# A New Kind of Ternary Copolymer for Ionic Conduction

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ABSTRACT: Two novel ternary copolymers, MNEC-TPC-LDABS and MMEC-TPC-LD-ABS, were synthesized by condensation copolymerization of mannitol-containing oligomeric side chains (MNEC) or melamine-containing oligomeric side chains (MMEC) with terephthaloyl chloride (TPC) and lithium 2,5-diaminobenzene sulfonate (LDABS), respectively, to become thermally stable and mechanically strong ionic conductors. Incorporating anionic groups  $(SO_3^{2-})$  into the structure of copolymers increases mobile cation concentration and introducing MNEC and MMEC enhances ionic conductivity via flexible chain motion assistance. The conductivity ( $\sigma$ ) of MNEC-TPC-LDABS is 7.82  $\times$  10<sup>-5</sup> S/cm and of MMEC-TPC-LDABS is 9.17  $\times$  10<sup>-5</sup> S/cm, both measured at 25°C. The crystallinity and  $T_g$  of the copolymers were greatly decreased by the incorporation of dendritic macromolecule units of MNEC or MMEC. The temperature dependencies of the ionic conductivity for two polymers show curved Arrhenius plots, which suggest that ionic conduction is closely associated with segmental motion of the polymer hosts. The conductivity of the polymer electrolytes obeys the Williams-Landel-Ferry (WLF) and Vogel-Tammann-Fulcher (VTF) equation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 953-959, 1999

**Key words:** polymeric single-ionic conductor; dendritic macromolecule; ternary copolymer

# INTRODUCTION

Since Wright<sup>1</sup> reported in 1975 that polyethylene oxide (PEO) dissolved inorganic salts and showed ionic conductivities at ambient temperatures, the developments of ion-conductive macromolecules (solid macromolecular electrolytes) greatly increased.<sup>2-4</sup> These polymers are expected to be applied for electrochemical devices, such as allsolid-state batteries, sensors, displays, and so on.<sup>5</sup> The ionic conductive polymer such as the complexes of PEO and lithium salts that showed high ionic conductivity of  $10^{-5}$ - $10^{-4}$  S/cm at room temperature are characterized by a bi-ionic trans-

port 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 polymer electrolytes are used in 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 singleion 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 that were characterized by a single-ion transport mechanism were reported.<sup>6–15</sup> Most of them are the polyblends of ionomer oligomer with polyether or copolymers of ionomer oligomer with polyether low molecular weight ionomers. Usually, the polyblend electrolytes

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Figure 1 The structures of MNEC and MMEC.

show poor mechanical properties and the copolymer electrolytes show low conductivity.

To obtain polymeric single-ionic conductors with both good mechanical properties and high ionic conductivities, we synthesized the ternary copolymer (PEO-TPC-LDABS)<sup>16</sup> to become a good polymeric material with considerable mechanical properties and high ionic conductivity of 8.37  $\times$  10<sup>-6</sup> S/cm at 25°C. The conductivity of polymeric solid electrolyte can be enhanced by appending short oligomeric side chains of PEO to high molecular weight polymeric backbone.<sup>12,14,17</sup> For this reason, two dendritic macromolecules MNEC and MMEC (Fig. 1) were synthesized and condensation copolymerized separately with terephthaloyl chloride (TPC) and lithium 2,5-diaminobenzene sulfonate (LDABS), which obtain two novel copolymers (MNEC-TPC-LDABS and MMEC-TPC-LDABS). The crystallinity and glass transition temperature  $(T_g)$  of the copolymers greatly decrease by the incorporation of dendritic macromolecule units of MNEC and MMEC. The mechanical properties of the copolymers are still held good for their partially aromatic structures.

Free-standing films can be obtained. The physical properties as well as ion conductivity of the conducting copolymers were investigated.

# **EXPERIMENTAL**

#### Materials

2,5-Diaminobenzene sulfonic acid (DABSA) was purchased from Aldrich Chemical Co. TPC was prepared and purified according to the previously described method.<sup>18</sup> N,N-Dimethyl formamide (DMF) was azeotropically distilled with benzene to remove residual moisture before use.

# Instruments and Measurements

IR spectra were recorded on Alpha-Centauri FTIR spectrophotometer (KBr pellets). Elemental analyses were measured with 1106 Elemental analyzer (Carbol-Erba, Italy) and E1 Elemental analyzer (Vario, Germany). <sup>1</sup>H-NMR spectra were performed on Bruker-AM400 Nuclear Magnetic

Compound	ν(N—H)	ν(C==O) (PhCOO)	ν(C==O) (PhCON)	ν(S==0)	ν(O—H)	ν(C—O)	v(C—Cl)
MNEC	_	_	_	_	3516	1101	749
MMEC		_	—		3507	1104	746
MNEC-TPC-LDABS	3327	1690	1649	1180	3426	1113	732
MMEC-TPC- LDABS	3333	1697	1650	1172	3433	1113	731

Table I	IR Data	of Polymers
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#### Scheme 1

Resonance Spectrometer [dimethylsulfoxide-d6 (DMSO-d6) as solvents and tetramethylsilane (TMS) as internal standard]. Molecular weights were determined by Waters model-996 Gel Permeation Chromatographic instruments (GPC) or Vapour Pressure Osmometer (VPO). 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 300°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 were carried out using 12.9-mm (diameter) samples (compacted) and a two-point probe technique under the dry argon atmosphere.

#### **Preparation of Monomers and Polymers**

Synthesis of MNEC. A measure of 0.01 mol of mannitol and an appropriate amount of potassium hydroxide were dissolved into 4 mL water. Epichlorohydrin (0.30 mol) was added dropwise into the solution over a period of 6 h. The mixture was refluxed for 72 h, then the water and the unreactive epichlorohydrin were removed under vacuum. Ethanol (100 mL) was added to the mixture to dissolve mannitol-containing oligomeric side chains (MNEC). After cooling to room temperature, the inorganic salt was filtered off. MNEC was obtained after a large amount of ethanol was evaporated and dried under vacuum at 65°C for 3 days. IR results of MNEC are listed in Table I. Molecular weight was determined  $(M_n = 2200)$ .

Synthesis of MMEC. To a well-stirred solution of 0.01 mol melamine, an appropriate amount of potassium hydroxide and 25 mL of water, 0.03 mol of epichlorohydrin was added dropwise over a period of 15 h. Then, the experimental procedures were operated as described above. IR results of melamine-containing oligomeric side chains (MMEC) are also listed in Table I ( $M_n = 2350$ ).

Synthesis of MNEC-TPC-LDABS. MNEC-TPC-LDABS was prepared according to Scheme 1.

Table II <sup>1</sup>H-NMR Results of MNEC-TPC-LDABS and MMEC-TPC-LDABS

Copolymer       a       b       c       d       e       f $-OH$ $-OCH_2C$ $-CHO$ $CH_2C$ MNEC-TPC-LDABS       10.3       8.9       8.0       7.6       7.3       7.0       3.53       3.9       3.6       3.4         MMEC-TPC-LDABS       10.5       9.0       8.0       7.8       7.5       7.0       3.52       3.9       3.5       3.3         (a) $(d)H$ SO_3Li O         O		δ, ppm									
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Copolymer	a	b	с	d	e	f	—ОН	-OCH <sub>2</sub> C-	—СНО—	$\rm CH_2 Cl$
$\underbrace{\text{MMEC-TPC-LDABS} 10.5 9.0 8.0 7.8 7.5 7.0 3.52 3.9 3.5 3.3}_{(a)} \underbrace{(a)^{(d)}H}_{H} \underbrace{\text{SO}_{3}\text{Li}}_{H} O \underbrace{O}_{H}$	MNEC-TPC-LDABS	10.3	8.9	8.0	7.6	7.3	7.0	3.53	3.9	3.6	3.4
$(a)^{(d)H} \xrightarrow{SO_3Li} O_{H} \xrightarrow{O} U_{H}$	MMEC-TPC-LDABS	10.5	9.0	8.0	7.8	7.5	7.0	3.52	3.9	3.5	3.3
$-HN \prec$ $\rightarrow NH - C \rightarrow$	MNEC-TPC-LDABS MMEC-TPC-LDABS	10.3 10.5	8.9 9.0	8.0 8.0 (a)	7.6 7.8 (d)H	$\frac{7.3}{7.5}$ SO <sub>3</sub> L	7.0 7.0 i O	3.53 3.52	3.9 3.9	3.6 3.5	3.4 3.3



In the presence of triethylamine, the DABSA (0.1 mol) in 30 mL of DMF was added dropwise into a TPC solution of 70 mL DMF containing 0.2 mol of TPC over a time of 30 min. This solution was then added dropwise into MNEC (0.1 mol) solution of 50 mL DMF. After being stirred for 2.5 h, the mixture was poured into a 10-fold volume of acetone to precipitate the copolymer (MNEC-TPC-DABSA). The collected precipitate was washed several times with acetone.

A hot aqueous mixture of MNEC-TPC-DABSA was neutralized by lithium carbonate, then water was evaporated from the solution. Alcohol (200 mL) was added to the mixture to dissolve the inorganic salt, and then it was filtered. MNEC-TPC-LDABS was obtained after a large amount of ethanol evaporated and was dried under vacuum at 65°C for 3 days ( $\bar{M}_n = 1.7 \times 10^4$ ,  $\bar{M}_w = 4.0$ 



**Figure 2** DSC curves of copolymers, (1) MNEC-TPC-LDABS; (2) MMEC-TPC-LDABS.

 $\times~10^4$ ). IR data are also listed in Table I and  $^1\text{H-NMR}$  results of MNEC-TPC-LDABS are listed in Table II.

Synthesis of MMEC-TPC-LDABS. MMEC-TPC-LDABS was synthesized by the method represented by Scheme 2. All experimental procedures were same as that of MNEC-TPC-LDABS ( $\bar{M}_n = 1.2 \times 10^4$ ,  $\bar{M}_w = 3.3 \times 10^4$ ). IR data are also listed in Table I and <sup>1</sup>H-NMR results are also listed in Table II.

# **RESULTS AND DISCUSSION**

### **Physical Properties**

DSC curves of the copolymers are illustrated in Figure 2, showing characteristics of semicrystalline polymers. DSC data for these three polymers are summarized in Table III. It is noted that the  $T_g$  of the copolymer MNEC-TPC-LDABS and the copolymer MMEC-TPC-LDABS was more greatly decreased by the incorporation of dendritic macromolecule units of MNEC and MMEC than that of PEO-TPC-LDABS.<sup>16</sup> The flow temperature of the copolymers shows that the copolymers can only be used in the temperature range under

Table II	DSC	Data	of	Copol	ymers
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Sample	$T_g$ (°C)	$T_m$ (°C)	$\Delta C_p$
MNEC-TPC-LDABS MMEC-TPC-LDABS	$\begin{array}{c} -40 \\ -58 \end{array}$	$220.7 \\ 114.7$	$\begin{array}{c} 0.743 \\ 0.812 \end{array}$

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Yield Strength (MPa)
PEO-TPC-LDABS	170.0	13.7	220	12.9
MNEC-TPC-LDABS	154.0	13.0	220	12.3
MMEC-TPC-LDABS	140.0	12.9	230	11.7

Table IV Tensile Properties of Conducting Polymers

130°C, which are wider than that of PEO-TPC-LDABS.

# **Mechanical Properties**

Tensile properties of three copolymers summarized from stress-strain curves are listed in Table IV. It is noted that three copolymers all exhibited good mechanical properties. Compared with those of PEO-TPC-LDABS copolymer, the tensile strength, the Young's modulus, and the elongation at the break of MNEC-TPC-LDABS and MMEC-TPC-LDABS have little decrease, which suggests that mechanical properties of MNEC-TPC-LDABS and MMEC-TPC-LDABS still held good after the introduction of flexible branched  $-(CH_2CHO)_n -$ The reason is that the chain ĊH<sub>2</sub>Cl main chain of polymers is a rigid aromatic polyamide.

# Ionic Conductivity and Its Temperature Dependence

The conductivities of typical PEO complexes with alkali metals are between  $10^{-6}$  and  $10^{-9}$  S/cm at ambient temperature.<sup>19</sup> In recent years, we found that the ionic conductivity of solid macromolecular electrolyte could reach  $10^{-4}$  S/cm at room temperature,<sup>20</sup> even though their mechanical properties are not good. To increase the mechanical properties of the polymeric ionic conductor, we introduced the rigid ring into the main chain of the ternary copolymer (PEO-TPC-LDABS),<sup>16</sup> of which the ionic conductivity is  $8.37 \times 10^{-6}$  S/cm at 25°C. Here, the PEO in the ternary copolymer was replaced with MNEC and MMEC, which affords MNEC-TPC-LDABS and MMEC-TPC-LDABS. The conductivities of the novel ternary copolymer are 10-fold higher than that of PEO-TPC-LDABS, which are  $7.82 \times 10^{-5}$  and 9.17imes 10<sup>-5</sup> S/cm separately, and the mechanic properties are nearly same as the above polymers.

Arrhenius plots of conductivity of copolymers are shown in Figure 3, which consists of all curves. This behavior is characteristic of amorphous materials and implies that the process of ionic conduction is associated with the renewal of free volumes of polymers. Therefore, the Williams–Landel–Ferry (WLF) equation, which proved 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<sup>21</sup>:

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

where  $C_1$  and  $C_2$  are contants, and  $\sigma(T)$  and  $\sigma(T_g)$  are the conductivity at temperature T and glass transition temperature  $T_g$ , respectively. In



Figure 3 Arrhenius plots of copolymers.

Sample	$\sigma(T_g)~(\mathrm{S/cm})$	$C_1 \; (^{\circ}\mathrm{C})$	$C_2 \; (^{\circ}\mathrm{C})$	$f_g \; ( imes 10^{-2})$	$\alpha_f  ( imes 10^{-4})$
MNEC-TPC-LDABS	$9.0 imes 10^{-9}\ 4.5 imes 10^{-11}$	7.6	53.8 44 0	5.7 4 3	10.6
WLF		17.4	51.6	2.5	4.8

Table V WLF Parameters of Conducting Polymers

this work, the  $\sigma(T_g)$  is determined by a nonlinear imitation 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  $1/\log[\sigma(T)/\sigma(T_g)]$  versus (T $-T_{g}$ ) - 1. The WLF parameters are listed in Table V, together with the free-volume fraction  $(f_g)$  at  $T_g$  and the coefficient of thermal expansion  $(\alpha_f)$ , which are calculated according to the equations  $f_g = 1/2.303C_1$ ,  $\alpha_f = 1/2.303 C_1C_2$ , respectively. The WLF parameters of conductivity of copolymers are roughly consistent and comparable with the universal values ( $C_1 = 17.4, C_2$ = 51.6) that verifies the close relationship between ionic conduction and segmental motion of polymer hosts.

More often, ionic conductivity in electric materials is described by the VTF (Vogel–Tammann–Fulcher) equation  $^{22-24}$ :

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

where A and B are constants and  $T_0$  is the ideal temperature at which the configurational entropy become zero. The parameters  $T_0$ , A, and B obtained by a nonlinear least-squares analysis of the conductivity data are listed in Table VI. Substitution of these parameters into eq. (2) gives a series of straight lines with a regression factor of more than 0.996 (Fig. 4), revealing the considerable dependence of ionic conductivity on the segmental motion of polymeric hosts.

According to the configurational entropy theory of Gibbs and DiMarzio, parameter B of the VTF equation may be written as<sup>25</sup>

 $B = T_0 S c^* \Delta \mu / K \Delta C_p T \tag{3}$ 

where  $\Delta C_p$  is the change in heat capacity during the glass transition,  $\Delta \mu$  is the molar energy barrier of segmental rearrangement, and  $Sc^*$  is the minimum configurational entropy required for such a rearrangement. An approximation of  $Sc^*$  is K ln 2, where K is the Boltzmann constant. Using  $\Delta C_p$  values determined from DSC results,  $\Delta \mu$  is calculated and also listed in Table VI. The  $\Delta \mu$  values of the nearly amorphous copolymers are independent of the kind of copolymers, revealing further that there is the same basic process between ionic transfer and segmental motion.

The availability of WLF and VTF equations for describing the conductivity data led to the conclusion that conduction of  $Li^+$  ions is carried out by segmental motion of the polyelectrolyte host.

# CONCLUSIONS

MNEC-TPC-LDABS and MMEC-TPC-LDABS copolymers were prepared as a new type of polymeric solid electrolyte that showed good mechanical properties and high conductivity. The crystallinity and  $T_g$  of the copolymers greatly decreased by the incorporation of dendritic macromolecule units of MNEC and MMEC. The curved Arrhenius plots of conductivity suggest that there is a close correlation between ionic conduction and segmental motion, which is verified by the validity of WLF and VTF empirical equations analyzing the obtained conductivity data.

Table VI VTF Parameters of Conducting Polymers

Sample	A	В	$T_0$ (°C)	$T_g$ – $T_0$ (°C)	$\Delta C_p~({\rm J/gc})$	$\Delta \mu (\text{KJ/g})$
MNEC-TPC-LDABS MMEC-TPC-LDABS	$\begin{array}{c} 24.9\\ 22.4\end{array}$	$1117.2 \\ 1054.4$	$-93.2 \\ -89.7$	$\begin{array}{c} 53.2\\ 31.7\end{array}$	$\begin{array}{c} 0.743\\ 0.812\end{array}$	$4.9 \\ 5.1$



Figure 4 VTF plots of conductivity of copolymers.

# REFERENCES

- 1. Fenton, D. E.; Parker, J. M.; Wright, P. V. Polymer 1973, 14, 589.
- Ranter, M. A.; Shriver, D. F. Chem Rev 1988, 88, 109.
- 3. Watanabe, M.; Ogata, N. Br Polym J 1988, 20, 181.
- Kaneko, M.; Wohrle, D. Adv Polym Sci 1988, 84, 141.
- Przyluski, J.; Wieczorek, W.; Florjanczyk, Z. Mater Sci Forum 1993, 122, 131.

- Bannister, D. J.; Davies, G. R.; Ward, I. M.; McIntyre, J. E. Polymer 1984, 25, 1291.
- Ganapathiappan, S.; Chen, K.; Shriver, D. F. J Am Chem Soc 1989, 111, 4091.
- Hardy, L. C.; Shriver, D. F. J Am Chem Soc 1985, 107, 3823.
- 9. Tsuchida, E.; Shigehara, K. Mol Cryst Liq Cryst 1984, 106, 361.
- Zhou, G. B.; Ishrat, M.; Smid, J. Polym Commun 1989, 30, 52.
- Lonergan, M. C.; Ratner, M. A.; Shriver, D. F. J Am Chem Soc 1995, 117, 2344.
- Zhou, G. B.; Khan, I. M.; Smid, J. Macromolecules 1993, 26, 2202.
- Xu, H. S.; Yang, C. C. J Polym Sci Part B: Polym Phys 1995, 33, 745.
- Zhang, S. S.; Liu, Q. G.; Yang, L. L. Polymer 1994, 35, 3740.
- 15. Ohno, H.; Ito, K. Polymer 1995, 36, 891.
- Wang, Y. P.; Lei, Y. H.; Wang, R. M. J Appl Polym Sci 1998, 69, 835.
- 17. Wright, P. V. J Macromol Sci Chem 1989, A26, 519.
- 18. Rose, N. C. J Chem Educ 1967, 44(5), 283.
- Tsuchida, E.; Takeoka, S. in Macromolecule–Metal Complexes; Ciardelli, F.; Tsuchida, E.; Wohrle, D. Eds.; Springer: Berlin, 1996, p 153.
- Wang, Y. P.; Feng, H. Y.; Fu, Z. S.; Tsuchida, E.; Takeoka, S.; Ohta, T. Polym Adv Technol 1991, 2, 295.
- Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
- 22. Vogel, H. Phys Z 1921, 22, 645.
- Tammann, V. G.; Hesse, W. Z. Anorg Allg Chem 1926, 156, 245.
- 24. Fulcher, G. C. J Am Ceram Soc 1925, 8, 339.
- 25. Gibbs, J. H.; DiMarzio, E. A. J Chem Phys 1958, 28, 373.