

Synthesis, Characterization, and Properties of Two-Component Amphiphilic Polyoxyethylene-Containing Multiblock Copolymers

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ABSTRACT: Amphiphilic (oxyethylene–oxypropylene) and (oxyethylene–styrene) multiblock copolymers, both with high molecular weights, were synthesized by coupling poly(ethylene glycol) (PEG) with poly(propylene glycol) (PPG) or with telechelic dihydroxy polystyrene using 2,4-toluene diisocyanate as a coupling agent, respectively. The polymerization conditions were investigated. The products were purified and characterized by IR, ¹H-NMR spectroscopy, and membrane osmometry and identified as multiblock copolymers. Crystallinity of the two kinds of multiblock copolymers was determined by DSC. They showed good emulsifying properties. Their complexes with LiClO₄ showed high room-temperature conductivities from

3×10^{-5} to 4×10^{-4} S/cm at 30°C. High molecular weight (oxyethylene–oxypropylene) multiblock copolymers, at a weight ratio of PEG/PPG = 6/4, behave like thermoplastic elastomers. The (oxyethylene–styrene) copolymer functions as a good compatibilizer for the blend of chlorohydrin rubber and polystyrene. An amount of only 3 wt %, based on the blend, is needed to increase the tensile strength of the blend almost sixfold. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1295–1301, 2005

Key words: multiblock copolymers; crystal structures; amphiphiles; compatibilization; thermoplastics

INTRODUCTION

Block and graft copolymers, containing hydrophilic polyoxyethylene (PEO) segments and hydrophobic segments, have attracted much attention because they are not only amphiphilic, but their PEO segments are also nonionic, crystalline, and can complex monovalent metallic ions.^{1–3} They have many uses, including polymeric surfactants, phase-transfer catalyst, solid polymer electrolyte, and compatibilizers in polymer blending, to cite but a few.

Oxyethylene–styrene diblock copolymers were synthesized by O'Malley et al.⁴ and Xie et al.⁵ by a sequential anionic polymerization of styrene and ethylene oxide with cumyl potassium and α -phenyl ethyl potassium as initiator, respectively. Ueda and Nagai⁶ synthesized diblock copolymers of styrene and ethylene oxide through polycondensation between azobiscyanopentanoyl chloride and poly(ethylene glycol) (PEG), followed by thermal decomposition in the presence of styrene. Shimura et al.⁷ prepared oxyethylene–styrene multiblock copolymers by coupling telechelic

dihydroxyl polystyrene with PEG, using 4,4'-diphenylmethane diisocyanate as a coupling agent and indicated that films cast from benzene solution of products showed a tensile strength of 13 MPa and 44% elongation. Booth and coworkers⁸ used dichloromethane, KOH, PEG (molecular weight 400), and monohydroxyl-terminated polystyrene to prepare oxymethylene-linked (oxyethylene–styrene) triblock copolymer and showed that its complex with LiCF₃SO₃ had a conductivity < $1 \cdot 10^{-5}$ S/cm. Xie and Guo⁹ prepared a kind of amphiphilic (oxyethylene–butadiene) multiblock copolymers and indicated that the copolymers exhibited excellent emulsifying properties. Most (oxyethylene–oxypropylene) block copolymers were synthesized in liquid form with low molecular weight in the range of 3000–5000 by sequential anionic polymerization using alkali catalyst, such as CsOH.¹⁰ Sangen et al.¹¹ polymerized propylene oxide under a cationic ring-opening reaction, followed by treating with butyl lithium and *p*-toluene sulfonyl chloride and then with PEG to give triblock copolymer. Ding et al.¹² prepared (oxyethylene–oxypropylene) diblock copolymers with 18-crown-6 ether and potassium salt of methoxypropanol by sequential anionic polymerization. However, until now no (oxyethylene–oxypropylene) multiblock copolymer with high molecular weight has been prepared.

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This article deals with the synthesis, characterization, and properties of the urethane-linked, high molecular weight (oxyethylene–oxypropylene) multiblock copolymers and (oxyethylene–styrene) multiblock copolymers, to obtain solid multiphase copolymers, which possess not only crystalline property, emulsifying property, and ion-conduction property, but also exhibit their compatibilizing effect on the blending of oil-resistant chlorohydrin rubber with polystyrene.

EXPERIMENTAL

Materials

Poly(propylene glycol) (PPG, molecular weight 1950; Nanking Plastics Manufacturer, China) and poly(ethylene glycol) (PEG, various molecular weights; Baker Co., Paris, KY) were dried by azeotropic distillation with toluene separately. Telechelic dihydroxyl polystyrene (THPS) was synthesized as follows.¹³ Living polystyrene, obtained by anionic polymerization of styrene with lithium 1-methyl dihydronaphthalide as dianionic initiator, was terminated successively with ethylene oxide and acetic acid. The molecular weight of THPS was determined with a Knauer vapor pressure osmometer (VPO; Knauer GmbH, Berlin, Germany). 2,4-Toluene diisocyanate (TDI) was purified by distillation under reduced pressure. Toluene was dried overnight with a 4-Å molecular sieve. Dibutyltin dilaurate was chemically pure with 18 wt % Sn content. Polystyrene, with molecular weight of 2×10^5 , was a product of Asahi Chemical Industry Co. (Tokyo, Japan). Chlorohydrin rubber, with molecular weight of 5×10^5 , was purchased from Wuhan Organic Synthetic Materials Factory (China). Other reagents were chemically pure.

Synthesis and purification of two-component multiblock copolymers

For the synthesis of (oxyethylene–styrene) multiblock copolymer, THPS, PEG, and dibutyltin dilaurate were dissolved in toluene and heated to 60°C. TDI was added during stirring and the reaction was carried out at 60°C for 5 h. For the synthesis of (oxyethylene–oxypropylene) multiblock copolymer, PEG first reacted with TDI in toluene in the presence of dibutyltin dilaurate at 65°C, followed by addition of PPG and further reaction for 5 h. Both polymerizations were terminated with methanol containing a small amount of 2,6-di-*tert*-butyl-4-methyl-phenol for 30 min. The reaction mixture was poured into a culture dish to evaporate the solvent under an infrared lamp. The crude product was extracted three times with water overnight to remove the unreacted PEG or its homopolymer. The dried residue was further extracted

with ethyl ether three times to remove the unreacted PPG or THPS. After evaporation, the residue was dried in a vacuum desiccator. The efficiency of purification was verified by extractions of a mixture of PEO and PPG or THPS in the same way.

Intrinsic viscosities of the purified products were determined with a Ubbelohde viscosimeter at $25 \pm 0.1^\circ\text{C}$ using CHCl_3 as solvent, followed by calculation according to the following equation¹⁴:

$$[\eta] = 2^{1/2}(\eta_{sp} - \ln \eta_r)^{1/2}/C$$

Characterization of the multiblock copolymers

IR spectra were taken with an IR-408 infrared spectrophotometer (Shimadzu, Kyoto, Japan). ¹H-NMR spectra were recorded with an AC-80 spectrometer (Bruker, Darmstadt, Germany) using CDCl_3 as solvent and TMS as an internal standard. Number-average molecular weights of the copolymers were determined with a modified Bruss membrane osmometer, using tetrahydrofuran as solvent. Number-average molecular weights of the THPS were determined with Knauer VPO apparatus, using CHCl_3 as solvent. Its functionality was determined by isocyanate method to be 2.00 ± 0.10 .

Crystallinity of the multiblock copolymers

Crystallinity was determined from DSC curves using a PE DSC-4 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of $10^\circ\text{C}/\text{min}$ and a sample weight of about 10 mg. The crystallinity (X_c) was 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, equal to 210 J/g.¹⁵

Emulsifying property of the multiblock copolymers

The emulsifying property was measured as emulsifying volume,⁹ which was determined as follows: a 0.2-g sample was dissolved in 30 mL toluene, which was added to 70 mL distilled water. The mixture was vigorously shaken for 5 min and poured into a 100-mL measuring cylinder with a cover. After standing for 24 h, the emulsifying volume was measured by subtracting the volume of the lower water layer from the total volume.

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

A 0.6-g sample of the multiblock copolymer was dissolved in 15 mL benzene, to which a certain amount of

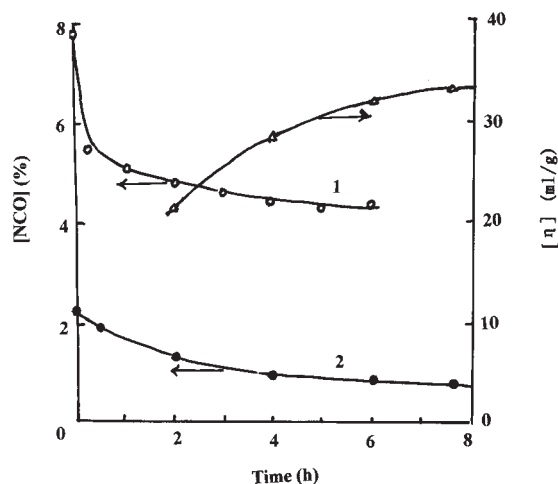


Figure 1 Change of NCO% and $[\eta]$ of the (oxyethylene-oxypropylene) copolymer versus polymerization time.

ethanolic solution of LiClO_4 (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. The complex was hot pressed in a die into pellets (~ 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminum discs at 80°C and then kept in a vacuum desiccator with fresh P_2O_5 .

The ac conductivity was measured at 30°C with a DDS-11 conductometer using copper disc electrodes operating 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; reproducible results were usually obtained.

Blending of chlorohydrin rubber with polystyrene

Different proportions of polystyrene and chlorohydrin rubber, with or without a small amount of the (oxyethylene-styrene) multiblock block, were blended on a hot mill at 160°C for 6 min. Then the blend was hot pressed under 10 MPa at 160°C for 10 min and cut into specimens. The tensile strength and ultimate elongation were measured on a DL-2500 tensile tester at an extension rate of 300 mm/min. The permanent set was measured as % elongation 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

During synthesis of (oxyethylene-oxypropylene) multiblock copolymers, when PEG reacts with excess TDI at molar ratio of NCO/OH = 2.2, using 0.5% dibutyltine dilaurate as catalyst at 60°C , the change of NCO% versus time is shown as curve 1 in Figure 1. It can be seen that the reaction takes place quickly at the

beginning, then gradually leveling off at about 3 h. When the NCO-terminated PEG formed was further reacted with PPG, NCO% of the product decreased gradually and then reached a constant level within 6 h, as shown as curve 2 in Figure 1. The relatively slow reaction rate is because the terminated NCO group is in the *ortho* position of TDI, which is less reactive than the NCO group in the *para* position of TDI, and also because the secondary OH group of PPG is less reactive than the primary OH group of PEG and PPG.

Figure 1 also indicates that $[\eta]$ of the copolymer formed during reaction of NCO-terminated PEG with PPG increases gradually and levels off at 6 h. This result showed that the step polymerization almost finished at 6 h.

Figure 2 illustrates that at the total molar ratio of NCO/OH of 1.1–1.15, $[\eta]$ of the product is the highest and the yield approaches a maximum. Excess TDI lowers the molecular weight of the product. Theoretically, the molecular weight of the product should be the highest at a molar ratio of NCO/OH = 1. The above result may be attributable to the consumption of a small amount of TDI by the moisture in the polymerization system. The optimum prepolymer concentration is 20–25 g/100 mL, and the optimum dibutyltine dilaurate catalyst concentration is 0.5–0.7%. The reduced catalyst concentration causes decreases of yield, whereas the excess catalyst concentration causes gelation.

The crude product usually contains a small amount of PEG, PPG, or THPS. A preliminary experiment showed that water can dissolve PEG and ethyl ether can remove PPG or THPS. In the case of the copolymer containing a large proportion of PEO blocks, it is

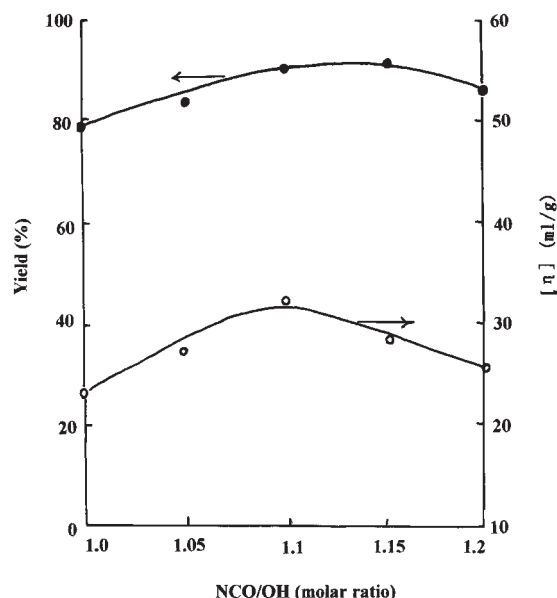


Figure 2 Effect of molar ratio of NCO/OH on yield and $[\eta]$ of the (oxyethylene-oxypropylene) copolymer.

TABLE I
Effects of Molecular Weight and Feeding Weight Ratio of the Prepolymers on the Yield of Purified Copolymers

PEG/PPG (or PS)	Yield (%)			
	$M_{\text{PEG}} = 3400$ $M_{\text{PPG}} = 1950$	$M_{\text{PEG}} = 6000$ $M_{\text{PPG}} = 1950$	$M_{\text{PEG}} = 20000$ $M_{\text{PPG}} = 1950$	$M_{\text{PEG}} = 2000$ $M_{\text{THPS}} = 7780$
9/1	96.3	97.1		93.3
8/2	97.2	97.1		92.2
7/3	93.5	96.2	85.3	92.4
6/4	98.1	95.1	85.4	92.5
5/5	91.5	91.5	86.9	92.5
4/6	97.2	92.4	86.3	90.6
3/7	96.2	92.5	87.4	

better to dissolve the crude product in CHCl_3 solution first, then extract with water, to avoid some loss of the block copolymer. The efficiency of purification was verified by extractions of a mixture of PEO and PPG or THPS in the same way.

Table I denotes the yield of purified multiblock copolymers using different feeding weight fractions and different molecular weights of PEG. The yield of purified (oxyethylene–oxypropylene) multiblock copolymers reaches $95 \pm 3\%$. However, when the molecular weight of PEG increases to 20,000, the yield decreases to about $86.5 \pm 1\%$. The yield of purified (oxyethylene–styrene) copolymers is $92 \pm 1.5\%$.

Characterization of the multiblock copolymers

The IR spectrum of the purified (oxyethylene–styrene) multiblock copolymer indicated absorption peaks at 1530, 3300, and 3500 cm^{-1} for the NH group; a peak at 1720 cm^{-1} for the C=O group; peaks at 700, 740, 850, 950, 1450, 1800, and 3050 cm^{-1} for the phenyl group; and peaks at 1060–1150 cm^{-1} for the ether group. The $^1\text{H-NMR}$ spectrum of the purified (oxyethylene–styrene) multiblock copolymer showed the presence of phenyl protons at $\delta = 6.5\text{--}7.0$ ppm and alkyl protons next to oxygen at 3.6 and 3.8 ppm. These data demonstrated that the purified product is indeed a block copolymer of styrene and ethylene oxide linked by a urethane group.

The IR spectrum of the purified (oxyethylene–oxypropylene) multiblock copolymer showed absorption peaks at 1530, 3300, and 3500 cm^{-1} for the NH group; a peak at 1720 cm^{-1} for the C=O groups;

peaks at 1380, 2850–2950 cm^{-1} for the CH_3 , CH_2 , CH groups; and peaks at 1060–1150 cm^{-1} for the ether group. The $^1\text{H-NMR}$ spectrum of the purified (oxyethylene–oxypropylene) multiblock copolymer indicated the presence of CH_3 protons at 1.15 ppm and protons of $-\text{CH}_2-$ at 3.6–3.8 ppm. The above data demonstrated that the purified product is indeed the block copolymer of ethylene oxide and propylene oxide linked by a urethane group.

From the height of the integrals of the peaks in the $^1\text{H-NMR}$ spectrum, the proportions of these different blocks were calculated. It is shown in Table II that the composition of the purified copolymer obtained is quite close to that of the feeding prepolymer mixtures. Table II also shows the structural parameters of the two copolymers, which were calculated from the molecular weights of the copolymers and prepolymers, determined by membrane osmometry and VPO, respectively. It can be noted that both block copolymers contain a number of blocks for PEO and PS or PPO.

Crystallinity of the (oxyethylene–oxypropylene) multiblock copolymers and (oxyethylene–styrene) multiblock copolymers

Table III shows that both kinds of multiblock copolymers possess a crystalline segment. The crystallinity determined by DSC method increases with increasing weight fraction of PEO because only the PEO block can crystallize. At the same weight fraction of PEO blocks, PPO blocks seem to lower the crystallinity of the copolymer more obviously than PS blocks. This result is probably the result of the greater compatibil-

TABLE II
Structural Parameters of the Multiblock Copolymers, Calculated from the Molecular Weights of Prepolymers and Copolymers and the Composition Calculated from $^1\text{H-NMR}$ Data

Feeding wt ratio PEG/PPG/THPS	Composition PEO/PEO/PS	$M_n \times 10^{-3}$			$M_{\text{ncop}} \times 10^{-3}$	No. of blocks		
		PEG	PPG	THPS		PEO	PPO	PS
30/70/0	31.2/68.8/0	3.4	1.95		114	10.5	40.2	
60/0/40	60.8/0/39.2	6.0		7.78	135	13.7		6.8

TABLE III
Melt Enthalpy and Crystallinity of Two Kinds of
Multiblock Copolymers Determined by DSC

PEG/PPG (wt ratio)	PEG/PS (wt ratio)	$M_{\text{PEG}} \times 10^{-3}$	ΔH_m (J/g)	X_c (%)
9/1		2	33.9	15.2
7/3		2	28.9	12.9
9/1		3.4	89.5	40.4
6/4		20	195.8	88.3
5/5		20	176.5	79.6
4/6		20	120.9	54.5
3/7		20	93.7	42.3
	9/1	2	74.9	33.8
	8/2	2	66.5	30.3
	7/3	2	58.1	26.2
	5/5	2	23.0	10.3
	4/6	2	23.9	10.8

ity of PEO with PPO than that of PEO with PS, given that PPO is more similar to PEO than to PS in structure. Thus PPO blocks more easily hinder the crystallization of PEO than PS blocks.

Crystallinity of the block copolymers obviously increases with molecular weight of PEG used in synthesis because the larger the molecular weight of PEG, the greater the probability for PEO segments to crystallize.

Emulsifying properties of the (oxyethylene–oxypropylene) multiblock copolymers and (oxyethylene–styrene) multiblock copolymers

Both kinds of polyoxyethylene-containing multiblock copolymers are amphiphilic and can emulsify a toluene/water system. Table IV indicates that at a weight ratio of PEO/PPO or PEO/PS = 5/5, the emulsifying volume exhibits a maximum value. This result can be interpreted by the fact that PEO blocks are hydrophilic

and PS or PPO blocks are hydrophobic. It is interesting to note that the emulsifying volumes of (oxyethylene–oxypropylene) copolymers are larger than those of the (oxyethylene–styrene) copolymers. This phenomenon can be explained by the fact that the molecular weight of THPS is 7780, which is much higher than that of PPG, with molecular weight of 1950, resulting in more emulsifying centers in the (oxyethylene–oxypropylene) copolymer system than in the (oxyethylene–styrene) copolymer system.

The emulsifying volume varies with molecular weight of the PEG used in synthesis of (oxyethylene–oxypropylene) copolymer. The block copolymer with molecular weight of 2000 seems to show the highest emulsifying volume. This result may be explained by the fact that with increasing molecular weight of PEG used in synthesis of multiblock copolymer, the number of PEO blocks diminishes, resulting in decreasing emulsifying sites and lowering emulsifying ability. For PEG whose molecular weight is too low, the amount of TDI used is too high, thus also decreasing the emulsifying ability. The emulsion obtained is very stable; no separation phenomenon occurred after standing for several months.

Ion conductivity of LiClO_4 complexes of the two kinds of multiblock copolymers

Polyoxyethylene can form a complex with alkali metallic ions. Wright¹⁶ discovered that this complex can transport ions under electric field, thus showing ion conductivity. However, the ion conductivity is very low at room temperature, having a magnitude of only $<10^{-7}$ S/cm, because of its high crystallinity. The oxyethylene-containing block or graft copolymers were investigated for their ability to enhance ion conductivity at room temperature.

TABLE IV
Effects of Feeding Weight Ratios of Prepolymers and Molecular Weight of PEG Used
in Synthesis on the Emulsifying Volume

PEG/PPG	PEG/THPS	Emulsifying volume (mL)/ $M_{\text{PEG}} \times 10^{-3} =$					
		1.0	2.0	3.4	6.0	10.0	2.0
9/1		34	41	38	36		
8/2		36	45	40	38		
7/3		40	48	45	40	36	
6/4		43	52	46	43	40	
5/5			62	45	44	42	
4/6			52	42	41	37	
3/7			47	41	39	36	
	9/1						30
	8/2						44
	7/3						47
	6/4						49
	5/5						53
	4/6						50

TABLE V
Effects of Molecular Weight of PEG and Feeding Weight Ratios on Room-Temperature Conductivity of the Multiblock Copolymer Complexed with LiClO₄

PEG/PPG	PPG/THPS	$M_{\text{PEG}} \times 10^{-3}$	$M_{\text{THPS}} \times 10^{-3}$	$\delta \times 10^{-4}$ (S/cm)
9/1		1.0		4.6
7/3		1.0		1.35
6/4		1.0		0.75
9/1		3.4		4.0
8/2		3.4		1.05
7/3		3.4		0.75
9/1		6.0		1.66
	8/2	2.0	6.17	0.47
	7/3	2.0	6.17	0.26
	9/1	3.4	7.78	1.54

In this article LiClO₄ complexes of both kinds of multiblock copolymers were prepared and their ion conductivities were studied. The results shown in Table V indicate that most complexes exhibit conductivity about 10⁻⁴ S/cm at 30°C. The conductivity decreases with decreasing PEO content and with increasing molecular weight of PEO blocks. The latter phenomenon is because the higher the molecular weight of PEG used in synthesis, the higher is the crystallinity, which retards the ion transportation. The (oxyethylene-styrene) copolymer shows lower conductivity than that of the (oxyethylene-oxypropylene) copolymer with the same weight fraction of PEO blocks. This result is probably attributable to the higher crystallinity of the (oxyethylene-styrene) copolymer than that of the (oxyethylene-oxypropylene) copolymer, as listed in Table III, and also because the PEO blocks are more compatible with PPO blocks, which inhibit the crystallization of the PEO blocks more effectively than the PS blocks.

Mechanical properties of the PEO-PPO multiblock copolymers

The (oxyethylene-oxypropylene) multiblock copolymers, synthesized from PEG with molecular weight of

TABLE VI
Mechanical Properties of the (Oxyethylene-Oxypropylene) Multiblock Copolymers^a

PEG/PPG (wt ratio)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
6/4	4.16	220	50
5/5	4.80	460	120
4/6	3.41	1010	150
3/7	1.19	410	50

^a $M_{\text{PEG}} = 20,000$.

20,000 and feeding weight ratio of PEG/PPG higher than 5/5, possess tensile strength > 4 MPa, as shown in Table VI. With decreasing feeding ratio of PEG/PPG, both the tensile strength and ultimate strength first increases and then decreases. When the feeding weight ratio of PEG/PPG is 6/4, it functions as a thermoplastic elastomer with larger ultimate elongation and lower permanent set. This result is because PEG with higher molecular weight can form crystalline phase and physical crosslinkage, whereas PPO blocks are soft and flexible.

Blending of polystyrene (PS) with chlorohydrin rubber (CHR) using (oxyethylene-styrene) multiblock copolymer as compatibilizer

Table VII shows the effect of the (oxyethylene-styrene) copolymer as a compatibilizer on the mechanical properties of the PS/CHR blends. The blend at a weight ratio of PS/CHR = 3/7, in the absence of the multiblock copolymer, shows very low tensile strength. However, after adding a small amount of the (oxyethylene-styrene) multiblock copolymer to the blend during mixing, the tensile strength of the blend increases concomitantly with the amount of multiblock copolymer added. A maximum tensile strength occurred at 3 wt % multiblock copolymer based on the blend. The blend exhibits good thermoplastic elastomer behavior. Thus the multiblock copol-

TABLE VII
Effect of (Oxyethylene-Styrene) Multiblock Copolymer (PEO-PS) on the Mechanical Properties of the PS/CHR Blends

PS/CHR (wt ratio)	PEO-PS/blend (wt %)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
3/7	0	1.65	130	52
3/7	1	4.20	280	40
3/7	2	6.20	400	30
3/7	3	8.98	500	25
3/7	5	8.47	420	56
3/7	10	7.25	320	89
1/9	3	3.25	1080	210
2/8	3	6.48	770	120
3/7	3	8.98	500	25
4/6	3	10.87	270	42
5/5	3	14.95	155	56

mer is a good compatibilizer for these blends. This result can be explained by the fact that PS blocks can be miscible with the PS phase, and the PEO blocks can be compatible with the ether linkage of the rubber phase of CHR. Thus the two phases can be linked by the multiblock copolymer.

Table VII also shows that in the presence of 3 wt % (oxyethylene-styrene) multiblock copolymer, the blends of PS/CHR at different weight ratios show different mechanical properties. The tensile strength of the blends increases with the weight ratio of PS/CHR. At a weight ratio of PS/CHR = 3/7-4/6, the blends function as good thermoplastic elastomers, whereas at a weight ratio of PS/CHR = 5/5, the blends function as toughened plastics.

CONCLUSIONS

The (oxyethylene-styrene) and (oxyethylene-oxypropylene) multiblock copolymers with high molecular weights were synthesized by coupling PEG and THPS or PPG together with TDI, respectively. The products can be purified by water extraction to remove PEG and ether extraction to remove PPG or THPS successively and identified to be the multiblock copolymers. Both kinds of copolymers showed some crystallinities attributed to the crystalline PEO blocks and good emulsifying properties attributed to the hydrophilic PEO blocks and hydrophobic PPO or PS blocks. Their complexes with LiClO_4 exhibit very good ion conductivity in the range of 3×10^{-5} to 4×10^{-4} S/cm at 30°C, given that the crystallinity of PEO blocks was lowered by the other kinds of blocks. The (oxyethylene-oxypropylene) multiblock copolymers, at a weight ratio of PEG/PPG = 6/4, behave like a thermoplastic elastomer because the crystalline PEO acts as physical crosslinkage in the soft PPO phase. The

(oxyethylene-styrene) multiblock copolymer functions as a good compatibilizer for the blends of polystyrene and chlorohydrin rubber because PS blocks are miscible with the polystyrene phase, whereas the PEO blocks are compatible with the polyether chains of the chlorohydrin rubber phase. Thus the two phases can be linked by the multiblock copolymer. An amount of only 3 wt %, based on the blend, is needed to enhance the tensile strength of the blend sixfold, thus causing the blend to act as a thermoplastic elastomer.

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