

Synthesis and Properties of Multiblock Copolymers of Styrene and Propylene Oxide

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ABSTRACT: Multiblock copolymers of styrene and propylene oxide were synthesized by coupling together polypropylene glycol and telechelic dihydroxyl polystyrene with 2,4-toluene diisocyanate (TDI) as the coupling agent. The results showed that it was better to terminate the telechelic dihydroxyl polystyrene with TDI first, then react with polypropylene glycol. The copolymer obtained in this two-step method possesses less homopolymers than that obtained when all the three reagents reacted together in one step. The crude product can be purified by extractions with absolute ethyl alcohol and decalin in order to remove the unreacted polypropylene glycol and polystyrene respectively. The purified products were characterized by IR, ^1H NMR, GPC, membrane osmometry, elemental analysis, and shown to be multiblock copolymers of styrene and propylene oxide. The multiblock copolymer exhibits two glass transition temperatures (T_g) and behaves like a thermoplastic elastomer at 20—30% polystyrene content. Addition of 2% of the copolymers to the blends of polystyrene and epichlorohydrin rubber improves evidently their mechanical properties and causes the two T_g 's become closer.

KEY WORDS Block Copolymer / Styrene-Propylene Oxide Block Copolymer / Thermoplastic Elastomer / Compatibilizer /

Szwarc and Richards¹ attempted to synthesize a triblock copolymer of styrene and propylene oxide using sodium α -methylstyrene tetramer as an initiator, but failed due to the chain transfer reaction of propylene oxide. Tobolsky *et al.*² obtained the block copolymer through reaction of isocyanate terminated polypropylene glycol with *t*-butyl hydrogen peroxide to form a product which then initiated the radical polymerization of styrene. The product obtained after fractionation was shown to be block copolymer of styrene and propylene oxide. Kawamura *et al.*³ used 4,4'-diisocyanate diphenyl disulfide as an initiator for photopolymerization of styrene and thus obtained telechelic diisocyanate polystyrene in 50% conversion, which then reacted with polypropylene glycol to form block copolymer. Hsiue⁴ synthesized styrene-propylene oxide-styrene triblock copolymer by first

preparing isocyanate terminated polystyrene which then reacted with polypropylene glycol. The molecular weight of the triblock copolymer was reported to be 8×10^4 .

This paper deals with the synthesis of multiblock copolymer of styrene and propylene oxide by coupling reaction of telechelic dihydroxyl polystyrene, TDI and polypropylene glycol and also the study of their properties in order to obtain a new polymeric material containing no double bonds for use as a thermoplastic elastomer and a compatibilizer in the blending of epichlorohydrin rubber and polystyrene.

EXPERIMENTAL

Materials

Telechelic dihydroxyl polystyrenes with different molecular weight from 0.86×10^4 to

1.65×10^4 were prepared by anionic polymerization of styrene using lithium α -methylnaphthalene as a dianionic initiator, then terminating with ethylene oxide and neutralizing with acetic acid.⁵ Polypropylene glycol with number-average molecular weight (\bar{M}_n) of 2000 was produced by Dow Chemical Company and dried by azeotropic distillation with toluene. Functionality of the above two prepolymers was determined by isocyanate method⁵ to be 2.00 ± 0.02 . 2,4-Toluene diisocyanate (TDI) was purified by distillation under reduced pressure. The distillate at 105°C/4 mmHg was collected and preserved under nitrogen atmosphere and protection from light. Toluene was dried by standing over 4A molecular sieve overnight. Dibutyl dilaurate and epichlorohydrin rubber with viscosity-average molecular weight (\bar{M}_v) of 6×10^5 and polystyrene with weight-average molecular weight (\bar{M}_w) of 1×10^5 were used as received.

One-Step Method for Synthesis of the Block Copolymers

The telechelic dihydroxyl polystyrene was dissolved in 25 ml dried toluene to which the dried polypropylene glycol was added under stirring. The total amount of the two prepolymers was 10 g. Dibutyltin dilaurate (0.2% based on the solution) was then introduced *via* a syringe and the mixture heated to 60°C. Then a calculated amount of TDI was added under stirring and the reaction was carried out at 60°C for 2 days. Samples were taken out for analysis of isocyanate group and viscosity of the solution at intervals. The isocyanate group was determined by back titration of *n*-butylamine after reaction.

Two-Step Method for Synthesis of the Block Copolymers

The telechelic dihydroxyl polystyrene was dissolved in 25 ml dried toluene to which dibutyltin dilaurate solution was added. A calculated amount of TDI based on total hydroxyl group content of both telechelic dihydroxyl

polystyrene and polypropylene glycol according to the weight ratio of PST/PPO desired was added under stirring at 40°C. After reaction for 2 h, polypropylene glycol was then introduced and the reaction carried out for 46 h at 60°C. The total amount of the two prepolymers was 10 g.

Purification of the Block Copolymers

The polymerization solution was added slowly to 4 times its volume of ethyl alcohol. After centrifuging, the precipitate was washed several times with ethyl alcohol in order to remove unreacted polypropylene glycol. After drying, the precipitate was extracted with decalin in order to remove unreacted polystyrene. The purified product was then washed with ethyl alcohol and dried under vacuum.

Characterization of the Block Copolymers

The molecular weight and molecular weight distribution of telechelic dihydroxyl polystyrene were determined by GPC on LC-4A liquid chromatography apparatus with differential refractive index detector. The number-average molecular weight of the block copolymer was measured by Bruss membrane osmometer. The IR spectra of the block copolymers were obtained with SP3-300 spectrophotometer and ¹H NMR spectra recorded by a EM-360 spectrometer (60 MHz). Oxygen content of the block copolymer was analyzed by automatic elemental analyzer and composition of the polyether in the copolymer can thus be calculated. Glass transition temperatures were measured by DDV-III-EA apparatus with a heating rate of 3°C min⁻¹ at 110 Hz. Mechanical properties were measured by DL-250A tensile tester with a stretching speed at 300 mm min⁻¹. The specimens were prepared by pressing under pressure at 110°C for 20 min and annealing to room temperature. Melt index was determined by XRZ-400-1 melt index apparatus at 145°C with 2.1 kg load.

Blending of epichlorohydrin rubber and

polystyrene was carried out on a hot mill at 155°C for 5 min. Intrinsic viscosity $[\eta]$ was determined in toluene at 25°C.

RESULTS AND DISCUSSION

One-Step Method

Figure 1 shows the relation between the reaction time and the conversion of isocyanate group and the relative viscosity of the polymerization solution. It can be seen that at the beginning of reaction conversion of NCO group rose very quickly to about 80% within 2 h. Then the reaction proceeded slowly so that the rest of NCO groups needed 46 h to react completely. This is attributed to the lower reactivity of the NCO groups in the *ortho* position of TDI than that in the *para* position and also to the lower reactivity of secondary hydroxyl groups of polypropylene glycol than

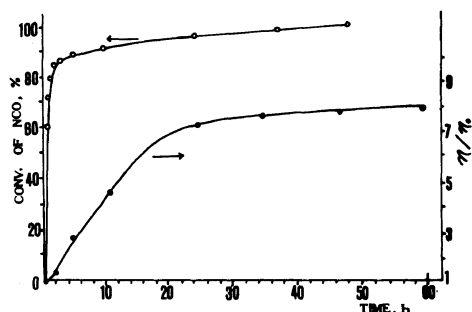


Figure 1. Relation between reaction time and the conversion of NCO groups, and relative viscosity of the polymerization solution in one-step reaction.

Table I. Effects of molar ratio of NCO/OH on one-step reaction

NCO/OH	$[\eta]$	Oxygen content	PPO/%	
	dl g^{-1}	%	Exptl	Calcd
1.00	0.87	15.21	52.3	65.6
1.05	1.05	15.75	54.2	65.4
1.10	1.42	16.49	56.7	65.2
1.15	2.01	19.00	65.3	65.0
1.20	∞	—	—	—
1.30	∞	—	—	—

that of primary hydroxyl end groups of both the polystyrene and polypropylene glycol. The viscosity of the polymerization solution increases gradually in the first 20 h and then slowly. Increase of viscosity implies the coupling of the end groups of the prepolymers. In the last period both conversion of NCO and viscosity increased slowly due to lower concentration of functional groups.

The effect of molar ratio of NCO/OH on the one-step reaction was shown in Table I. When NCO/OH was =1.10, the coupling reaction was not complete and the content of polyether (PPO) was lower than the calculated value. When NCO/OH=1.15, the content of polyether units approached to the calculated value. But if NCO/OH was larger than 1.15, gelation occurred. The reason for NCO/OH in excess is probably due to that a small amount of impurities including water remaining in the reagents consumed some TDI.

Amount of toluene used as solvent also has some effect on the coupling reaction. If toluene used was too little, there appeared some white precipitates in the course of the reaction and no product with higher molecular weight was obtained. The relation between the amount of

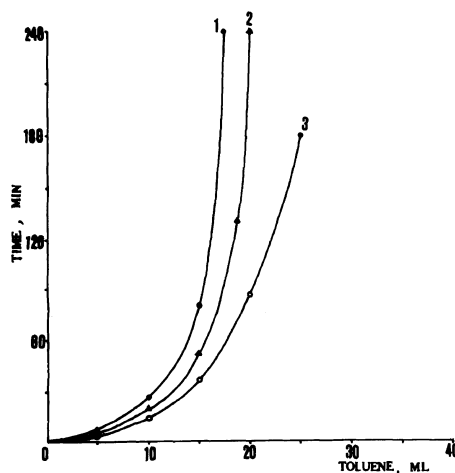


Figure 2. Effects of the amount of solvent and the molecular weight of polystyrene on the time of precipitation during one-step reaction. $\bar{M}_n \times 10^{-4}$ of PSt: 1, 0.84; 2, 1.52; 3, 2.40.

toluene used, the molecular weight of the telechelic dihydroxyl polystyrene and the time when the white precipitate began to occur was shown in Figure 2. The larger the molecular weight of polystyrene was, the more easily the precipitate formed or the more solvent was needed to prevent from precipitation.

Two-Step Method

In order to prevent the telechelic dihydroxyl polystyrene from coupling together, a two-step coupling method was used, *i.e.*, the α,ω -dihydroxyl polystyrene was first reacted with TDI to form poly(styrene diisocyanate), which then reacted with polypropylene glycol. It

was confirmed by GPC that no coupled polystyrene was produced.

It is better to carry out the coupling reaction at 60°C than at 40°C, since the molecular weight of the product obtained at 60°C is higher than that at 40°C and the polyether content of product prepared at 60°C was nearer to the calculated value, as shown in Table II. This implies that the coupling reaction seems not complete at 40°C within 46 h.

Purification of the Block Copolymers

GPC curve of the crude product obtained by one-step method (curve ABCDE in Figure 3) was compared with that of a mixture of telechelic dihydroxyl polystyrene and polypropylene glycol. This indicates that there is still some homopolymers existing in the crude product obtained by one-step method.

The crude product can be purified by extractions with ethyl alcohol and decalin, as demonstrated by GPC curves in Figure 3. Curve FBCDE represents the GPC curve of the product after extraction with ethyl alcohol. The GPC curve of the product after extractions with ethyl alcohol and decalin is represented by FCDE curve which shows no homopolymers as compared with dashed curve. The products obtained by two-step method usually contain only a little homopolymers.

Table II. Effects of reaction temperature on the block copolymers obtained by two-step method^a

PSt/PPO wt ratio	Temp at 2nd step °C	$[\eta]$ dl g ⁻¹	PPO/%	
			Exptl	Calcd
2/8	40	1.64	53.4	73.8
2/8	60	2.23	69.5	73.8
3/7	40	1.58	48.8	65.0
3/7	60	2.10	65.1	65.0

^a NCO/OH = 1.15. \bar{M}_n of PSt = 1.12×10^4 . The first step was at 40°C for 2 h and the second step for 46 h.

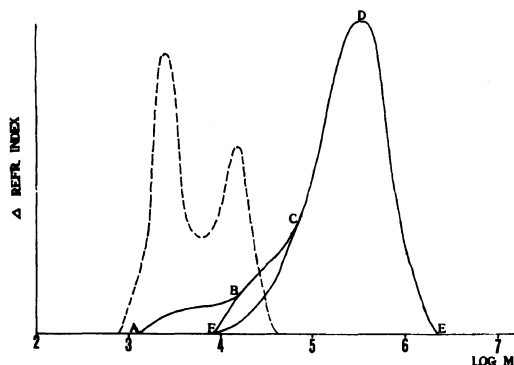


Figure 3. GPC curves of a product obtained in one-step method before and after extractions: Curve ABCDE, crude product before extraction; FBCDE, after extraction with ethyl alcohol; FCDE, after extractions with ethyl alcohol and decalin. Dashed curve, GPC curve of a mixture of the polypropylene glycol and telechelic dihydroxyl polystyrene.

Characterization of the Purified Block Copolymers

The purified block copolymers were characterized by IR and ¹H NMR. The IR spectra showed the absorption peaks of urethane groups at 3308 and 1725 cm⁻¹, those of phenyl groups at 3025, 3060, 3080, 1600, 1530, 775, and 695 cm⁻¹ and those of ether groups at 1050–1150 cm⁻¹. ¹H NMR spectra indicated the presence of phenyl protons at δ 6.5 and δ 6.95, alkyl protons next to oxygen at δ 3.35 and δ 3.55 and protons from CH₃ and CH₂-CH at δ 1.10. These data demonstrate that the purified products are indeed block copolymers of styrene and propylene oxide coupled by

Table III. Structural parameters of the block copolymers obtained by two-step method

wt ratio PSt/PPO	\bar{M}_n^a of used PSt $\times 10^{-4}$	\bar{M}_n^b of block copolymer $\times 10^{-4}$	Calcd. No. of blocks in the copolymers ^c
2.1/7.9	1.14	14.5	6.34
3/7	1.14	7.92	5.16
3/7	1.14	15.4	9.10
3/7	0.86	14.7	11.3
3/7	1.65	13.5	5.90
4/6	1.14	14.9	11.5

^a GPC. ^b Bruss membrane osmometry.^c The value was calculated as follows: No. of blocks in the copolymer = No. of PSt in the block copolymer + No. of coupled PPO in the block copolymer. No. of coupled PPO in the block copolymer = No. of PSt in the block copolymer 1.

$$\text{No. of PSt} = \frac{\text{wt of PSt}}{\text{wt of PSt} + \text{wt of PPO}} \times \frac{\bar{M}_n \text{ of copolymer}}{\bar{M}_n \text{ of PSt}}$$

TDI.

Structural parameters of the block copolymers are listed in Table III. It can be deduced that: (1) the block copolymers are rather multiblock copolymers; (2) when the weight ratio of PSt/PPO and also \bar{M}_n of the telechelic dihydroxyl polystyrene were kept unchanged, both the average number of the polystyrene blocks and the length of the coupled PPO block decrease with decreasing \bar{M}_n of the block copolymers.

Properties of the Multiblock Copolymers

Dynamical mechanical analysis of the purified block copolymers shows that they exhibit two transition temperatures at 108 and -47°C , which correspond to the T_g 's of polystyrene and polypropylene oxide respectively. This implies that there occurs microphase separation in the block copolymer.

The mechanical properties of the block copolymer with \bar{M}_n of 14.5×10^4 — 15.5×10^4 were listed in Table IV, which shows that when polystyrene content is 20—30%, the copoly-

Table IV. Effects of weight ratio of PSt/PPO on mechanical properties of the block copolymers

PSt/PPO	Tensile strength	Elongation	Permanent set	Melt index
wt ratio	MPa	%	%	g/10 min
2/8	7.6	667	16	3.6
2.5/7.5	10.5	634	14	4.0
3/7	13.1	402	10	5.4
4/6	14.6	134	36	6.3

mers behave like thermoplastic elastomers, exhibiting high elongation, low permanent set and suitable melt index. With increase of polystyrene content, the tensile strength and modulus of the block copolymers increase, while elongation decreases. When the polystyrene content reaches 40%, elongation decreases evidently, while the tensile strength and permanent set become larger, and so the block copolymers belong to toughened plastics. These behaviors are similar to that of SBS block copolymers⁶ and the superstructure of the multiblock copolymers can be described as polystyrene domains, formed by aggregation of polystyrene blocks, dispersed in a continuous phase of polypropylene oxide. When the polystyrene content is above 40%, the polystyrene domains may be connected together and tend to form continuous phase, showing the properties of plastics.

\bar{M}_n of the polystyrene block exerts an important influence on the mechanical properties of the block copolymers (Table V). When \bar{M}_n of the polystyrene blocks is $>1.14 \times 10^4$, tensile strength increases slowly with \bar{M}_n of the polystyrene blocks; but when \bar{M}_n of the polystyrene blocks is $<0.86 \times 10^4$, tensile strength of the copolymer decreases significantly and permanent set tends to increase with decreasing \bar{M}_n of the polystyrene blocks. This can be interpreted as that too short polystyrene blocks cannot form domains efficiently, as demonstrated by the well known SBS block copolymers.⁶

Table V. Effects of \bar{M}_n of the PSt block on mechanical properties of the block copolymer^a

$\bar{M}_n \times 10^{-4}$ of PSt block	Tensile strength	Elongation	Permanent
	MPa	%	%
1.65	13.6	426	10
1.14	13.1	402	10
0.86	11.9	417	12
0.57	8.8	450	17

^a PSt: PPO = 3:7.**Table VI.** Effects of the block copolymer^a on the mechanical properties of the blend^b

Block copolymer/ Blend	Tensile strength	Elongation	Permanent set	Shore hardness
	MPa	%	%	
%				
0	4.7	363	19	66
1	10.0	717	11	—
2	11.5	721	6	46
3	9.9	732	12	—
4	9.2	751	12	44
6	8.4	878	15	44
8	7.1	788	19	43
10	7.1	797	22	41

^a Composition of the block copolymer, PSt: PPO = 3:7 (weight ratio).^b Composition of the blend, PSt: ECHR = 3:7 (weight ratio).

When epichlorohydrin rubber was blended with polystyrene alone, the tensile strength was rather low and the permanent set somewhat large. However, if 1–4% of the above mentioned multiblock copolymer of styrene and propylene oxide was added to the blend, the mechanical properties were improved quite a lot, as shown in Table VI. It indicates that the multiblock copolymer can act as a compatibilizer and only a small amount of it is needed. If the block copolymer was used more than 4% of the blend, the tensile strength decreased

Table VII. Glass transition temperature of polystyrene (PSt), epichlorohydrin rubber (ECHR), and their blends

Samples	T_{g1}	T_{g2}
PSt	—	114
ECHR	−15	—
Blend of PSt: ECHR = 3:7	−5	109
Blend of PSt: ECHR = 3:7 and 2% copolymer	−1	85

and permanent set increased with further increasing amount of compatibilizer. Dynamic mechanical analysis shows that T_g 's of the blend are -5°C and 109°C , while those of the blend with addition of 2% block copolymer are -1°C and 85°C (Table VII). The inward shift of T_g 's as compared to those of individual homopolymers denotes that the block copolymer enhances the compatibility of epichlorohydrin rubber and polystyrene. It can be explained by the similar structure between PPO block of the block copolymer and the epichlorohydrin rubber. However, the less shift of T_{g1} is probably due to some difference between the structure of epichlorohydrin rubber and PPO blocks and also a larger difference between their molecular weight.

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