Synthesis and Properties of Unsaturated Polyoxyethylene and Its Graft Copolymers with Styrene

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ABSTRACT: The unsaturated polyoxyethylene (PEO) was synthesized by copolymerization of ethylene oxide with allyl glycidyl ether in toluene using bimetallic-oxo-alkoxide as a catalyst. The effects of polymerization conditions on conversion and intrinsic viscosity of the copolymer were studied. The unsaturated copolymer was characterized with infrared spectra, ^{1}H NMR, and wide-angle X-ray diffraction. The relationship between crystallinity of the copolymers and conductivity of their $LiClO_4$ complexes were investigated. The copolymer with $\sim$ 65 wt % PEO content exhibits a room temperature conductivity of 1×10^{-4} S cm^{-1} at a molar ratio of EO/Li = 20. The unsaturated PEO was graft-copolymerized with styrene using 2,2′-azobis(isobutyronitrile) as initiator in toluene, with grafting efficiency $\sim$ 50%. The purified graft copolymer was characterized with infrared spectra, ^{1}H NMR, and wide-angle X-ray diffraction, and was shown to have good emulsifying properties and a phase-transfer catalytic property. $LiClO_4$ complex of the graft copolymer with 70 wt % PEO content exhibits a room temperature conductivity approaching 1×10^{-4} S cm^{-1} at molar ratio of EO/Li = 20/1. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2417–2425, 1998

Key words: polyoxyethylene; graft copolymerization; styrene; allyl glycidyl ether; conductivity; amphiphilic copolymer

INTRODUCTION

Since Wright[1] discovered that fast ion transport took place in the complex between polyoxyethylene (PEO) and various alkali metal salts at $\sim$ 100°C and Armand[2] pointed out potential application of the PEO complexes to solid electrolytes in high-energy density batteries, widespread interest has developed in the PEO complexes. However, the main disadvantages of using the high molecular weight PEO is the high crystallinity, which reduces the ionic conductivity at room temperature. Thus, many research works have paid attention to the use of PEO-containing block copolymers,[3,4] comb or graft copolymers,[5,6] crosslinked polymers,[7] interpenetrating polymer networks,[8] and polymer blends[9] to replace the high molecular weight PEO to raise both the room temperature conductivity and the mechanical strength. PEO and its copolymers can be synthesized by ring-opening polymerization of ethylene oxide (EO) using different kinds of catalysts. Osgan and Teyssie[10] used the bimetallic-oxo-alkoxide catalyst for polymerization of alkylene oxides. Hsieh[11] and Kuntz[12] studied the copolymerization of epichlorohydrin and propylene oxide with allyl glycidyl ether (AGE) using AlR_3-H_2O-$Zn(acac)_2$ and $Zn(C_2H_5)_2$-H_2O-$R_2Al(acac)$ as catalysts, respectively, in order to obtain an unsaturated type of chlorohydrin rubber or polypropylene

oxide rubber for vulcanization with sulfur. Alloin and Sanchez[13] used Vandenberg catalyst or potassium *t*-butoxide as initiator in ring-opening copolymerization of EO and AGE at 100°C for 24 h under pressure, followed by using dibenzoyl peroxide to crosslink the unsaturated copolymer. They indicated that the Li^+ complexed network showed a room temperature conductivity above 5 $\times$ 10^{-5} S cm^{-1}. In 1985, Ito and colleagues[14] synthesized polystyrene (PSt) grafted with PEO (i.e., PSt-*g*-PEO) using methacrylate-terminated PEO macromer. At the same time, we synthesized PEO-*g*-PSt using epoxy-terminated polystyrene macromer[15] and studied its emulsifying property.

This article deals with the synthesis of the unsaturated PEO *via* copolymerization of EO and AGE using the bimetallic-oxo-alkoxide as catalyst and synthesis of its graft copolymers (PEO-*g*-PSt) *via* copolymerization of the unsaturated PEO with styrene (St). The goals of our work are to: (1) decrease the crystallinity of PEO to enhance the conductivity of its complex with Li salt; (2) increase the strength of EO-AGE copolymer by graft copolymerization with St; and (3) use the amphiphilic graft copolymer as emulsifier and phase-transfer catalyst.

EXPERIMENTAL

Materials

All of the reagents and solvents were chemically pure except $LiClO_4 \cdot 3H_2O$, which was an analytical reagent. EO and St were purified and dried as usual.[15,16] AGE was prepared by reacting allyl alcohol with epichlorohydrin using boron trifluoride etherate as a catalyst at 55°C for 4 h, followed by dropping 50% NaOH into the mixture at 20°C and stirring for 4 h. The crude product was washed with water and distilled under reduced pressure. Bimetallic-oxo-alkoxide catalyst was prepared by reaction between aluminium isopropoxide and zinc acetate as follows: solution of 9 g zinc acetate and 20.4 g freshly distilled aluminium isopropoxide in 50 mL decahydronaphthalene was refluxed for 8 h, followed by distillation to remove isopropyl acetate formed. After refluxing further for 8–9 h and cooling, the product was distilled under reduced pressure till dry, then dissolved in 180 mL petroleum ether and filtered. The filtrate contained the bimetallic-oxo-alkoxide, which was analyzed by titration with

EDTA to determine the concentration of Al^{3+} and Zn^{2+} ions.

Copolymerization of EO and AGE to Form the Unsaturated PEO

To calculated amounts of AGE and toluene solution of EO was added a certain amount of bimetallic-oxo-alkoxide solution with stirring under nitrogen atmosphere. Copolymerization was conducted at 60°C for 10 h and terminated with a 1% ethanol solution of hydrochloric acid. The copolymer was precipitated and washed three times with petroleum ether containing antioxidant 264. Then, the unsaturated PEO was vacuum-dried to constant weight.

Graft Copolymerization of St on the Unsaturated PEO

The unsaturated PEO containing 9.8 wt % AGE—determined by ^{1}H NMR, and with a molecular weight of 12.2×10^4 determined by membrane osmometer—was dissolved in dimethylformamide (DMF), and St was added. After purging with nitrogen gas, a calculated amount of 2,2′-azobis(isobutyronitrile) (AIBN) was added with stirring. The graft copolymerization was conducted at 70°C for 20 h and terminated with dioxane containing *p*-hydroxyphenol. The solvent was evaporated and the residue vacuum-dried at 40°C. The crude product was weighed and purified by extraction with 20% ethanol three times each for 12 h to remove the unreacted copolymer of EO and AGE. After drying, the product was weighed and further extracted with hot cyclohexane three times each for 12 h to remove homopolymer of St. The purified product was vacuum-dried and weighed.

Grafting efficiency and content of PEO in the graft copolymer were calculated as follows:

$$G.E. \ (\%) = \frac{(Wt._{CrP.} - Wt._{PSt} - Wt._{PAE}) \times 100}{(Wt._{CrP} - Wt._{PAE})}$$

PEO content (%)

$$= \left(1 - \frac{(Wt._{CrP} - Wt._{PAE}) \times G.E./100}{Wt._{PuP}}\right)(100 - 9.8)$$

where G.E. is grafting efficiency, CrP is the crude product, PAE is the AGE-EO copolymer charged, PuP is the purified product, and 9.8 is the AGE wt % of PAE.

Characterization

Intrinsic viscosity of the unsaturated PEO copolymer was determined by Ubbelohde viscometer at $35 \pm 0.1°C$ using water as solvent. Infrared (IR) spectra of both the unsaturated copolymer and the graft copolymer were taken by the PE-580B IR spectrophotometer. ^{1}H NMR spectra of both copolymers were obtained by the Bruker AC-80 NMR spectrometer, using D_2O as solvent and tetramethyl silane as internal standard. Crystallinity of the copolymers and their complexes was determined by wide-angle X-ray diffraction using a Rigaku 3015 X-ray diffractometer and calculated according to the literature.[16]

Preparation of the LiClO$_4$ Complex of the Copolymers and Measurement of Conductivity[17]

An accurately weighed amount of the copolymer sample was dissolved in benzene, and a calculated amount of tetrahydrofuran solution of Li-ClO$_4$ was added with a measuring pipet during stirring. Then, the solution was poured into a culture dish and evaporated. After vacuum-drying, the complex was hot-pressed in a die into a pellet ($\sim$ 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminium disks at 80°C and then kept in a vacuum desiccator with fresh P_2O_5 for 1 day. Ac conductivity was measured with a DDS-11 conductometer using copper electrodes operated at a frequency of 1100–1200 Hz and a voltage of 1.2 V. Before measurement, the sample was equilibrated with P_2O_5 in the conductivity cell for 1 day. The determination was repeated once more. Usually, no further reduction in conductivity at room temperature was observed.

Emulsifying Property of the Graft Copolymer

The emulsifying property was represented by emulsifying volume,[18] which was determined as follows: a weighed amount of graft copolymer sample was dissolved in 10 mL DMF. To the solution was added 30 mL toluene and 10 mL water. After shaking for 10 min, the mixture was poured into a 100-mL measuring cylinder and covered. After standing for 48 h, the difference between the total volume of the mixture and the volume of lower layer of water containing DMF was recorded as emulsifying volume.

Phase-Transfer Catalytic Property[18] of the Graft Polymer

A weighed amount of the graft copolymer was mixed with 1 g (accurately weighed) solid potas-

Figure 1 Effect of total monomer concentration on the copolymerization (EO/AGE = 90/10 molar ratio, catalyst/monomers = 5 wt %).

sium phenolate, 2 mL n-butyl bromide, and 40 mL toluene. Reaction of the mixture was conducted with stirring at 90°C for 4.5 h. After reaction, a small amount of distilled water was added. Conversion of potassium phenolate was obtained by titration of the unreacted potassium phenolate using standard hydrochloric acid.

RESULTS AND DISCUSSION

Copolymerization of EO with AGE

Figure 1 shows the effect of total monomer concentration on the conversion and [η] of the copolymer obtained. At 60°C, when AGE and the catalyst were 10 wt % and 5 wt % (based on total monomers, respectively), the optimum monomer concentration was 20 wt % with respect to both conversion and [η] of the copolymer. In the case of low monomer concentration, the copolymerization rate is low and the amount of impurities—which induce chain transfer and chain termination—becomes relatively high as regard to initiator, thus resulting in lowering the molecular weight of the copolymer. In the case of too-high monomer concentration, too many macromolecules are adsorbed on the surface of the catalyst associates[10] and inhibit the further reaction of the active centers with monomers.

Figure 2   Effect of temperature on copolymerization.

The optimum reaction temperature is 60°C, at which the conversion reaches high level, whereas the molecular weight of the copolymer is the highest (as shown in Fig. 2). This can be explained by the fact that the chain transfer and chain termination rates increase much faster than the chain propagation rate with increasing temperature, thus resulting in decreasing molecular weight of the copolymer at higher temperatures.

The effect of catalyst amount on the copolymerization is indicated in Figure 3. At a catalyst amount of 5 wt %, based on total monomers, the conversion at 10 h can exceed 90%. This amount corresponds to the molar ratio of catalyst/total monomers $\sim$ 0.52/100, which demonstrates that the catalytic efficiency of bimetallic-oxo-alkoxide is not high. Osgan and Tayssie[10] indicated that, when this catalyst is used in polymerization of propylene oxide, the real active centers only amount to $<$ 4% of the total amount of the catalyst. It was attributed to the reason that the catalyst molecules tend to associate and only those on the surface of the associates are active. The maximum [η] occurs at a catalyst amount of 4 wt %. Excess amount of catalyst causes the decrease of molecular weight of the copolymer. The low molecular weight copolymer dissolved in the filtrate, thus resulting in decreasing conversion.

Figure 4 shows that the conversion increases quickly at the beginning of copolymerization and levels off after 10 h. [η] of the copolymers changes similarly with copolymerization time. These phenomena are probably due to too many macromolecules formed at the later stage of copolymeriza-

Figure 3   Effect of catalyst amount on copolymerization.

tion, which are adsorbed on the active centers on the surface of the catalyst associates and reduce further propagation of the active centers.

With increasing charging wt % of AGE to 25 wt %, based on total monomers, conversion decreases gradually and then decreases sharply, whereas [η] of the copolymer diminishes likewise but more

Figure 4   Effect of time on copolymerization.

Figure 5 Effect of charging wt % of AGE on copolymerization.

Figure 6 ¹H NMR spectrum of unsaturated PEO.

obviously (as shown in Fig. 5). This implies that the copolymerization activity of AGE is lower than that of EO; in other words, active chains ended with the AGE unit possessing lower activity, and more tend to induce chain transfer or chain termination.

Characterization of the Unsaturated PEO

IR spectrum of the copolymer indicated absorption peaks at 990 and 1645 cm^{-1} for C=C, absorption peaks at 950 cm^{-1} and 1150–1050 cm^{-1} for C—O—C, and absorption peaks at 1350–1150 cm^{-1}, 1460 cm^{-1}, and 2800–3000 cm^{-1} for CH_2. ¹H NMR spectrum shows peaks at 3.6δ for proton (a), 5.2δ for proton (b), 4.43δ for proton (c), 5.7δ for proton (d) and 4.0δ for proton (e) (Fig. 6). These two spectra demonstrated the existence of EO and AGE units in the unsaturated PEO molecules.

Properties of the Unsaturated PEO

The micrographs under the polarized microscope indicated that the size of spherulites was reduced as the charging AGE % increased. The crystallinity obtained from wide-angle X-ray diffraction analysis (Fig. 7) decreased obviously, with increasing amount of AGE used in copolymerization. The same figure illustrates that, when the unsaturated PEO was complexed with $LiClO_4$, the crystallinity diminishes further with increasing amount of $LiClO_4$ complexed. This is probably because the complexation of PEO with $LiClO_4$

partially destroys the PEO crystals. The room temperature conductivity of the $LiClO_4$ complex of the unsaturated PEO changes with PEO con-

Figure 7 Change of crystallinity of unsaturated copolymers with PEO content and with EO/Li molar ratio (○, copolymer; ●, $LiClO_4$ complex with molar ratio of EO/Li = 20/1; △, $LiClO_4$ complex of the copolymer containing ~ 70% PEO).

PEO(wt.%)

Figure 8   Room temperature conductivity of the unsaturated copolymer complexed with LiClO$_4$ vs. PEO content and molar ratio of EO/Li.

tent (as shown in Fig. 8). Maximum conductivity occurred at ~ 65% PEO content. This may be interpreted as the higher the PEO content, the higher the crystallinity the copolymer possesses, which retards ion mobility. On the contrary, too-high AGE content is also not beneficial to conductivity, because the large side groups of AGE units inhibit ion mobility, even though crystallinity of the copolymer is reduced. The same figure indicated that, for the copolymer containing 70% PEO, the maximum conductivity occurs at EO/Li = ~ 20/1. This is attributed to the fact that, when the amount of LiClO$_4$ complexed is too low, the crystallinity of the copolymer complex is high, which retards the ion conductivity, whereas excess LiClO$_4$ enhances the interaction between Li$^+$ ions and PEO segments, thus retarding Li$^+$ ion transportation.

Graft Copolymerization of the Unsaturated PEO with St

AIBN/monomer(%)

Figure 9   Effect of reactants concentration or amount of initiator on grafting efficiency (at 70°C).

No reaction occurred between St and PEO, containing no unsaturated side groups, in the presence of AIBN and DMF. However, graft copolymer formed during the reaction of the unsaturated PEO with St in the presence of AIBN. Figure 9 shows the effects of reactant concentration and initiator amount on the grafting efficiency. Maximum grafting efficiency occurs at a total reactant concentration of 0.2 g mL^{-1}, because too-high reactant concentration causes the viscosity of the copolymerization to increase markedly, thus resulting in retarding the diffusion of the active centers. With increasing amount of AIBN used grafting efficiency increases significantly at first and then decreases gradually. The latter phenomenon is probably because excess initiator increases the probability of chain transfer, thus increasing the homopolymer of St.

Grafting efficiency diminishes as the charging amount of the unsaturated PEO increases (Fig. 10), probably due to the reduction of collision probability between St and the unsaturated PEO, caused by the increased viscosity of copolymerization system containing a higher amount of PEO.

Figure 10 Effect of copolymerization temperature and charging wt % of the unsaturated PEO (at 60°C) on grafting efficiency.

The optimum copolymerization temperature occurs at 70°C, as illustrated in the same figure. This may be attributed to the reason that the rates of chain transfer and chain termination increase more quickly than that of chain propagation with temperature, thus resulting in an increasing homopolymer of St. Grafting efficiency increased with copolymerization time and leveled off after 28 h.

Characterization of the Purified Graft Copolymers

IR spectrum of the purified graft copolymer showed absorption peaks at 1460 cm^{-1} and 1150–1350 cm^{-1} for CH$_2$ groups; those at 950 cm^{-1} and 1050–1150 cm^{-1} for C—O—C groups; and those at 1500, 1600, 750, and 700 cm^{-1} for phenyl groups, whereas the absorption peaks at 1645 cm^{-1} and 990 cm^{-1} for double bounds disappeared. ^{1}H NMR spectrum of the purified graft copolymer indicated the peak at 3.6δ for protons of ether group, peaks at 6.6δ and 7.1δ for phenyl protons, and also a weak peak at 1.1δ for CH$_3$ protons, which are derived from the AIBN initiator. Both spectra demonstrated that the purified graft copolymer consists of both PEO and PSt units.

Properties of the Graft Copolymers

Crystallinity of the graft copolymers decreases with decreasing PEO content, whereas conductivity of their complexes with LiClO$_4$ at 25°C exhibits a maximum value for the graft copolymer con-

taining ～ 70% PEO (Fig. 11, curves c and d). This implies that, when PEO content is > 60%, a decrease of crystallinity is beneficial to the increase of room temperature conductivity. But, if PEO content is < 60%, PEO cannot form continuous phase and hence the ionic conductivity diminishes seriously. Crystallinity of the graft copolymer is lowered after complexed with LiClO$_4$. The lower the EO/Li molar ratio, the lower the crystallinity (as shown in Fig. 11, curve b). Crystallinity becomes 0 when EO/Li molar ratio = 4/1. Maximum conductivity occurs at molar ratio of EO/Li = ～ 20/1 (Fig. 11, curve a). This phenomenon indicates that small amount of LiClO$_4$ complexed with the graft copolymer can lower crystallinity of PEO, thus favoring the transportation of Li$^+$ ions through the vacant oxygen atoms of the spiral PEO structure. However, if LiClO$_4$ is in excess, although the number of Li$^+$ ions increases but the interaction between the Li$^+$ ions and PEO segments was enhanced, this raised the microviscosity of the complex, thus resulting in lower mobility of Li$^+$ ions and conductivity.

Figure 12 illustrates that the emulsifying volume, which represents the emulsifying property of the graft copolymer, increases with the amount of copolymer added to the toluene/water system, due to the increase of emulsifying centers. A maximum emulsifying volume occurs at the graft copolymer containing ～ 70% PEO. This implies that the emulsifying property is related to both the

Figure 11 Crystallinity and room temperature conductivity of the graft copolymer complexed with LiClO$_4$ vs. PEO content and molar ratio of EO/Li.

hydrophilic PEO segments and the hydrophobic PSt segments.

The phase-transfer catalytic behavior of the graft copolymer in the Williamson reaction of solid potassium phenolate with *n*-butyl bromide is shown in Figure 13. Conversion of potassium phenolate is very low in the absence of the graft copolymer. However, the conversion increases to 50% in the presence of PEO, whereas it increases to ~ 80% in the presence of 10% graft copolymer based on potassium phenolate. Then, the conversion increases gradually with the amount of graft copolymer added. This fact can be interpreted as PEO segments can complex with the K^+ ion, and hydrophobic PSt grafts favor the transfer of phenolate into the organic phase, thus enhancing the conversion. A maximum conversion exists for the graft copolymer containing ~ 70% PEO content, because both PSt and PEO segments play the role of phase-transfer action.

CONCLUSIONS

The double bond-containing PEO can be obtained by copolymerization of EO with AGE using bime-

Figure 13 Effect of amount of the graft copolymer and its PEO content on the conversion of potassium phenolate (KOPh) in the Williamson reaction.

tallic-oxo-alkoxide as catalyst. When AGE and the catalyst are 10 wt % and 5 wt %, based on total monomers, respectively, conversion reaches 90%, and [η] of the copolymer is 150 mL g^{-1}. Maximum conductivity of the LiClO$_4$ complexed copolymer occurred at ~ 65% PEO content and reaches 10^{-4} S cm^{-1} at 25°C. Unsaturated PEO can be graft-copolymerized with St with a grafting efficiency ~ 50%. Conductivity of the graft copolymer complexed with LiClO$_4$ at 25°C approaches 1×10^{-4} S cm^{-1}, when its PEO content is 70 wt % and molar ratio of EO/Li = 20/1. The graft copolymer showed good emulsifying property and phase-transfer catalytic activity in the Williamson reaction.

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Figure 12 Effect of amount of the graft copolymer and its PEO content on the emulsifying volume.

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