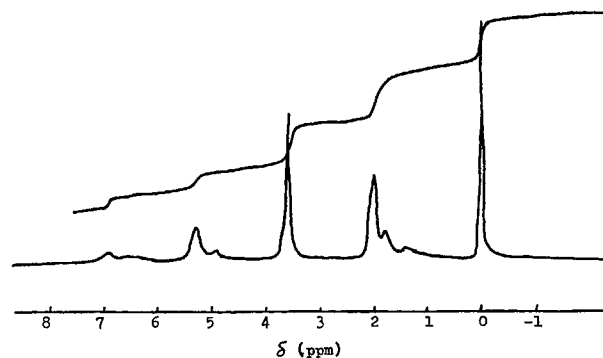

Figure 3 ^{1}H-NMR spectrum of the purified multiblock copolymer.

Table II   Structural Parameters of the Multiblock Copolymers

THPS/THPB/PEG[a] (Charging Wt)	$M_{nCop}{}^{c} \times 10^{-5}$	Wt %[b]			No. of Blocks		
		PS	PB	PEO	PS	PB	PEG
10/10/80	2.72	5.9	8.4	85.7	2.3	5.0	58.3
15/15/70	2.80	9.4	14.8	75.8	3.7	9.1	53.1
20/20/60	2.21	12.8	17.8	66.4	4.0	8.7	36.7
20/40/40	1.33	13.7	39.4	46.9	2.6	11.6	15.6
30/50/20	1.97	20.6	51.6	27.8	5.7	22.4	13.7

[a] $M_{nTHPS} = 7110$, $M_{nTHPB} = 4530$, $M_{nPEG} = 4000$.
[b] Composition calculated from ^{1}H-NMR data.
[c] Number average molecular weight of the copolymer.

with about 75% PEO blocks seems to exhibit optimum phase transfer catalyst behavior, giving high conversion of potassium phenolate. This is probably because the phase transfer catalyst needs not only the ability of PEO blocks to complex with K^+ ions, but also the ability of hydrophobic PS and PB blocks to carry the complex into organic solution. The molecular weight of the PEO blocks also has an influence on the conversion of potassium phenolate, as shown in Figure 7. With increasing molecular weight of the PEO blocks, the catalytic efficiency of the copolymer in the Williamson reaction is also enhanced. This can probably be explained by the fact that the higher the molecular

weight of the PEO blocks, the easier it is for the PEO segments to form a spiral structure which can complex with the K^+ ions, resulting in high conversion of potassium phenolate to produce n-butyl phenolate.

Conductivity of the LiClO₄ Complexes of the Multiblock Copolymers

Conductivity of the complex shows a maximum value with change of EO/Li molar ratio, as illustrated in Figure 8. The maximum conductivity occurs at an EO/Li molar ratio of about 20. This may be attributed to the fact that when salt concentration is lower, there exist empty oxygen sites of PEO segments available for cation transport, and thus Li^+ can transport more freely through the amorphous phase of PEO. With increasing Li^+ concentration, the ionic carriers increase and at the same time the incorporation of LiClO₄ inhibits the crystallization of PEO, resulting in increased conductivity. However, if the salt concentration was too high, although the ionic carriers increased greatly, the interaction between Li^+ and PEO segments was significantly
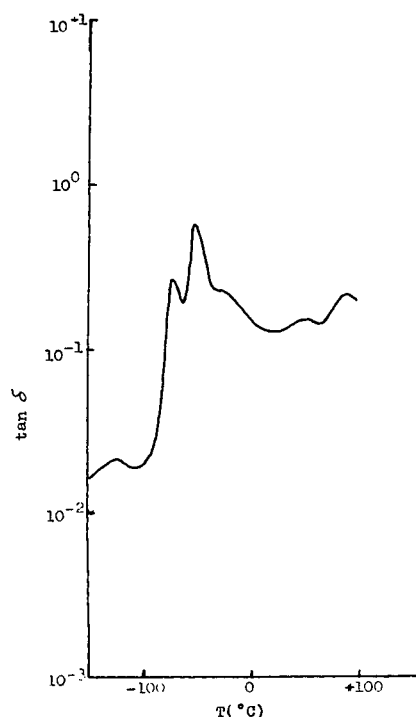

Figure 4   Dynamic mechanical spectrum of the purified multiblock copolymer.
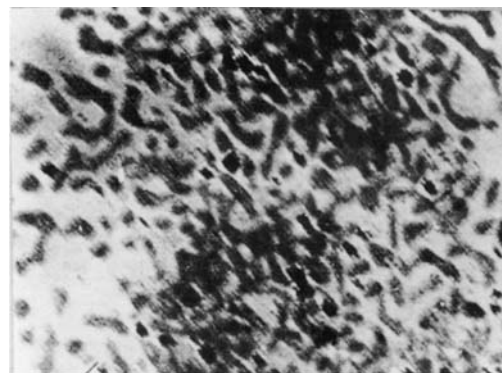

Figure 5   TEM microphotograph of the purified multiblock copolymer ($5 \times 10^4 \times$).
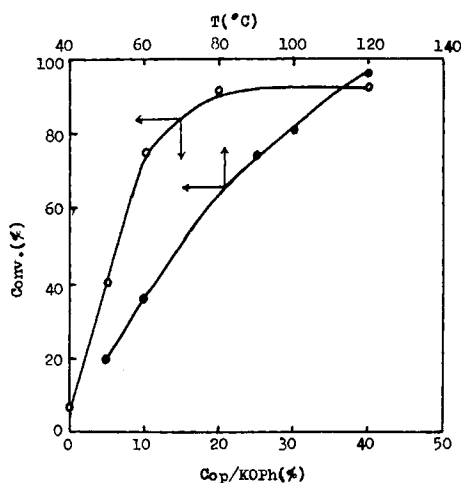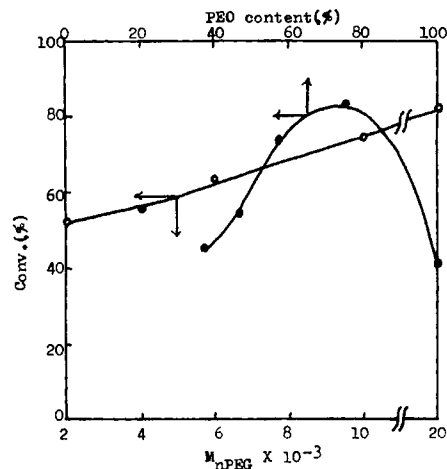
Table III Effects of Charging Weight Ratio and Molecular Weight of PEG used in Synthesis on Water Absorbency and Emulsifying Volume (EV)

THPS/THPB/PEG (Wt Ratio)	PEO Content (%)	M_{nPEG}	H_2O (%)	EV (mL)
10/10/80	85.7	4000	—	35.0
15/15/70	75.5	4000	286	—
20/20/60	66.4	4000	250	47.5
25/25/50	56.3	4000	196	65.5
30/30/40	46.5	4000	155	73.0
20/50/30	37.1	4000	88	70.0
30/50/20	27.6	4000	17	55.6
25/25/50	58.8	1000	105	83.0
25/25/50	57.2	2000	152	76.2
25/25/50	56.3	4000	191	65.5
25/25/50	55.6	6000	267	54.2
25/25/50	54.7	10000	291	53.0
25/25/50	53.3	20000	357	50.0

$M_{nTHPS} = 7110$, $M_{nTHPB} = 4530$.

enhanced. This makes the mobility of ions decrease and thus lowers the conductivity.
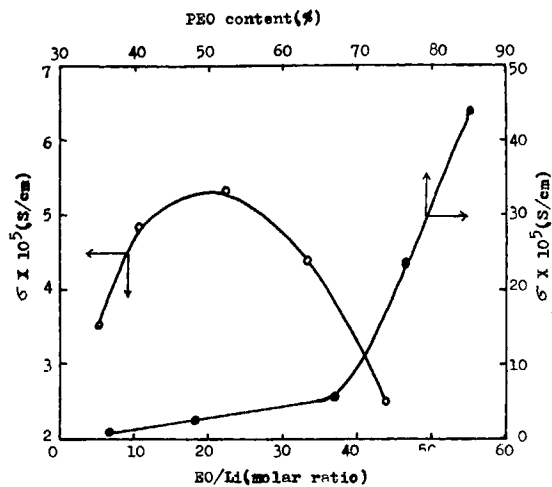
The PEO content of the multiblock copolymer affects greatly on the conductivity of the copolymers, as shown in Figure 8. The conductivity increases slowly with PEO content up to 66% and increases quickly with PEO content above 66%. This is probably attributed to the change of PEO phase from dispersed phases to continuous phase, as the PEO content is above 66%. At nearly the same PEO content (66%), the conductivity of the copolymers di-

Figure 7 Effects of PEO content (1) and molecular weight of PEG (2) used in synthesis on the conversion of potassium phenolate: (1) $M_{nPEG} = 4000$; (2) charging weight ratio of PS/PB/PEG = 25/25/50.

minishes with increasing molecular weight of PEG used in synthesis (Fig. 9) due to the increased crystallinity, which reduces the room temperature conductivity. Figure 9 also indicates the decrease of crystallinity determined by WAXD with decreasing molecular weight of PEG. Almost no crystalline part exists in the copolymer containing PEO blocks with molecular weight of 2,000.

CONCLUSION

Multiblock copolymers of ethylene oxide, styrene, and butadiene can be obtained with molecular

Figure 6 Effects of amount of the copolymer (1) and reaction temperature (2) on the conversion of potassium phenolate: (1) PEO content = 57%, 90°C; (2) Cop/KOPh = 0.1.

Figure 8 Effects of EO/Li molar ratio (1) and PEO content (2) on the conductivity of the LiClO$_4$ complex at 35°C: (1) PEO = 66%; (2) EO/Li = 22.
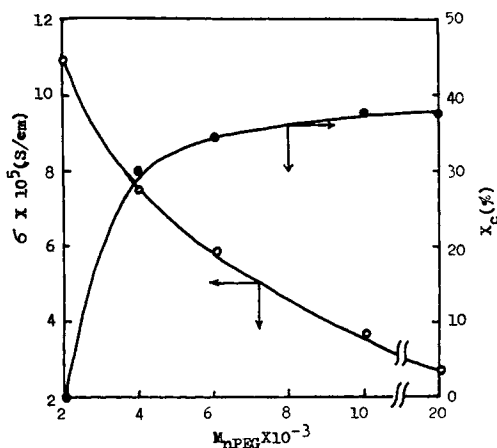
Figure 9   Effects of molecular weight of PEG used in synthesis on the crystallinity (X_c) of the copolymers and conductivity of the $LiClO_4$ complexes: charging weight ratio of PS/PB/PEG = 20/20/60.

weight of 10^5 by coupling THPS, THPB, and PEG together with TDI. The copolymers are amphiphilic and exhibit very good emulsifying properties. The emulsifying ability of the copolymer is optimum at about 47% PEO content. The copolymers show phase transfer catalytic activity in Williamson reaction. The catalytic activity of the copolymer is optimum at about 76% PEO content. The $LiClO_4$ complex of the multiblock copolymer containing 76% PEO can show an ionic conductivity of 2.3 $\times 10^{-4}$ S/cm at 35°C.

REFERENCES

1. D. H. Richards and M. Szwarc, *Trans. Faraday Soc.,* **55,** 1644 (1959).
2. H. Q. Xie and P. G. Zhou, *Polym. Eng. Sci.,* **25,** 32 (1985).
3. Y. Shimura and W. S. Lin, *J. Polym. Sci. A-1,* **8,** 2171 (1970).
4. M. Gerrais and B. Gallot, *Macromol. Chem.,* **178,** 1577 (1977).
5. R. Rahman and Y. Avny, *J. Macromol. Sci.-Chem.,* **A13,** 953 (1979).
6. General Motors Corp., Canadian patent, 939,868 (1970).
7. E. Hirate, *Polym. Prepr.,* **15,** 177 (1974).
8. J. P. Kennedy and Y. Hongu, *Polym. Bull.,* **13,** 115 (1985).
9. H. Q. Xie, X. Y. Chen, and J. S. Guo, *Angew. Makromol. Chem.,* **200,** 49 (1992).
10. H. Q. Xie, Z. S. Liu, and J. S. Guo, *Polymer,* **35,** 4914 (1994).
11. H. Q. Xie and X. Chen, *Polymer J.,* **20,** 153 (1988).
12. N. Kornblum and A. P. Luric, *J. Amer. Chem. Soc.,* **81,** 2710 (1959).
13. H. Q. Xie and P. G. Zhou, *Adv. Chem. Ser.,* **211,** 139 (1986).