Synthesis and properties of oxymethylene-linked oxyethylene–oxypropylene–styrene multiblock copolymers

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Oxymethylene-linked multiblock copolymers with two or three components (oxyethylene–oxypropylene–styrene) (EO–PO–St) were synthesized by coupling polyethylene glycol with polypropylene glycol and/or telechelic dihydroxyl polystyrene, using dichloromethane as coupling agent and KOH as catalyst. The copolymers were purified, characterized by i.r., ^{1}H n.m.r., g.p.c. and membrane osmometry, and were shown to be multiblock copolymers. D.s.c. and wide angle X-ray diffraction indicated the crystallinity of the copolymer, which depended on the molecular weight and content of polyoxyethylene (PEO) blocks. The multiblock copolymers exhibit good emulsifying properties and good phase transfer catalyst properties in Williamson reactions. The tensile strength of the copolymer increases with polystyrene and PEO content as well as with the molecular weight of PEO blocks. The $LiClO_4$ complex of the multiblock copolymer (EO/PO = 95/5) shows very good room temperature conductivity, which reaches 5.8×10^{-4} S cm^{-1} at 25°C and 1.2×10^{-3} S cm^{-1} at 30°C.

(Keywords: block copolymer; amphiphilic copolymer; solid polymer electrolyte)

INTRODUCTION

Since Wright[1] discovered that ion transport took place in the complexes between polyoxyethylene (PEO) and various alkali metal salts, and Armand[2] pointed out potential applications of the PEO complexes as solid electrolytes in high energy density batteries, widespread interest has been aroused in the development of these complexes. The main disadvantage of using high molecular weight PEO is its high crystallinity, which reduces the ionic conductivity at room temperature. Hence recent research has focused on the use of PEO-containing block copolymers[3,4], graft copolymers[5,6] and crosslinked polymers[7], in order to raise both the room temperature conductivity and the mechanical strength.

Shimura and Lin[8] synthesized oxyethylene–styrene (EO–St) multiblock copolymers by coupling telechelic dihydroxyl polystyrene with polyethylene glycol (PEG) using 4,4′-diphenylmethane diisocyanate as coupling agent, and studied their mechanical properties. We[9] prepared oxypropylene–styrene (PO–St) multiblock copolymers through coupling telechelic dihydroxyl polystyrene with polypropylene glycol (PPG) using 2,4-toluene diisocyanate (TDI) as coupling agent. Booth and co-workers[10] synthesized oxymethylene-linked PEO by reaction of dichloromethane with PEG (molecular weight 400) in the presence of KOH, and indicated that the conductivity of its complex with $LiCF_3SO_3$ reached 4×10^{-5} S cm^{-1} at 20°C. Two years later the same workers[11] used dichloromethane, KOH, PEG (molecular weight 400) and monohydroxyl-terminated polystyrene to prepare oxymethylene-linked EO–St multiblock copolymer, and showed that its complex with $LiCF_3SO_3$ had a conductivity lower than 1×10^{-5} S cm^{-1}. Recently, we reported the synthesis and properties of urethane-linked EO–PO, EO–St and EO–PO–St multiblock copolymers[12] and noted that the conductivity of their $LiClO_4$ complex approached 1×10^{-4} S cm^{-1} at 25°C.

This paper deals with the synthesis, characterization and properties of oxymethylene-linked EO–PO, EO–St and EO–PO–St multiblock copolymers through reaction of dichloromethane, PEG with different molecular weights, PPG and telechelic dihydroxyl polystyrene, in order to obtain copolymers that exhibit not only good emulsifying properties and phase transfer catalyst properties but also high room temperature conductivity, when complexed with $LiClO_4$. The aim in using the telechelic dihydroxyl polystyrene instead of monohydroxyl-terminated polystyrene is to increase the number of polystyrene (PSt) blocks and hence the chain length of the multiblock copolymer through coupling with dichloromethane.

EXPERIMENTAL

Materials

All the reagents, except KOH and $LiClO_4$ which were analytical reagents, were chemically pure. TDI was

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purified by distillation under reduced pressure. PEG with different molecular weights (Japan) and PPG with molecular weight of 1000 (Nanking Plastics Manufacturer, P.R. China) were dried by azeotropic distillation with toluene. Dichloromethane was dried overnight with a 4 Å molecular sieve.

Telechelic dihydroxyl polystyrene (THPS) with different molecular weights was synthesized by anionic polymerization of purified St using lithium α-methylnaphthalene as a dianionic initiator, followed by termination with purified ethylene oxide and neutralization with acetic acid[9]. Functionality of the THPS, PEG and PPG was determined by the isocyanate method to be 2.00±0.10.

Synthesis and purification of the multiblock copolymers

To a mixture of 10 g KOH powder and 100 ml CH_2Cl_2 was added slowly a certain amount of liquid PEG or its CH_2Cl_2 solution and CH_2Cl_2 solution of THPS during stirring. Additional amounts (5 g) of KOH were added at 0.5 h, 1.5 h and 3.0 h from the beginning of the reaction. PPG was added at 1.5 h. The reaction was carried out at room temperature during stirring for 16 h. Then the reaction mixture was poured into an evaporating dish to vaporize most of the unreacted CH_2Cl_2. The residue was dissolved in toluene and the solution decanted from the salt sediment. The crude product was precipitated out by adding petroleum ether (b.p. 90–120°C) to the solution and was dried under i.r. lamp.

The crude product was purified by extraction with hot cyclohexane three times, so as to remove the unreacted PPG, THPS, their homopolymers and copolymers. The residue after drying was extracted with distilled water three times in order to remove the unreacted PEG and its homopolymers. The purified product was vacuum dried and weighed. If the charging amount of PEG during synthesis was higher than 80 wt%, the unreacted PEG and its homopolymer were removed first by dissolving the crude product in CH_2Cl_2, followed by extracting the solution with distilled water three times and evaporating CH_2Cl_2 off. Then the residue was extracted with hot cyclohexane three times.

Characterization of the purified multiblock copolymers

The number average molecular weights of THPS and the multiblock copolymers were determined by Knauer VPO apparatus using $CHCl_3$ as solvent and Bruss membrane osmometer using dimethylformamide as solvent, respectively. The i.r. spectra of the multiblock copolymers were recorded on an IR-408 spectrophotometer using KBr pellets. The composition of the multiblock copolymer was calculated according to the ^1H n.m.r. spectrum taken with a Bruker AC-80 NMR spectrometer, using $CDCl_3$ as solvent and tetramethylsilane as internal standard. G.p.c. curves of the copolymers were obtained with a LC-4A type apparatus using a column filled with polystyrene gel and tetrahydrofuran as eluent.

Crystallinity of the multiblock copolymers

Crystallinity was determined from d.s.c. curves using a PE DSC-4 differential scanning calorimeter combined with a computer, at a heating rate of 10°C min^{-1} and a sample weight of about 10 mg. The crystallinity (X_c) was then calculated from the heat of fusion ΔH_f: $X_c = \Delta H_f / \Delta H_{100}$, where ΔH_{100} represents the heat of fusion of crystalline PEO and is equal to 210 J g^{-1} (ref. 13). The crystallinity of the copolymers was also measured by wide angle X-ray diffraction (WAXD) using Rigaku 3015 apparatus with a scanning rate of 2° min^{-1}. Crystallinity was calculated according to a published method[14].

Emulsifying volume

Copolymer (0.2 g) was dissolved in 30 ml toluene and then 70 ml water was added. The mixture was shaken thoroughly for 5 min and then poured into a 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 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.

Preparation of $LiClO_4$ complex of the copolymer and measurement of its conductivity

Copolymer (0.6 g) was dissolved in 15 ml benzene to which a certain amount of ethanolic solution of $LiClO_4$ (so as to make EO/Li = 20/1) was added during stirring. The mixture was evaporated and the complex formed was vacuum dried, followed by drying over P_2O_5 in a desiccator for 2 days.

The complex was hot-pressed in a die into pellets (about 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminium discs at 80°C and then kept in a vacuum desiccator with fresh P_2O_5 for 2 days.

A.c. conductivity was measured at different temperatures with a DDS-11 conductometer using copper disc electrodes operated at a frequency of 1100–1200 Hz. Before measurement, the sample was equilibrated with P_2O_5 in the conductivity cell for 2 days. The determination was repeated once more. Reproducible results were usually obtained.

Mechanical properties of the copolymers

The specimens were prepared from the copolymer cast from CH_2Cl_2 solution. The tensile strength, ultimate elongation and permanent set were measured on an XL-2500 tensile tester at an extension rate of 300 mm min^{-1}. The permanent set was measured as per cent elongation when the specimen was broken and reunited after 3 min.

RESULTS AND DISCUSSION

Synthesis and purification of the multiblock copolymers

Optimum synthesis conditions for obtaining a purified copolymer yield of over 65% and copolymer molecular weight of 5×10^4 to 11×10^4 consist of: (1) addition of KOH powder at different times of the reaction, namely 0.5 h, 1.5 h and 3.0 h; (2) reaction temperature of 20–25°C; (3) addition of PEG and THPS at the beginning of reaction and addition of PPG at 1.5 h from the beginning of reaction.

The g.p.c. curve of the purified copolymer (*Figure 1*) shows that the purification procedure is efficient and only a very small amount of PEG, PPG ot THPS remained (elution volume > 16 ml) in the purified copolymer. The molecular weights of EO–PO, EO–St and EO–PO–St multiblock copolymers obtained are 5×10^4–7.5×10^4, 8.5×10^4–11×10^4 and 6.0×10^4–8.5×10^4, respectively, as determined by membrane osmometry.

Characterization of the purified copolymers

I.r. spectra of the purified block copolymers indicated absorption peaks at 2850–2950 cm^{-1} for CH_2 and CH groups, peaks at 1150–1060 cm^{-1} for C–O–C groups, peaks at 700, 740, 1450, 1500 and 1600 cm^{-1} for the benzene ring of PSt blocks and a peak at 1380 cm^{-1} for the methyl groups of PPG blocks. ^{1}H n.m.r. spectra showed the presence of alkyl protons next to oxygen at 3.6 and 3.8 ppm, alkyl protons between two oxygen atoms at 4.8 ppm, protons of benzene at 6.8 and 7.2 ppm and methyl protons at 1.1–1.2 ppm. These data demonstrate that the purified products are oxymethylene-linked block copolymers of EO, PO and/or St. From the height of the integrals, the proportions of these blocks were calculated and it is shown in *Table 1* that the composition of the purified copolymers obtained is close to the charging weight ratio of prepolymers. *Table 1* also shows the structure parameters of the block copolymers, which were calculated from the molecular weights of the copolymers and prepolymers determined by membrane osmometry and v.p.o., respectively. Thus it can be deduced that the block copolymers are really multiblock copolymers. When the molecular weight of THPS was lower, the number of PSt blocks became larger.

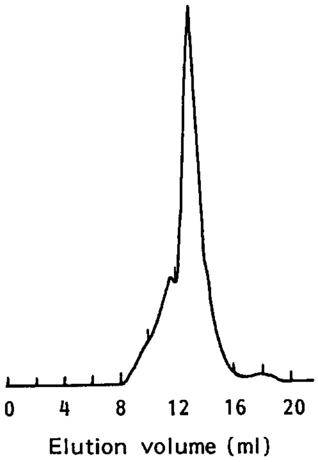

Figure 1 G.p.c. curve of the oxymethylene-linked multiblock copolymer (charging wt ratio PEG/PPG/THPS = 65/10/25, $M_{n,PEG} = 600$, $M_{n,PPG} = 1000$, $M_{n,THPS} = 6860$)

Table 1 Structural parameters of multiblock copolymers

Charging wt ratio PEG/PPG/THPS	$M_{n,copol}$ $\times 10^{-4}$	$M_{n,block}$			Wt% (n.m.r.)			No. of blocks		
		PEG	PPG	THPS	PEO	PPO	PSt	PEO	PPO	PSt
50/50/0	4.9	1000	1000	–	46.6	53.4	–	22.8	26.2	–
70/30/0	5.1	1000	1000	–	68.4	31.6	–	34.9	16.1	–
70/0/30	9.6	400	–	2220	68.5	–	31.5	164	–	13.7
75/5/20	7.5	600	1000	6860	80.3	4.5	15.2	100	3.4	1.7
65/10/25	7.8	600	1000	6860	68.4	12.8	18.7	89.1	10.1	2.1

Crystallinity of the multiblock copolymers

Table 2 indicates that the crystallinity measured by d.s.c. increases with increasing molecular weight of PEG and decreases markedly when the copolymer is complexed with $LiClO_4$. The crystallinity measured by d.s.c. is near to that measured by WAXD. The lower the PEO content in the block copolymer, the lower is the crystallinity. At the same content of PEO, PPO blocks seems to lower the crystallinity more severely than the PSt blocks, probably because there is greater compatibility between PPO and PEO than between PEO and PSt.

Mechanical properties of the multiblock copolymers

As shown in *Table 3*, the tensile strength of EO–PO multiblock copolymer decreases with increasing PPO

Table 2 Crystallinity of the multiblock copolymers

Charging wt ratio PEG/PPG/THPS	M_n			D.s.c.		
	PEG	PPG	THPS	ΔH_f (J g^{-1})	X_c(%)	WAXD, X_c (%)
100/0/0	600	–	–	69.5	33.1	30.2
100/0/0	1000	–	–	82.6	39.3	40.3
100/0/0	2000	–	–	100.4	47.8	51.3
100/0/0[a]	1000	–	–	27.7	13.2	11.4
85/0/15	1000	–	9980	74.3	35.4	38.1
85/5/10	1000	1000	9980	66.9	31.9	–
75/5/20	600	1000	6860	–	–	12.8
65/10/25	600	1000	6860	–	–	0

[a] Complex with $LiClO_4$: EO/Li = 20/1

Table 3 Mechanical properties[a] of the multiblock copolymers at 22°C

Charging wt ratio PEG/PPG/THPS[b]	$M_{n,PEG}$	$M_{n,copol}$ $\times 10^{-4}$	σ (MPa)	ε (%)	δ (%)
100/0/0	600	11.3	92	640	460
95/5/0	600	7.5	85	40	0
90/10/0	600	5.0	57	30	0
85/15/0	600	4.9	50	30	0
75/25/0	600	4.9	47	30	0
95/0/5	600	9.7	102	50	10
90/0/10	600	11.0	111	60	20
85/0/15	600	8.2	106	80	20
75/0/25	600	10.1	88	130	40
90/5/5	600	6.1	109	30	5
85/5/10	600	6.8	105	30	10
80/5/15	600	6.2	93	70	20
75/5/20	600	7.5	84	180	80
80/10/10	600	8.5	74	40	0
65/10/25	600	7.8	51	50	0

[a] σ, ε and δ are tensile strength, ultimate elongation and permanent set, respectively

[b] $M_{n,PPO} = 1000$, $M_{n,THPS} = 6860$

Table 4 Emulsifying volume of the multiblock copolymers

Charging wt ratio PEG/PPG/THPS[a]	Amount of copolymer (g)	Emulsifying volume (ml)
95/5/0	0.20	36
90/10/0	0.20	38
85/15/0	0.20	40
75/25/0	0.20	43
95/0/5	0.20	39
90/0/10	0.20	41
85/0/15	0.20	43
75/0/25	0.20	46
90/5/5	0.20	41
80/10/10	0.20	44
75/5/25	0.20	46
65/10/25	0.10	39
65/10/25	0.20	43
65/10/25	0.30	44
65/10/25	0.50	46
55/20/25	0.20	41
45/30/25	0.20	39

[a] $M_{n,PEO}=600$, $M_{n,PPG}=1000$, $M_{n,THPS}=6860$

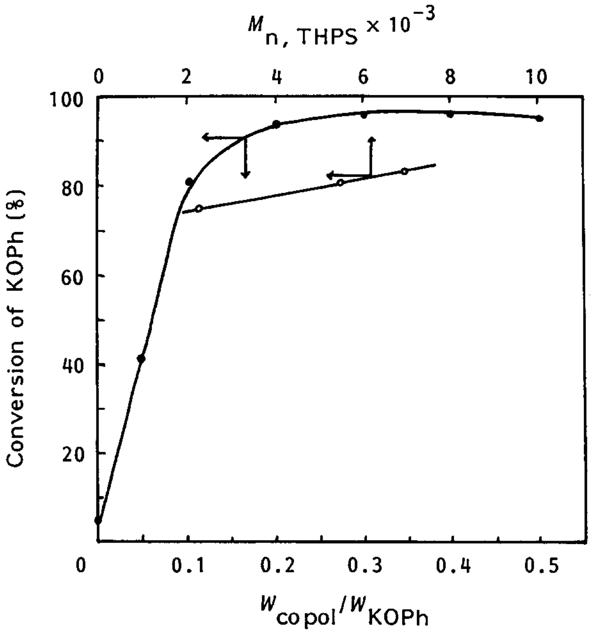

Figure 2 Effect of amount of the multiblock copolymers and molecular weight of THPS used in synthesis on the conversion of potassium phenolate. ●, PEG/PPG/THPS = 65/10/25, $M_{n,PEG}=600$, $M_{n,PPG}=1000$, $M_{n,THPS}=6860$; ○, PEG/THPS = 90/10, $M_{n,PEG}=600$, $W_{copol}/W_{KOPh}=0.1$

content, whereas the ultimate elongation and permanent set drop severely. This result may be attributed to the fact that the crystallinity of PEO, which decreases with increasing PPO content, plays an important role in the mechanical properties. PEO blocks can form crystalline domains at room temperature, whereas PPO blocks cannot. The resilience of the copolymer is poor and does not increase with PPO content, probably because of the low molecular weight of PPG (only 1000) used. The tensile strength of the EO–St multiblock copolymers exhibits a maximum value at 10–15% PSt content. This implies that both PSt and PEO blocks contribute to the strength of copolymer. However, if the PSt block content exceeds 15%, the crystallinity of PEO is greatly reduced, resulting in lowering of the strength. In the series of EO–PO–St multiblock copolymers with 5% PPO content, maximum tensile strength occurs at 5–10% PSt content. Comparison of different types of the multiblock copolymers indicates the order of decreasing tensile strength and molecular weight as: EO–St > EO–PO–St > EO–PO.

Emulsifying properties of the multiblock copolymers

The emulsifying properties of amphiphilic copolymer can be expressed by their emulsifying volumes. The emulsifying volume of various multiblock copolymers increases with the amount of multiblock copolymer used and changes with the hydrophobic PSt or PPO content, as shown in *Table 4*. A maximum value is reached at a PEO content of about 75%. This result may be attributed to the composition of the water/toluene (70/30 by volume) system and the formation of oil in water emulsion, which requires more hydrophilic content than hydrophobic content. The emulsion formed is quite stable and does not separate into layers during storage for 1 month.

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 2* 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. The phase transfer catalytic effect increases somewhat with the molecular weight of the PSt blocks, probably owing to the increased solubility of the copolymer containing longer PSt blocks in toluene, resulting in higher conversion of potassium phenolate.

Table 5 shows the effect of different proportions of three kinds of blocks on the conversion of potassium phenolate. The copolymer with about 75% PEO blocks seems to

Table 5 Effect of different composition of multiblock copolymers on conversion of potassium phenolate (KOPh) in Williamson reaction

Charging wt ratio PEG/PPG/THPS[a]	Copolymer/KOPh (wt ratio)	Conversion (%)
–	0	5
100/0/0	0.10	60
95/5/5	0.10	71
80/10/10	0.10	80
75/5/20	0.10	86
65/10/25	0.10	81
65/10/25	0.30	96
65/10/25[b]	0.30	94
55/20/25	0.10	76
45/30/25	0.10	61
95/0/5	0.10	74
90/0/10	0.10	80
85/0/15	0.10	84
75/0/25	0.10	87
95/5/0	0.10	65
90/10/0	0.10	71
85/15/0	0.10	74
75/25/0	0.10	78

[a] $M_{n,PEG}=600$, $M_{n,PPG}=1000$, $M_{n,THPS}=6860$
[b] The copolymer was recovered and used again

Table 6 Effect of composition of the multiblock copolymers on the conductivity of their $LiClO_4$ complexes[a] at 25°C

Charging wt ratio PEG/PPG/THPS	$M_{n,PEG}$	$M_{n,PPG}$	$M_{n,THPS}$	$M_{nc} \times 10^{-4}$	Conductivity $\times 10^4$ (S cm^{-1})
100/0/0	600	–	–	11.3	4.80
100/0/0	1000	–	–	8.4	4.30
100/0/0	2000	–	–	10.5	0.71
90/0/10	400	–	2220	–	2.01
80/0/20	400	–	2220	–	1.40
70/0/30	400	–	2220	9.6	0.34
95/5/5	400	1000	2220	–	3.86
80/5/15	400	1000	2220	–	1.46
95/5/0	600	1000	–	7.5	5.80
90/10/0	600	1000	–	5.0	2.20
85/15/0	600	1000	–	4.9	1.81
75/25/0	600	1000	–	4.9	0.64
95/0/5	600	–	6860	9.7	3.30
90/0/10	600	–	6860	11.0	2.05
85/0/15	600	–	6860	8.2	1.80
75/0/25	600	–	6860	10.1	0.68
90/5/5	600	1000	6860	6.1	4.20
85/5/10	600	1000	6860	6.8	2.65
80/5/15	600	1000	6860	6.2	1.55
80/10/10	600	1000	6860	8.5	2.81
75/5/20	600	1000	6860	7.5	1.16
65/10/25	600	1000	6860	7.8	0.34
45/30/25	600	1000	6850	–	0.058
85/0/15	1000	1000	9980	–	1.30
85/5/10	1000	1000	9980	–	2.85
80/5/15	1000	1000	9980	–	1.85

[a] EO/Li = 20/1

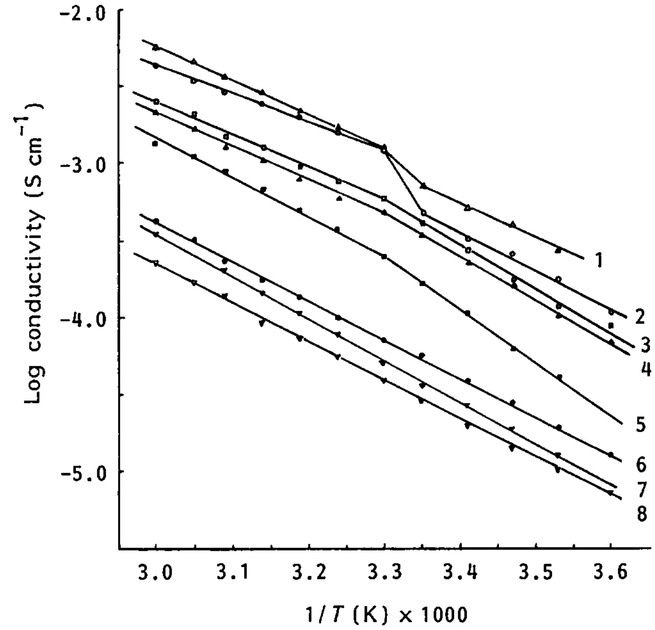

Figure 3 Plot of log conductivity *versus* reciprocal temperature. Multiblock copolymers from PEG/PPG/THPS: 1, 95/5/0; 2, 100/0/0; 3, 90/5/5; 4, 95/0/5; 5, 80/5/15; 6, 75/25/0; 7, 65/10/25; $M_{n,PEG} = 600$, $M_{n,PPG} = 1000$, $M_{n,THPS} = 6860$; 8, PEG/THPS = 70/30, $M_{n,PEG} = 400$, $M_{n,THPS} = 2220$

exhibit optimum phase transfer catalyst behaviour, 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 blocks to carry the complex into organic solution. At the same PEO content, the catalytic activity of different copolymers decreases in the following order: EO–St > EO–PO–St > EO–PO. This result may be explained by the order of decreasing solubility in toluene: PSt > PPO > PEO.

This kind of phase transfer catalyst can be recovered and used again. Almost no catalytic activity was lost when the recovered block copolymer was used again in the Williamson reaction, as shown in *Table 5*.

Conductivity of the $LiClO_4$ complexes of the multiblock copolymers

Since most research concerning the $LiClO_4$ complexes of PEO has demonstrated that for conduction purposes the optimum molar ratio of EO/Li is about 20/1, all the $LiClO_4$ complexes of the multiblock copolymers were made at this molar ratio. *Table 6* indicates that the conductivity of oxymethylene-linked PEO diminishes with increasing molecular weight of PEO blocks, owing to the increased crystallinity which reduces the room temperature conductivity.

As the PEO content of the block copolymer decreases, the conductivity of the copolymer is lowered, especially below 65 wt% PEO, at which level the copolymer cannot form the continuous phase that is necessary for ionic conduction. The EO–PO multiblock copolymer with 5% PPO content exhibits the highest conductivity, even higher than the oxymethylene-linked PEO. However, with further increase of PPO content, the conductivity diminishes. This phenomenon can be explained by a balance between the enhancement of conductivity due to lowering of crystallinity by PPO blocks and the lowering of conductivity due to decrease of PEO blocks. In the case of EO–PO–St multiblock copolymers, high conductivity occurs at PEO/PPO/PSt = 90/5/5.

In a comparison of different types of multiblock copolymers, conductivity decreases in the following order: EO–PO > EO–PO–St > EO–St.

Figure 3 illustrates the Arrhenius plots of conductivity *versus* temperature. Plots 1 and 2 are composed of two straight lines with a discontinuity, plots 3, 4 and 5 consist of two straight lines, whereas plots 6, 7 and 8 are a single straight line. A plot of two straight lines implies the existence of crystalline PEO in the $LiClO_4$ complex at lower temperature.

CONCLUSION

Three types of purified oxymethylene-linked PEO-containing multiblock copolymers can be obtained with molecular weight between 5×10^4 and 11×10^4, and a yield higher than 65%. The copolymers show some crystallinity, which increases with molecular weight and content of PEO blocks. Incorporation of PPO or PSt blocks can lower crystallinity, but the effect of PPO is more evident than that of PSt. The copolymers are amphiphilic and so exhibit good emulsifying properties. The emulsifying ability of the copolymer is optimum at 75% PEO content. The copolymers show phase transfer catalytic activity in Williamson reactions. The catalytic activity of the copolymer is optimum at 75% PEO content and is almost unchanged when the recovered copolymer is used again. The tensile strength increases with the molecular weight and content of PEO blocks as well as the PSt blocks. The $LiClO_4$ complex of the EO–PO multiblock copolymer from a charging weight ratio of PEG/PPG = 95/5 during synthesis shows very good room temperature conductivity, reaching $5.8 \times 10^{-4}\,S\,cm^{-1}$ at 25°C and $1.2 \times 10^{-3}\,S\,cm^{-1}$ at 30°C.

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