

MOLECULAR DESIGN SYNTHESIS AND PROPERTIES OF SIX KINDS OF MULTIPHASE (STYRENE-ETHYLENE OXIDE) COPOLYMERS

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Multiphase copolymers of styrene (S) and ethylene oxide (EO) are amphiphilic, because of the hydrophobic and amorphous polystyrene (PS) segments and the hydrophilic and crystalline polyoxyethylene (PEO). They have many uses including polymeric surfactants, electrostatic charge reducers, compatibilizer in polymer blending, phase transfer catalysts or solid polymer electrolytes. These copolymers include different types of block copolymers, graft copolymers and star-shaped block copolymers.

In this paper recent progress including our works concerning the molecular design, synthesis, purification, characterization and various properties of six kinds of multiphase (styrene-ethylene oxide) copolymers, namely, PS-PEO diblock copolymers, PS-PEO-PS and PEO-PS-PEO triblock copolymers, $(PS)_2(PEO)_2$ star-shaped block copolymers, PEO-g-PS and PS-g-PEO graft copolymers are reviewed. The structure of these six kinds of copolymers is pictorially represented as follows:



PEO-PS-PEO



PS-PEO



PS-PEO-PS



$(PS)_2(PEO)_2$



PEO-g-PS



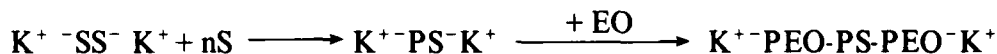
PS-g-PEO

where — represents PS block and ~~~~ PEO block.

1. PEO-PS-PEO triblock copolymers

Szwarc^[1] first reported the synthesis of a PEO-PS-PEO block copolymer (BAB type). He used a successive anionic polymerization of S and EO in tetrahydrofuran that was initiated by naphthalenyl sodium. Finaz and Rempp^[2] described the preparation of a BAB block copolymer with a disodium compound of α -methylstyrene tetramer as the initiator. Zgonnik^[3] used biphenylpotassium as the initiator and tetrahydrofuran as the solvent in a successive polymerization of S and EO to form also a BAB block copolymer. A dipotassium compound of α -methylstyrene tetramer was used by Marti^[4] for the preparation of the same type block polymer.

PEO-PS-PEO triblock copolymers were synthesized by the authors through successive dianionic polymerization of S and EO in toluene using alkali metal naphthalene as initiator as follows^[5]:



The results showed that the activity of alkali metal naphthalenes decreased in the following order: potassium naphthalene > sodium naphthalene > lithium naphthalene. The last of these barely initiates the block copolymerization of EO with the PS anion. If EO was polymerized first and then styrene added, the latter could not be polymerized, since the alkalinity of alkoxide anion is less than that of styrene. In block copolymerization the polymerization rate of EO is far less than that in homopolymerization and much longer time was needed to reach high conversion.

In the course of this block copolymerization a strange phenomenon was observed. After adding EO to living polystyrene and copolymerizing at 60 °C for 8h, bead-like particles appeared uniformly suspended in the copolymerization system. The particles disappeared after shaking and reappeared after setting in 60 °C thermostat. This phenomenon was closely related to the block lengths of PEO and PS (Table 1).

Table 1 Effect of molecular weight of the PEO block on the size of suspended beads

$\overline{M}_{n \text{ Cop}} \times 10^{-3}$	$\overline{M}_{n \text{ PS}} \times 10^{-3}$	$\overline{M}_{n \text{ PEO}} \times 10^{-3}$	Observation
22.7	12.7	10.0	Small beads
25.5	11.5	14.0	Larger beads
28.7	8.6	20.1	Much larger beads with diameter of 1–2mm.

When the molecular weight of either block was too small, only a homogeneous solution of amber color was observed. No such phenomenon appeared for mixed solution of homopolymers with almost the same molecular weight as the blocks. When the copolymerization was terminated, the solution was poured into a culture dish and warmed under an infrared lamp. After a few minutes of heating, a polygonal network of lines appeared on the surface of the solution, which disappeared on shaking and reappeared on setting. Even after the block copolymer was purified, its toluene solution still showed this unusual mesomorphic phenomenon.

The reason for the above phenomenon is probably that a repelling effect produced by thermodynamic incompatibility between hydrophilic polyoxyethylene blocks and hydrophobic polystyrene blocks and the resulting formation of domains of hydrophilic crystallizable polyoxyethylene blocks and hydrophobic polystyrene blocks. When light passed through the solution with these two kinds of domains, refraction of light occurred. When the molecular weight of the one block was sufficiently small, it was difficult to form domains, hence homogeneous solutions of amber color resulted. If the polymerization system was stirred the block domains were destroyed and the system exhibited no suspended beads. The polygonal network line appearance on the surface of the solution perhaps was also due to the domain state of the triblock copolymer.

Water and cyclohexane were used separately for extracting the homopolymers of EO and S from the block copolymer. The efficiency of the extractions was evaluated.

Two extractions for each solvent efficiently separated the homopolymers from the copolymer. According to GPC results, the elution count (V_e) of PS was 46, and its molecular weight distribution was narrow. However, after block copolymerization with EO, the V_e shifted to 43, which indicates a molecular weight increase and the disappearance of PS after extraction. The ^1H NMR spectrum of the copolymer indicated that the two peaks at 6.4 and 6.9 δ are due to the phenyl ring protons, the single peak at 3.5 δ is from the methylene group in the $-\text{OCH}_2\text{CH}_2-$ and the peak at 1.4 δ is due to the $\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2-$ group. Thus, the purified polymer contains both S units and oxyethylene units. TBA curve showed two maxima at 56° and 93°C, corresponding to the T_m of PEO and T_g of PS. All these results indicate that the purified polymer is really a block copolymer.

Two diffuse diffraction rings were observed in the electron diffraction pattern of triblock sample with $\overline{M}_{n\text{PS}} = 41,400$ and $\overline{M}_{n\text{PEO}} = 37,000$. The small angle laser light scattering H_v pattern exhibited diffuse four leaves. A TEM micrograph showed a rod-like aggregate aligned somewhat parallel, indicating that the blocks exist in lamellae.

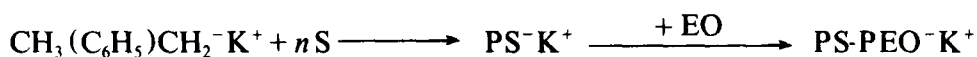
Toluene solution of the triblock copolymer (10wt. %) was a viscous liquid. When poured onto a glass plate, it took days to dry. In comparison, the viscosity for the solution of the homopolymer mixture was lower and the film formed only after several minutes. Under polarized microscope the triblock copolymer with $\overline{M}_{n\text{PS}} = 12,700$ and $\overline{M}_{n\text{PEO}} = 10,000$ in toluene solution exhibited a change from transparent and isotropic to a phase-separated anisotropic form with the increase of copolymer concentration. The depolarizing effect increased with the increase of copolymer concentration.

2. PS-PEO diblock copolymers

The PS-PEO block copolymer (AB type) was synthesized by O'Malley et al., using a successive anionic polymerization of S and EO with cumylpotassium as initiator^[2,4,6]. Minoura^[7] reported the preparation of an AB block copolymer by first dissolving PEO in S and then stirring the mixture with very high speed to produce free radicals and initiate the polymerization of styrene. The product obtained was not well characterized, however, and a large amount of homopolymers might be produced.

Recently Ueda and Nagai^[8] synthesized block copolymer of S and EO through polycondensation between azobis-cyanopentanoyl chloride and polyethylene glycol, followed by thermal decomposition in the presence of styrene. Yuruk and Ozdemir^[9] prepared the block copolymer using polymeric azocarbamate as an initiator, which was obtained by capping polyethylene glycol with aliphatic diisocyanate and subsequently by reacting this intermediate with azobiscyanopentanol. The macroazocarbamate was then used to initiate free radical polymerization of S at elevated temperature. Niwa et al.^[10] synthesized a macroinitiator through reaction of sodium ω -methoxypolyethylene glycol with tribromoacetyl chloride. Styrene was initiated with the macroinitiator in the presence of manganese carbonyl to form block copolymer.

PS-PEO diblock copolymers were synthesized by us through successive anionic polymerization of S and EO with α -phenyl ethyl potassium as a new initiator in toluene according to the following equation^[11,12]:



During the polymerization of styrene using this initiator, an induction period was observed. Length of the induction period decreased with increasing temperature of polymerization. Induction period can be somewhat shortened by adding a certain amount of tetrahydrofuran corresponding to the equivalent amount of α -phenyl ethyl potassium, but not very obviously. Probably the existence of induction period was not due to association of catalyst, but due to the increase of catalyst solubility in toluene with the increase of temperature, resulting in the change from heterogeneous phase to homogeneous phase and shortening of induction period.

Increase of temperature for the copolymerization of living PS with EO from 10 °C to 30 °C enhanced the conversion of EO obviously. At 30 °C 92% conversion of EO reached within 11h.

Water and cyclohexane were also proved to be used effectively as extracting agents for PEO and PS homopolymers. The diblock copolymer after purified by extractions appears white and granular, insoluble in cyclohexane, swelling in water but soluble in benzene, toluene, tetrahydrofuran and acetone.

IR spectrum of the purified diblock copolymer indicated a characteristic peak at 1120cm^{-1} for the ether linkage, a multipeak at 1610 and 3040cm^{-1} for the benzene ring and a single peak at 2930cm^{-1} for the methylene group. The ^1H NMR spectrum of the PS-PEO copolymer showed the same characteristic peaks as that of the PEO-PS-PEO copolymer.

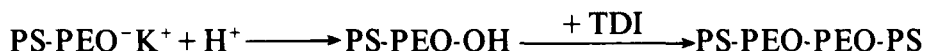
However, the peak in the GPC curve appears somewhat wider than that of the PEO-PS-PEO triblock copolymer. This increase in peak width is probably due to the poor solubility of α -phenyl ethyl potassium in toluene. DSC curve demonstrated the T_m of the PEO block, the T_g of the PS block, an exothermic transition of liquid crystals at about 180 °C and a single decomposition temperature (T_d) of the copolymer. However, two T_d 's occurred for the blend of homopolymers.

3. PS-PEO-PS triblock copolymers

The PS-PEO-PS block copolymer (ABA type) cannot be obtained directly by anionic polymerization because of the weak alkalinity of the PEO anion, which cannot initiate the polymerization of styrene. Therefore, Finaz and Rempp^[2] reported the synthesis of an ABA block copolymer by treating the PS anion with an excess of COCl_2 in toluene. This mixture was then reacted with polyethylene glycol in the presence of pyridine. Such type of copolymer was also prepared by Orhan^[13] via a reaction of polyethylene glycol with diisocyanate to form the isocyanate-capped prepolymer. The NCO group was then reacted with dihydroperoxide to peroxy carbamate, which then initiated radical polymerization of styrene. Obviously, the product obtained by radical polymerization had wide molecular weight distribution and contained an amount of homopolymer from chain transfer.

Seiler^[14] obtained the same type of copolymer by coupling an AB block copolymer with one hydroxyl end group and using butadiene diepoxide as the coupling agent. Lundberg^[15] combined a PS containing one OH group with polyethylene glycol by using toluene 2,4-diisocyanate as the coupling agent in the synthesis of a PS-PEO-PS copolymer.

We obtained the PS-PEO-PS block copolymer by coupling PS-PEO block copolymer with toluene 2,4-diisocyanate as outlined below^[11, 12]:



The crude product can be purified by fractional precipitation, using toluene as solvent and petroleum ether as precipitant. The condition that the diblock copolymer just began to precipitate was determined as precipitation point first, then the crude triblock copolymer was fractionally precipitated according to this condition. At the precipitation point most of the diblock copolymer remained in the solution, whereas most of the precipitate was the triblock copolymer. The $\overline{M}_n$ of the triblock copolymer obtained was almost twice as much as that of the diblock copolymer used. For example, $\overline{M}_n$ of one sample of the diblock copolymer was determined by membrane osmometry to be 2.75×10^4 and after coupling with toluene 2, 4-diisocyanate it became 5.84×10^4 . The ratio of these two $\overline{M}_n$ is 2.12.

The emulsifying properties of the block copolymers were studied by Riess and his coworkers^[6], who demonstrated that the PS-PEO block copolymer could act as a nonionic surfactant in the emulsification of a water-toluene mixture and the preparation of a microemulsion with the addition of a cosurfactant. They also correlated the molecular characteristics of the block copolymers to the emulsifying properties.

The emulsifying properties of the block copolymers in the water/toluene system was measured by us using a conductometric method^[11]. An emulsion was formed by adding water to the toluene solution. When the emulsion changed from the oily continuous phase to aqueous continuous phase, an abrupt rise in conductivity was detected. The conductivity began to fall when the amount of water added reached a critical value, over which the emulsion was destroyed, and phase separation into two layers resulted. The critical amount of water added per definite weight of copolymer was defined as the emulsifying ability of the block copolymer. Our results indicated that the emulsifying ability of the block copolymers increased with PEO content. At a similar PEO content, $\overline{M}_n$ and concentration, the emulsifying ability decreases in the following order: PEO-g-PS > PEO-PS-PEO > PS-PEO > PS-PEO-PS.

This difference is probably due to the following reasons: In the PEO-PS-PEO block copolymer, the PEO blocks are at both ends of the chain and easily interact with water. In the PS-PEO or PS-PEO-PS block copolymers, the PEO block is shielded by the PS block at one end or two ends of the chain, and the emulsifying ability is less. In the graft copolymer, hydrophobic PS grafts of equal length are distributed along the hydrophilic PEO chain. When water is added to this toluene solution, the PEO chain is probably in a ring-like structure in the toluene solution. Therefore the hydrophobic grafts are arranged outside the ring, and water is included within the ring. Hence, the emulsifying ability is enhanced.

Lotz and Kovacs^[17] investigated the crystalline properties of the block copolymers of S and EO and indicated their lamellar crystalline structure. Crystal et al.^[18] observed that the block copolymer cast from chloroform or ethylbenzene exhibited spherulite structure.

Our work showed that crystallinity of the block copolymers determined by WAXD increases with PEO content and decreases in the following order^[11]: PEO-PS-PEO > PEO-PS > PS-PEO-PS (Figure 1). Perhaps, in the PS-PEO-PS triblock copolymer, amorphous PS blocks at the ends of PEO block limit the folding of the PEO block. In the PEO-PS-PEO copolymer, however, the PEO blocks

situated at the ends of the chain can be folded more freely and easily, and thus, crystals can be formed more completely.

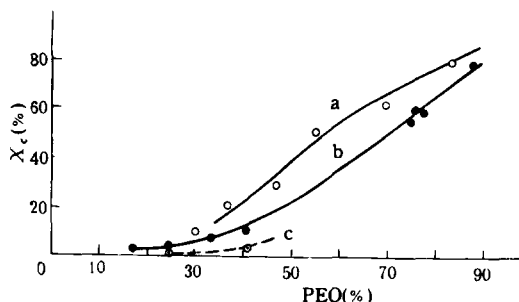
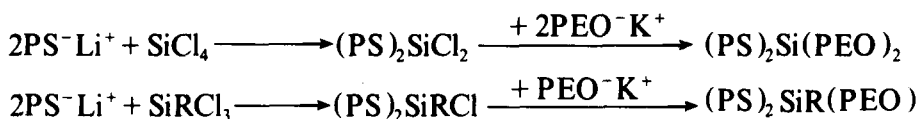


Fig.1 Relationship between PEO content and crystallinity (X_c):
(a) PEO-PS-PEO, (b) PEO-PS, and (c) PS-PEO-PS

4. Star-shaped block copolymers of S and EO

Huynh-Ba-Gia et al.^[19] obtained star-shaped PS (PEO)₂ block copolymer through polymerization of EO using a dianionic initiator formed by metallation of naphthalene terminated PS with potassium.

We prepared the star-shaped block copolymers with two arms of PS blocks and two arms of PEO blocks by coupling living PS anions first and then living PEO anions using SiCl₄ as the coupling agent and the star-shaped copolymers with two arms of PS blocks and one arm of PEO block using CH₃SiCl₃ as the coupling agent^[20, 21, 22] as follows:



When SiCl₄ was dropped into a solution of PS anions, the red color of the anion did not disappear even at a SiCl₄:PS anion ratio of 1:4. GPC analysis showed that only half of the PS anions were coupled. But when the ratio of SiCl₄:PS anions reached 1:2 the red color disappeared, while the GPC trace showed that most of the PS anions had changed into a product having the double molecular weight. These results indicate that only two atoms of chlorine in SiCl₄ can be exchanged vs. PS anions, due to steric hindrance. However, when PEO anions are coupled by SiCl₄, all the four chlorine atoms can react with the anions. Obviously, the steric hindrance of PEO anions is much less than that of PS anions.

Purification of the block copolymers is better carried out by first dissolving the crude product in toluene, then extracting the toluene solution with a large amount of water to remove the homopolymer of EO. This method can be used to prevent from losing some of the block copolymer during extraction with water. The homopolymer of S can be removed by extracting the residue of toluene solution after evaporation with diethyl ether. The purified star-shaped block copolymers are white, stable solids, soluble in benzene, toluene, tetrahydrofuran, chloroform, but slightly soluble in water, ethanol or diethyl ether.

GPC curves indicated that (PS)₂(PEO)₂ from SiCl₄ and (PS)₂(PEO) from CH₃SiCl₃ are rather pure, while (PS)₂(PEO) from SiCl₄ contained a small amount of

$(PS)_2(PEO)_2$. Molecular weight values of the purified $(PS)_2(PEO)_2$, determined by GPC, fit well with the values calculated on the basis of the molecular weight of PS and PEO precursors.

Both IR spectrum and ^1H NMR spectrum confirmed that the purified copolymer contains both monomeric units of S and EO. Torsional braid analysis of the purified copolymers indicated that two transition temperatures appear at 56° and $93^\circ C$ corresponding to the T_m of PEO and T_g of PS. This implies the occurrence of microphase separation and also indicates that the purified copolymer is really a block copolymer.

Crystallinity of the purified star-shaped block copolymers increases with the PEO content or with the molecular weight of the copolymers. When the copolymer is quenched in petroleum ether at $20^\circ C$, spherulites, observed under polarized microscope, seem to be more regular than those of the copolymer quenched at $0^\circ C$. Probably there was not enough time allowed for the PEO units to crystallize regularly into spherulites at $0^\circ C$. The spherulites were regular when the copolymer was cast from chloroform rather than from ethylbenzene, since chloroform is a good solvent for both PEO and PS blocks, while ethylbenzene is a good solvent for PS blocks, but a poor solvent for PEO blocks.

These star-shaped block copolymers exhibit the same peculiar mesomorphic behavior in toluene solution as PEO-PS-PEO triblock copolymers do.

Huynh-Ba-Gia et al.^[19] studied the emulsifying properties of their star-shaped block copolymer of S and EO using emulsifying volume to express the emulsifying properties. The emulsifying volume was taken as the total volume of water plus the benzene solution of the copolymer before mixing minus the volume of water separated after thoroughly mixing and then setting.

From the study of the emulsifying volume of the star-shaped block copolymers synthesized by us it showed that at constant amount and percentage of PEO in the copolymer, the smaller the molecular weight of the copolymer, and the higher the number of arms, the larger the emulsifying volume. This may be explained by the increase of emulsifying centers as the molecular weight of the copolymer decreases. The emulsifying volume increases with PEO content of the copolymer.

Kelly et al.^[23] observed that the PS-PEO block copolymer could form a toluene-soluble complex with potassium phenolate and used it as phase transfer catalyst in the Williamson reaction.

UV absorption indicated that the star-shaped block copolymers prepared could complex with alkali metal picrates^[20]. After addition of increasing amounts of the copolymer to a lithium picrate solution in tetrahydrofuran, the absorption maximum shifted to a larger and larger wavelength until it reached a certain value. The absorption spectra can be classified in two groups: the first group of spectra with a maximum absorption at relatively shorter wavelength (about 340nm) in the presence of smaller amounts of copolymer, indicates a complex of lithium bound peripherally by the PEO units, while the second group of spectra with a maximum absorption at longer wavelength (about 375nm) in the presence of larger amount of copolymer is attributed to the formation of a second complex, in which the PEO units are inserted into the ion pairs of the salt. Similar changes of the UV absorption occurred in the case of potassium or sodium picrates with the same limit wavelength of absorption at 380nm. However, the maximum absorption wavelength of the lowest absorption peak for the

picrates of lithium, sodium and potassium is located at 357, 363 and 366nm, respectively.

Lithium picrate is slightly soluble in chloroform or toluene, while sodium or potassium picrates are insoluble. Addition of the star-shaped block copolymer enhances the solubility of the alkali metal picrates in chloroform or toluene. The order of enhancing solubility of the alkali metal picrate in toluene is: star-shaped block copolymer > diblock copolymer > PEO. The star-shaped block copolymer with PEO contents of 40 — 50% exhibits the largest effect. The solubility of alkali metal picrates, complexed with the copolymer in toluene, decreases in the following order: $\text{Li} > \text{K} > \text{Na}$ (Table 2).

Table 2 Solubility of different alkali metal picrates (PiM) complexed with different PS-PEO block copolymers in toluene

Polymer	Content of PEO in wt (%)	Solubility in mmol / l		
		PiLi	PiNa	PiK
$(\text{PS})_2(\text{PEO})_2(1)$	53.9	14.5	4.0	11.1
$(\text{PS})_2(\text{PEO})_2(2)$	48.4	15.0	6.9	14.7
$(\text{PS})_2(\text{PEO})_2(3)$	38.7	14.6	6.5	13.2
$(\text{PS})_2(\text{PEO})_2(4)$	68.5	8.8	1.8	2.6
$(\text{PS})_2(\text{PEO})_2(5)$	28.0	4.5	1.3	2.4
$(\text{PS})(\text{PEO})$	49.0	6.2	2.6	5.4
$(\text{PS})_2(\text{PEO})$	33.0	4.9	2.1	3.1
PEO	100.0	5.8	1.6	2.4

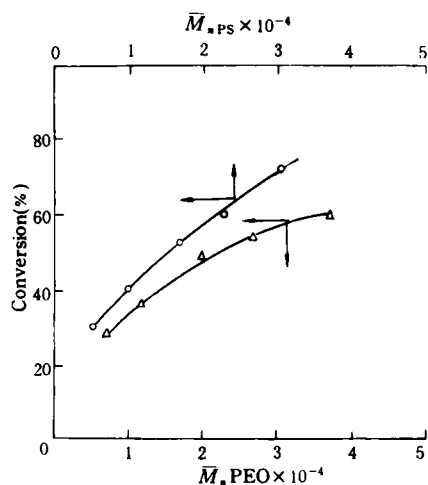


Fig. 2 Effect of molecular weights of PS block or PEO block on conversion of potassium phenolate during Williamson reaction

Since the PEO-containing copolymers can complex with alkali metal picrates, they were tried as phase transfer catalyst in the Williamson reaction. They evidently increase the yield of the reaction between solid potassium phenolate and butyl bromide in toluene. The order of catalytic efficiency is: star shaped block copolymer > diblock copolymer > PEO. The catalytic efficiency increases with the molecular weight of the PEO block and the PS block (Figure 2)

Ionic conductivity of salt complexes of the star-shaped copolymers of EO and S were studied by us^[24]. At a $\text{CH}_2\text{CH}_2\text{O}$ /cation ratio or $\text{EO}/\text{M} = 20$, all the Arrhenius conductivity plots consist of two straight-line regions with a discontinuity at a temperature range between 45 °C and 60 °C. Below 45 °C the crystalline

phase of PEO, the amorphous phase of PEO with dissolved salt and the polystyrene phase may exist together. DSC analysis demonstrated the endothermic melt peak of PEO, T_g of the polystyrene phase and also T_g of the PEO complex. In the temperature range of 45 — 60 °C, the crystalline phase of PEO melts gradually or changes into amorphous phase complexed with cations, thus markedly enhancing the cation transport and increasing the conductivity. Then the conductivity increases

gradually with further rise in temperature due to reduction of viscosity of the PEO melt. For the KCNS complex of the star-shaped block copolymer with $EO/K=20$, the conductivity reaches the value of $2 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C . At $EO/K=4.5$ the Arrhenius plot is linear from room temperature to 100°C . It implies that no phase transition from crystalline PEO to amorphous PEO occurs.

The conductivity decreases in the following order of cations: $K^+ > NH_4^+ > Na^+$. The DSC curve showed that T_m of the crystalline PEO in the NaCNS complexes decreases with the decrease of the EO/Na ratio, until T_m of PEO disappears at $EO/Na=4$ and T_m of the crystalline complex appears. WAXD also illustrates the same phenomenon.

At about the same PEO content of the copolymer and $EO/Na=20$, the less the molecular weight of PEO arms, the higher is the conductivity of the NaCNS complex. This is ascribed to the lower crystallinity of the copolymer with lower molecular weight of PEO. If the molecular weight of the PEO arms in the copolymer is kept almost constant, conductivity decreases with reduction of PEO content, since too much polystyrene, especially more than 60%, will make the PEO phase become discontinuous, restricting the cation transport through the copolymer complex and thus resulting in decrease of room temperature conductivity.

It is very interesting to reveal that the $FeCl_2$ complex exhibits conductivity even higher than NaCNS but lower than KCNS.

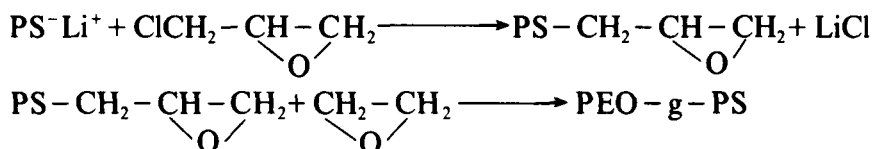
γ -Butyrolactone exerts significant influence on the conductivity of the NaCNS complex of the star-shaped block copolymer. On addition of 25% γ -butyrolactone the room temperature conductivity increases about 2.5 orders of magnitude, reaching the value of $2 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C . γ -Butyrolactone plays a role of plasticizer, increasing the polarity of the medium and decreasing the viscosity and the crystallinity of PEO, thus enhancing the ionic conductivity. DSC curves demonstrated that with increasing amount of γ -butyrolactone added, not only T_m and T_g of the PEO complex but also T_g of the polystyrene arms decreased. Thus γ -butyrolactone enhances the mobility of both the PEO segments and the PS segments.

The star-shaped block copolymers of S and EO can be used as compatibilizer for blending epichlorohydrin rubber and polystyrene. Mechanical properties of unvulcanized epichlorohydrin rubber is rather poor, possessing low tensile strength and very large ultimate elongation and permanent set. Blending this rubber with 30% polystyrene increases the tensile strength but decrease notably the ultimate elongation down to less than 100%. Addition of 2% star-shaped block copolymer of S and EO to the blend not only increases further the tensile strength, but also raising the ultimate elongation and decreases the permanent set. This demonstrates that the star-shaped block copolymer of EO and S enhances the interfacial adhesion of the two phases with two arms of PS blocks distributed in the PS phase and with two arms of PEO blocks distributed in the epichlorohydrin rubber phase.

5. PEO-g-PS copolymer of EO with uniform PS grafts

No work except ours has been published concerning the synthesis of EO copolymer with uniform PS grafts. We obtained these copolymers through copolymerization of epoxy ether terminated polystyrene macromonomer with EO in toluene using $i\text{-Bu}_3\text{Al-H}_2\text{O-H}_3\text{PO}_4$ -dimethyl aniline (DMA) as catalyst^[25]. The epoxy

ether terminated polystyrene was prepared by termination of living polystyrene anion with epichlorohydrin in cyclohexane. Synthesis of the macromonomer and its copolymerization with ethylene oxide are briefly denoted in the following equations:



The actual wt. % of PS containing epoxy end group in the macromonomer only amounts to 35% due to some side reactions between epichlorohydrin and the polystyrene anion.

According to the grafting efficiency or conversion of the macromonomer the quaternary catalyst ($i\text{-Bu}_3\text{Al-H}_2\text{O-H}_3\text{PO}_4\text{-DMA}$ catalyst) seems to be more effective than Vandenberg catalyst or bimetallic oxo-alkoxide catalyst. The optimum ratio of the four components of the quaternary catalyst is $i\text{-Bu}_3\text{Al} : \text{H}_3\text{PO}_4 : \text{H}_2\text{O} : \text{DMA} = 1.0 : 0.15 : 0.15 : 0.10$. The grafting efficiency increased with the amount of catalyst used, up to about 3% with respect to the total amount of EO and the macromonomer.

The grafting efficiency decreased with the increase of molecular weight of the macromonomer. This is attributed to the increase of viscosity and steric hindrance caused by the increase of molecular weight of the macromonomer. The grafting efficiency diminished as the macromonomer concentration increased. Evidently, this is caused by the lower reactivity and larger steric hindrance of the macromonomer as compared to EO, when higher concentration of the macromonomer was used in the copolymerization.

The rate of individual conversion of the macromonomer is much slower than that of EO probably due to the smaller mobility and larger steric hindrance of the macromonomer. After most of EO is consumed, the phenyl content of the product increases gradually with copolymerization time. Since the macromonomer does not homopolymerize easily due to steric hindrance and the quaternary catalyst has a long life with chain transfer, competition of the macromonomer with PEO molecules for reaction with active center may occur, resulting in more or less redistribution of polystyrene grafts.

The graft copolymer can be successively purified by extractions with cyclohexane and with 20% ethyl alcohol which is better than water for extraction.

The IR spectrum of the purified graft copolymer exhibited a strong absorption peak at 1120 cm^{-1} , a multipeak at 1610 and 3040 cm^{-1} and a peak at 2930 cm^{-1} which are the characteristic of the ether linkage, phenyl ring and methylene group respectively. Torsional braid analysis showed the melting temperature of PEO crystals and the T_g of PS which indicates microphase separation in the graft copolymer.

Average grafting number (N_g) of the purified graft copolymer can be calculated by the following equation :

$$N_g = \frac{M_{nc} \times W_g}{M_{ng}}$$

where M_{nc} and M_{ng} are the number average molecular weight of the copolymer and

the macromonomer determined by membrane osmometry and vapor pressure osmometry respectively, whereas W_g is the weight fraction of polystyrene in the copolymer. Average grafting number of these graft copolymers were determined to be 4—8 (Table 3)

Table 3 Structural parameters of some samples of PEO-g-PS copolymers

$M_{nc} \times 10^{-4}$	$M_{ng} \times 10^{-4}$	W_g	N_g
10.4	0.55	0.30	5.7
11.3	0.55	0.31	6.4
7.5	0.89	0.45	3.8
7.8	0.31	0.30	7.5
7.1	0.55	0.47	6.1

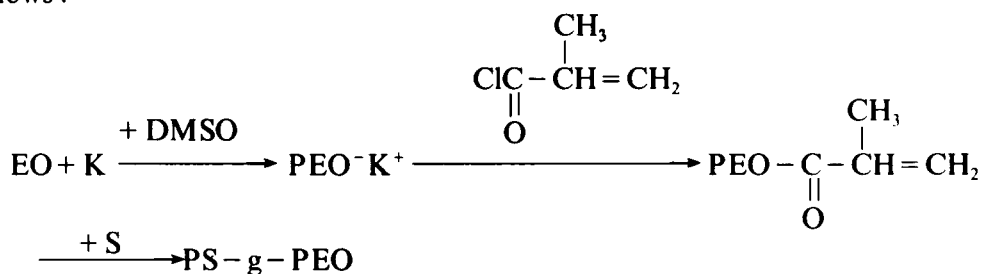
The emulsifying ability of this graft copolymer is higher than that of the block copolymers at the same PEO content as mentioned above.

The graft copolymer can absorb a large amount of water. The water-absorbing ability appears large and the quantity of water absorbed per PEO segments can reach 24. After absorption it changes from a white hard solid to an elastomer. Since water increases the distance between PEO chains and reduces the crystallinity of PEO, the PEO segment becomes flexible and the hydrophobic polystyrene grafts aggregate into domains, resulting in a network.

6. *PS-g-PEO, copolymers of S with uniform PEO grafts*

Ito et al.^[26, 27] synthesized graft copolymer of S with uniform PEO grafts through copolymerization of S with PEO macromonomer. They obtained PEO macromonomers using potassium tertiary butoxide as initiator and methacryloyl chloride or p-vinyl benzyl chloride as terminating agent.

This type of graft copolymers was obtained by us through copolymerization of styrene with PEO macromonomer which was synthesized by anionic polymerization of EO in dimethylsulfoxide using potassium naphthalene in tetrahydrofuran as initiator, followed by termination with methacryloyl chloride. The reactions are shown as follows :



This method of macromonomer synthesis^[28, 29] improved by us has the advantage of shorter reaction time and a larger range of molecular weight of the PEO macromonomer obtained than the usual method using potassium alcoholate as initiator. PEO macromonomers with molecular weight from 2×10^3 to 1.3×10^4 and $\overline{M}_w / \overline{M}_n = 1.07 - 1.12$ can be obtained by this method. The macromonomers as shown by UV, IR and ^1H NMR have one double bond in the molecule. The methacrylate terminated PEO macromonomers can be copolymerized with styrene having a reactivity ratio r_2 of 1.32 ± 0.12 which is higher than that of methyl

methacrylate during copolymerization with styrene ($r_2 = 0.57$). This is probably due to the larger size of the macromonomer which reduces the diffusion rate and increases the steric hindrance during copolymerization.

The PS-g-PEO copolymers were purified by extractions three times with diethyl ether and three times with water. GPC curve of the purified graft copolymer showed that they were free from contamination with the PEO macromonomer^[29].

This type of graft copolymers can also emulsify water / benzene system and enhance the Williamson reaction between solid potassium phenolate and benzene solution of butyl bromide. However, in comparison of the graft copolymers with different backbone structures but with the same uniform PEO grafts, the emulsifying ability and phase transfer catalytic efficiency of the copolymer decrease in the order: PMMA-g-PEO > PMA-g-PEO > PS-g-PEO, where PMMA is polymethyl methacrylate and PMA polymethyl acrylate. This may be attributed to the different conformation of the copolymer in benzene solution. The backbone of PS-g-PEO is not very flexible because of the steric hindrance of benzene rings, while PMA and PMMA backbones are more flexible in benzene, resulting in looser arrangements of PEO grafts in PMA-g-PEO or PMMA-g-PEO and larger probability of contact with water, thus increasing the emulsifying volume. The presence of methyl groups in PMMA-g-PEO makes the backbone more soluble in the organic phase than PMA-g-PEO and thus enhances the emulsifying power of the former. The effect of backbone on the phase transfer catalytic efficiency is also related to the conformation and solubility of the graft copolymers in toluene.

Metallic ion complex of the graft copolymer exhibits ionic conductivity decreasing in the order: KCNS > LiClO₄ > FeCl₂^[24]. For different kinds of copolymers with uniform PEO grafts, conductivity of the complexes increases in the order: PS-g-PEO < PMMA-g-PEO < PMA-g-PEO, while crystallinity of PEO complexes increases in the opposite order: PMA-g-PEO < PMMA-g-PEO < PS-g-PEO.

CONCLUSION

We have succeeded in synthesizing six kinds of multiphase (styrene-oxyethylene) copolymers, which differ in molecular architecture. PEO-PS-PEO triblock copolymer has been obtained by using successive dianionic polymerization, PEO-PS diblock copolymer through successive anionic polymerization initiated by a new initiator and PS-PEO-PS triblock copolymer through coupling of PEO-PS with toluene diisocyanate. Two kinds of graft copolymers with uniform grafts, namely, PEO-g-PS and PS-g-PEO have been prepared using macromonomer techniques. Epoxy ether terminated polystyrene macromonomers were synthesized and method of synthesizing PEO macromonomer was improved. By means of coupling living PS and PEO anions with SiCl₄ or CH₃SiCl₃, star-shaped block copolymers have been synthesized.

All of the above mentioned copolymers were purified by extraction or fractional precipitation and the purified products were characterized by IR, ¹H NMR, and GPC. DSC or torsional braid analysis curves showed that they were multiphase polymers. Some of them exhibit special mesomorphic phenomena in toluene solution. Special properties of some copolymers, such as emulsifying properties, crystalline properties, phase transfer catalytic effect, complexing properties with metallic ions and also ionic

conductivity of their metallic ion complex have been studied. They also show the possibility for use as a compatibilizer for the blend of epichlorohydrin rubber and polystyrene. The above mentioned properties have the promising prospect for industrial utilization.

Keywords :

Multiphase polymers; Amphiphilic copolymers; Graft copolymers; Block copolymers; Macromolecular design.

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