

Ternary Copolymer of Poly(ethylene oxide), Terephthalyl Chloride, and Lithium 2,5-Diaminobenzene Sulfonate for Ionic Conduction

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ABSTRACT: The ternary copolymers of poly(ethylene oxide) (PEO), terephthaloyl chloride (TPC), and lithium 2,5-diaminobenzene sulfonate (LDABS) have been synthesized by the separated copolymerization PEO, TPC, and LDABS. Three ternary copolymers, PEO_{0.12}-TPC_{0.50}-LDABS_{0.38}, PEO_{0.24}-TPC_{0.50}-LDABS_{0.26} and PEO_{0.36}-TPC_{0.51}-LDABS_{0.13}, are thermally stable and mechanically strong ionic conductors. The combination of immobilized anionic groups (SO₃⁻) incorporated into the copolymer to increase the mobile cation concentration and of PEO introduced to enhance ionic conductivity via flexible chain motion. PEO_{0.24}-TPC_{0.50}-LDABS_{0.26} was found to be a good polymeric material with good mechanical properties and a high ionic conductivity of 8.37×10^{-6} S/cm at 25°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 835–840, 1998

Key words: ternary copolymer; ionic conductivity; mechanical property; free volume theory; dynamic bond percolation theory

INTRODUCTION

Since Wright and coworkers¹ reported that the complexes of polyethylene oxide and lithium salts showed good ionic conductivity at room temperature, the study of solid ionic conductive polymers have blossomed.^{2–4} These polymers are expected to be applied for electrochemical devices, such as all-solid-state batteries, sensors, displays, and so on.⁵ The ionic conductive polymer, such as the complexes of polyethylene oxide and lithium salts that showed high ionic conductivity of 10^{-5} to 10^{-4} S/cm at room temperature, are characterized by a bi-ionic transport mechanism. The main drawback of these materials is the significant decrease in ionic conductivity with the direct current polarization. Such a decrease of direct current (dc) ionic conductivity is inconvenient when the poly-

mer electrolytes are used in the devices operating under dc polarization. For a number of applications, the ionic conductors with single-ion transport character are therefore required. Usually, the ionic conductivity of single-ion transport materials is lower than that of the bi-ion transport conductors, but the transport number of the cation is unity for the single-ion transport conductors, and the stable current in dc polarization can be provided. Several solid ionic conductive polymers characterized by a single-ion transport mechanism have been reported.^{6–15} Most of them are the polyblends of ionomer oligomer with polyether or copolymers of ionomer oligomer with polyether low-molecular ionomers. Usually, the polyblend electrolytes show poor mechanical property, and the copolymer electrolytes show low conductivity.

It is known that fiber from poly(*p*-phenylene terephthalamide) (PPTA) is a rigid rodlike polymer with high tensile strength, stiffness, crystallinity, and thermal stability. This wholly aromatic polyamide is very difficult to process due to

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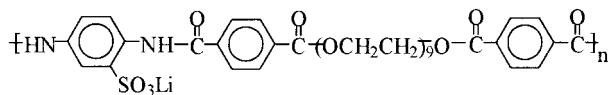
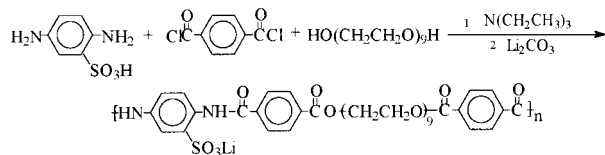


Figure 1 PEO-TPC-LDABS copolymer.

the lack of appropriate organic solvent. Recently, a water-soluble PPTA derivative,¹⁶ poly(*p*-phenylene sulfonic acid terephthalamide) (PPTS) has been prepared by polymerization of 1,4-diaminobenzene sulfonic acid with terephthalyl chloride. The sulfonate groups on the polymer backbone cause an interruption of the crystalline packing so that the hydrogen bonding and the regular packing of the polymer is impaired. In addition, the sulfonic acid forms strong hydrogen bonding with solvents, such as dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide, and *N,N*-dimethylformamide. But the conductivity of Na⁺ and Li⁺ poly(phenylene terephthalamide sulfonate salts) is very poor at room temperature. Until the temperature up to 250°C, the conductivity reaches to about 5×10^{-6} S/cm.

The conductivity of polymer electrolytes is generally enhanced by incorporation of additives. In order to obtain thermally stable and mechanically strong high conducting polymer, Y. Okamoto and coworkers¹⁷ synthesized oligo(ethylene oxide)-(3, 5, or 7 units of ethylene oxide) substituted ethylene carbonate and poly[oxyethylene-oligo(oxyethylene)]. These are high-boiling-point liquids with high dielectric constants as well as metal chelating properties. Polyelectrolyte systems were prepared by mixing Na⁺ and Li⁺ poly(phenylene terephthalamide sulfonate) salts with various amounts of modified ethylene carbonate and/or poly[oxyethylene-oligo(oxyethy-



Scheme 1 Synthesis of PEO-TPC-LDABS.

lene)]. The blends were found to have considerable mechanical strength and have ionic conductivities of 10^{-6} – 10^{-5} S/cm at 25°C. Although they have so many advantages, there is still a great drawback. They are unstable with the elapses of time because of phase separation, liquid leak, and volatilizing.

To overcome this disadvantage, a new kind of polyelectrolyte has been synthesized (its general formula is shown in Fig. 1). The sodium sulfonate as the carrier source of ion and PEO segment incorporated enhance ionic conductivity via flexible chain motion assistance and, hence, provide high conductivity due to the low dissociation energy of the sulfonates and to the greater solubility of the long PEO segment. Free-standing film can be obtained because of the excellent mechanical strength. The physical properties as well as ion conductivity of the electrolyte have been investigated.

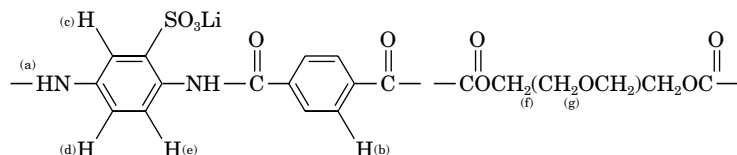
EXPERIMENTAL

Materials

2,5-Diaminobenzene sulfonic acid was purchased from Aldrich Chemical Co (USA). TPC was prepared and purified according to a method previously described.¹⁸ PEO was used after drying

Table I ¹H-NMR Results of Copolymers

Compounds	δ (ppm)						
	a	b	c	d	e	f	g
Polymer 1	10.5	8.8	8.0	7.6	7.2	3.3	3.0
Polymer 2	10.6	8.9	8.0	7.6	7.2	3.2	3.0
Polymer 3	10.3	8.9	8.0	7.6	7.2	3.5	3.0



PEO_{0.12}-TPC_{0.50}-LDABS_{0.38} (polymer 1) ($\bar{M}_n = 1.1 \times 10^4$, $\bar{M}_w = 2.7 \times 10^4$)

PEO_{0.24}-TPC_{0.50}-LDABS_{0.26} (polymer 2) ($\bar{M}_n = 7.0 \times 10^3$, $\bar{M}_w = 1.7 \times 10^4$)

PEO_{0.36}-TPC_{0.51}-LDABS_{0.13} (polymer 3) ($\bar{M}_n = 6.5 \times 10^3$, $\bar{M}_w = 1.7 \times 10^4$)

Scheme 2 Molar compositions and molecular weights of copolymers.

under vacuum at 65°C for 3 days. DMF was azeotropically distilled with benzene to remove residual moisture before use. The preparation of PEO-TPC-LDABS is showed in Scheme 1.

In the existence of triethylamine, the DABSA (0.1 mol) in 30 mL of DMF was added dropwise to a DMF solution (70 mL) containing TPC (0.2 mol) over a time of 30 min. Then the PEO (0.1 mol) in 30 mL DMF was added as before. The mixture was stirred for 2.5 h. Then all mixture was poured into ten-fold volume of water to precipitate the copolymer (PEO-TPC-DABSA). The collected precipitate was washed several times with water on a glass filter and dried in vacuum at 65°C for 3 days.

A hot aqueous solution of PEO-TPC-DABSA was neutralized by lithium carbonate. The neutralized PEO-TPC-LDABS precipitated when the solution cooled down. The salt was washed repeatedly with cold water and dried under vacuum at 65°C for 3 days.

Three different copolymers, as shown as Scheme 2, were obtained by controlling reaction ratios of PEO, TPC, and DABSA. Molecular weights of copolymers were obtained by gel permeation chromatography (GPC), and the results are also shown in Scheme 2. Molar composition of the copolymers was confirmed by elemental analysis. ¹H-NMR (400 MHz, DMSO-d₆) results of the copolymers are shown in Table I. Infrared (IR) spectra (Fig. 2) shows that $\nu(\text{C}=\text{O})$

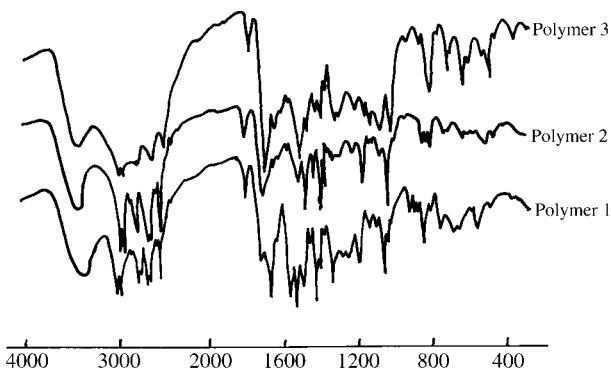
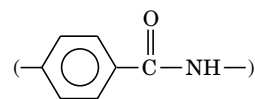
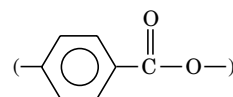


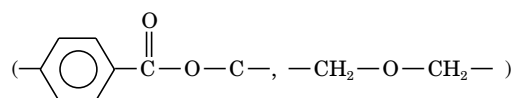
Figure 2 IR spectra of three ternary copolymers.



appear in 1650 cm⁻¹, $\nu(\text{C}=\text{O})$



appear in 1700 cm⁻¹, $\nu(\text{C---O---C})$



in 1030 cm⁻¹, and $\nu(\text{CH}_2)$ in 2910 and 2870 cm⁻¹. Wide absorption peaks of $\nu(\text{N---H})$ appearing in 3425 cm⁻¹ indicate that hydrogen bonds exist in different polymer bones.

Measurements

The differential scanning calorimetry (DSC) traces were obtained from a Du Pont 1090 thermal analyzer at a heating rate of 10°C/min under nitrogen. The polyelectrolyte systems were quenched to -150°C by liquid nitrogen before heating up to 100°C for the determination of any thermal transition. Uniaxial stress-strain testing was performed at room temperature (20°C) using a SHIMADZU AG-100KNE testing machine, with a crosshead speed of 50 mm/min. Dumbbell-shaped samples were stamped out with an ASTM D1708 die. Conductivity measurements

Table II DSC Data of Copolymer

Sample	T_g (°C)	T_c (°C) ^a	T_m (°C) ^b	ΔH (cal/g)
Polymer 1	-18	—	—	471
Polymer 2	-14	7	40	759
Polymer 3	-46	18	36	471

^a T_c is the temperature of crystallization.

^b T_m is the temperature of melting of crystals.

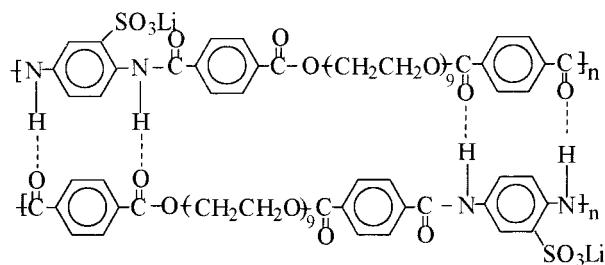


Figure 3 Hydrogen bonding between molecules of polymer 2.

were carried out using 12.9-mm (diameter) samples (compacted) and a two-point probe technique under a dry Argon atmosphere.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of these three copolymers were investigated by DSC. Their DSC traces are illustrated in Table II.

The glass transition temperature of the copolymer decreases with the increasing of the PEO segment content in copolymer. The T_g is -18°C for polymer 1, -14°C for polymer 2, and -46°C for polymer 3.

Two additional transitions are observed in polymers 2 and 3. These transition in polymer 2 originated from its regular structure enough to form hydrogen bonding between molecules of polymer 2 (see Fig. 3) and in polymer 3 originate from its PEO segment content enough to form a crystalline phase. The hydrogen bondings are also shown in IR spectra. Therefore, the exothermic peak at $0\text{--}20^\circ\text{C}$ is due to the crystallization, and the endothermic peak at $35\text{--}40^\circ\text{C}$ is due to the melting of this crystalline.

Mechanical Properties

Tensile properties obtained from stress-strain curves of the copolymers are summarized in Table

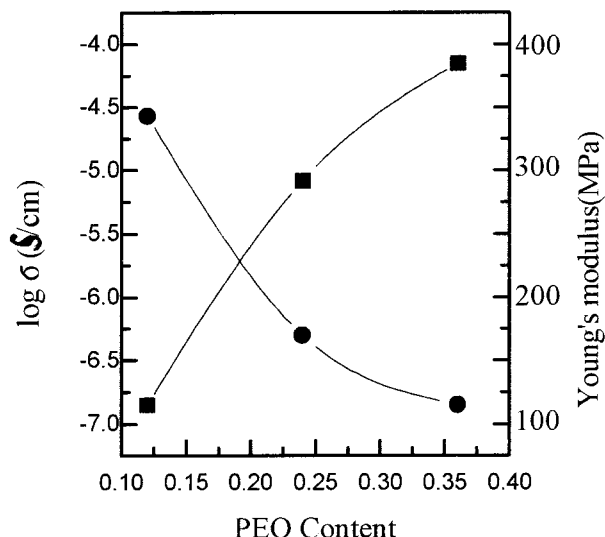


Figure 4 Log σ -PEO content-Young's modulus curves of the copolymers; (■), log σ -PEO content curve; (●), Young's modulus-PEO content curve.

III. It is noted that polymers 1 and 2 exhibited good mechanical properties, and polymer 3 is flexible at room temperature. The tensile strength and Young's modulus decreased, and the elongation at break increased with the increasing of PEO segment content. But the conductivity of the polymer 3 at room temperature decreases with the increasing of PEO segment content in copolymer. Figure 4 shows log σ -PEO content-Young's modulus curve of the copolymers. Obviously, the point of intersection in Figure 4 represent the best copolymer composition at which the polymer has both good mechanical property.

Ionic Conductivity and Its Temperature Dependence

Figure 5 shows the temperature dependence of the ionic conductivity of copolymers at different PEO content levels. Polymer 1 shows curved Arrhenius plot, but polymers 2 and 3 show straight-line Arrhenius plots, suggesting that they follow a different ion-transport mechanism.

Table III Tensile Properties

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Yield Strength (MPa)
Polymer 1	334.0	21.8	210	17.0
Polymer 2	170.0	13.7	220	12.9
Polymer 3	115.0	8.9	240	9.0

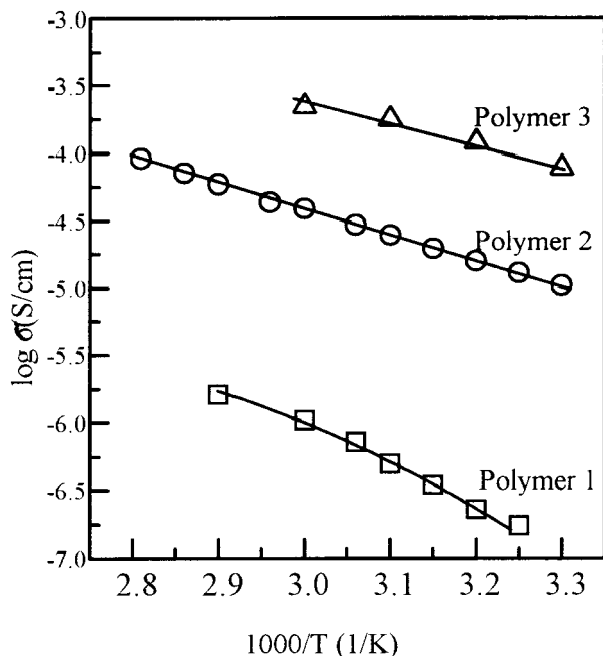


Figure 5 Arrhenius plots of copolymers.

A curved Arrhenius plot is a characteristic of amorphous materials and implies that the process of ionic conduction is associated with the renewal of free volume of polymer 1. Therefore, the Williams-Landel-Ferry (WLF) equation, which has proven to be universally available for describing properties related to the relaxation of free volume of amorphous polymers, may be used to analyze the conductivity data, as follows¹⁹:

$$\log(\sigma(T)/\sigma(T_g)) = C_1(T - T_g)/(C_2 + (T - T_g)) \quad (1)$$

Where C_1 and C_2 are constants, and $\sigma(T)$ and $\sigma(T_g)$ are conductivity at temperature T and glass transition temperature T_g , respectively.

In this work, the $\sigma(T_g)$ is determined by a nonlinear least-squares analysis of the conductivity data using a computer since it is too small to be

measured with an ordinary apparatus. Based on the obtained $\sigma(T_g)$ values, the WLF parameters C_1 and C_2 are derived from the intersection and slope of the straight line of $\log^{-1}[\sigma(T)/\sigma(T_g)]$ versus $(T - T_g)^{-1}$. The WLF parameters are listed in Table IV, together with the free-volume fraction (f_g) at T_g and the coefficient of thermal expansion (α_f), which are calculated according to the formulas $f_g = 1/2.303C_1$ and $\alpha_f = 1/2.303C_1C_2$, respectively. Only the WLF parameters of conductivity of polymer 1 are roughly consistent and comparable with the universal values ($C_1 = 17.4$ and $C_2 = 51.6$), which verifies the close relationship between ionic conduction and segmental motion of polymeric hosts. More often, ionic conductivity in electric materials is described by the VTF (Vogel-Tammann-Fulcher) equation, as follows²⁰⁻²²:

$$\sigma = AT^{-1/2} \exp(-B/(T - T_0)) \quad (2)$$

where A and B are constants, and T_0 is an ideal temperature, at which the configuration entropy become vanishing by small. The parameters T_0 , A , and B obtained by a nonlinear least-squares analysis of the conductivity data are listed in Table V. Only the $T_g - T_0$ value of polymer 1 is roughly close to the universal value ($T_g - T_0 = 52$), revealing the considerable dependence of ionic conductivity of polymer 1 on the segmental motion of polymeric hosts.

According to the configurational entropy theory of Gibbs et al., the parameter B of the VTF equation may be written as follows^{23,24}:

$$B = T_0 S_c^* \Delta\mu/k\Delta C_p T \quad (3)$$

Where ΔC_p is the change in heat capacity during the glass transition, $\Delta\mu$ is molar energy barrier of segmental rearrangement, and S_c^* is the minimum configurational entropy required for such a rearrangement. An approximation of S_c^* is $k \ln 2$, where k is Boltzmann constant. Using ΔC_p values

Table IV WLF Parameters of Conducting Polymers

Sample	T_g (°C)	δT_g (S/cm)	C_1	C_2 (°C)	f_g ($\times 10^{-2}$)	α ($\times 10^4$)
Polymer 1	18	2.8×10^{-10}	10.0	74.6	4.3	5.8
Polymer 2	-14	5.93×10^{-7}	5.4	147.0	8.0	5.5
Polymer 3	-46	6.64×10^{-6}	18.5	1219.5	0.3	0.2
WLF			17.4	51.6	2.5	4.8

Table V VTF Parameters of Conducting Polymer 3

Sample	A	B	T_0 (K)	$T_g - T_0$ (°C)	ΔC_p (J/gc)	$\Delta\mu$ (kJ/g)
Polymer 1	0.0071	644.8	255.5	35.5	0.512	4.6
Polymer 2	243.45	4064.8	14.8	244.2	—	—
Polymer 3	2.5385	1950.3	406.0	-179.0	—	—

determined from DSC results, $\Delta\mu$ is calculated and also listed in Table V.

The availability of WLF and VTF equations for describing the conductivity data of polymer 1 may let us conclude that conduction of Li^+ ions in polymer 1 is carried out by segmental motion of the polyelectrolyte host.

Linear Arrhenius plots of polymers 2 and 3 suggest that they follow a different conductive mechanism with polymer 1. This may be due to the existing of crystalline phase in these two polymers.

The free volume theory ignores ions transport in crystalline phase, namely, thermally activated ion hopping between preferred sites. The dynamic bond percolation theory (DBP) assumes, on the other hand, a solid-state-type jumping of ions along strings of sites, which occasionally connect together according to a liquid-state-type self-diffusion mechanism of the sites themselves. So, ion-transport in polymers 2 and 3 may follow the DBP theory, and the further discussion will be given in another article.

CONCLUSIONS

Three ternary copolymers with different PEO content level were prepared by the separated copolymerization of PEO, TPC, and LDABS. Contrary to polymers 1 and 3, polymer 2 has both a good mechanical property and high conductivity of 8.37×10^{-6} S/cm at 25°C. Ion transport in polymer 1 was confirmed to follow the free volume theory. Ion transport in polymers 2 and 3 may follow the DBP theory.

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