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PMDA–ODA–PSX–DABSA copolymer for ionic conduction

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A quaternary copolymer, containing 1,2,4,5-benzene tetracarboxylic dianhydride (PMDA), 4-aminophenyl ether (ODA), aminopropyldimethyl terminated polydimethylsiloxane (PSX) and 2,5-diaminobenzene sulfonic acid (DABSA), has been successfully synthesized to become an ionic conductor for electrochemical applications. It combines the functions of immobilized anionic groups (SO_3^-) incorporated into polyimide to increase mobile cation concentration and of PSX introduced to enhance ionic conductivity via flexible chain motion assistance. As a result, an improvement of multiple orders of magnitude for conductivity from each function has been achieved by this copolymer. These conductivities are also confirmed to be of an ionic nature.

(Keywords: quaternary copolymer; polyimide; ionic conductivity)

INTRODUCTION

Since polymers can be cast into thin films and stacked in multifilm cells to save weight, high-temperature ionic conducting polymers, as a new class of polymer electrolytes, have been proposed to replace ceramic electrolytes and molten salts in electrochemical cells to improve their performance[1,2]. The existing polyethylene oxides (PEO) and perfluorinated ionomers (Nafion) presently used in solid-state polymer batteries and sensors are, however, only able to work at temperatures below 125°C[3,4]. To obtain high-temperature polymer electrolytes, polyimides (PI) containing aromatic or heterocyclic rings (normally in combination) in the main-chain backbone have been selected as the copolymer host because they exhibit outstanding mechanical properties and excellent thermal and oxidative stability at temperatures above 250°C[5,6]. In our previous reports, polyimides were first incorporated with 2,5-diaminobenzene sulfonic acid (DABSA) to host cation via sulfonic groups[1,2] and then joined by polysiloxane (PSX) to make the polymer backbone flexible, thus enhancing the ion transport[7]. The ionic conductivity of lithium triflate-deoped PI–DABSA copolymer reached about 10^{-9} S cm^{-1} at 300°C (ca. 10^{-10} S cm^{-1} at 250°C) compared with that of pure polyimide (PMDA–ODA) of $< 10^{-14}$ S cm^{-1} at the same temperature. The lithium triflate-doped polyimide–polysiloxane (PI–PSX) segmented copolymer shows a conductivity of 10^{-7} S cm^{-1} at 300°C (10^{-8} S cm^{-1} at 250°C), still two orders of magnitude higher than that of polyimide containing DABSA. Based on the findings that either DABSA or PSX incorporation improves the ionic conductivity of polyimides, our investigation is now extended to the quaternary system of PMDA–ODA–PSX–DABSA copolymer, which is expected to combine the functions of DABSA and PSX to produce still better results for a real application.

In this paper, we report the successful synthesis of PMDA–ODA–PSX–DABSA copolymer with or without lithium dopant via a co-solvent system consisting of 1-methyl-2-pyrrolidinone (NMP) and tetrahydrofuran (THF), and the manipulation of the monomer addition sequence. The characterization of the copolymer was done by infra-red (i.r.) spectroscopy and differential scanning calorimetry (d.s.c.) measurement. Conductivities were measured at 20–300°C using the complex impedance method and the electronic transference numbers were evaluated by the d.c. polarization method. As a result, a much better ionic conductivity has been achieved (10^{-6} S cm^{-1} at 250°C), which is almost two orders of magnitude higher than that of PI–PSX and four orders of magnitude higher than that of DABSA containing polyimide. Finally, possible mechanisms for the conductivity enhancement are discussed.

EXPERIMENTAL

Reagents

The main reactants for polymerization were 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA, Aldrich, 97%), 4-aminophenyl ether (ODA, Aldrich, 97%), 2,5-diaminobenzenesulfonic acid (DABSA, Aldrich, 90%) and aminopropyldimethyl-terminated polydimethylsiloxane (PSX, i.e. PS 510 with an average molecular weight of 2500, obtained from Petrarch System). 1-Methyl-2-pyrrolidinone (NMP, Aldrich, 99+%) and tetrahydrofuran (THF, Fisher Scientific) were used as solvent.

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PDMA and ODA were purified by sublimation at around 240°C in vacuum. DABSA was stirred in water with activated carbon until boiling, followed by filtering. The monomer was then recrystallized three times from distilled water, washed with methanol twice and ether twice and dried under nitrogen. Purified PMDA and ODA as well as recrystallized DABSA were treated by powdering in a ceramic mortar to improve their solubility in the solvents. The lithium trifluoromethanesulfonate dopant ($LiCF_3SO_3$, 97%) was dried at 100°C for 4–5 h prior to use.

Copolymer synthesis and film preparation

Because PSX and aromatic monomers possess vastly different solubility behaviours, a co-solvent system consisting of NMP and THF is necessary to accomplish homogeneous solution copolymerization. Also, the sequence of adding the monomers becomes very important in the synthesis. In our experiments, 2,5-DABSA was first dissolved in NMP and stirred under a nitrogen stream at 50–60°C for 4–5 h; ODA and PSX dissolved in THF were subsequently added to the solution which was stirred at 35–40°C. PMDA was finally added and the mixture then stirred at the same temperature for more than 72 h. The procedure of lithium triflate incorporation was important, too, in preparing the copolymer–metal complex. Following our experience, $LiCF_3SO_3$ is added to the solution prior to PSX incorporation. After completion, the copolymer solution was refrigerated until film casting.

Conversion of the polyintermediates to the fully imidized copolymer was then accomplished by bulk thermal imidization, which involves casting the copolymer solution onto a glass slide and removing the solvent in a flowing nitrogen atmosphere at room temperature. Films were then subjected to scheduled heating in a nitrogen atmosphere at 60, 80, 100, 200 and 300°C for 1 h at each temperature. In certain cases, the copolymer was cast on a metal-coated glass slide to serve as an electrode for the conductivity measurement. In all cases, thermally and mechanically stable films 10–30 μm thick were obtained.

Characterization

A Hewlett-Packard (HP 4284A) precision LCR meter was employed to measure the magnitude of the real and imaginary impedance at frequencies from 20 Hz to 1 MHz in a temperature range of 20–300°C. It is interfaced with a personal computer to handle the data acquisition. Complex impedance spectra were plotted and the conductivity was evaluated by extrapolating the impedance arc to intercept the real axis. In all cases, the relative errors were estimated to be less than 10%. The electronic transference numbers were measured by the d.c. polarization method.

The i.r. spectroscopic measurements were carried out on a BioRad FT-IR (model FTS-40) spectrometer, incorporated with a SPC 3200 data acquisition system. The spectra were measured at room temperature under nitrogen in the wavenumber range 400–4000 cm^{-1}.

D.s.c. was used to determine the glass transition temperature (T_g) with a Dupont 910 DSC module at a heating rate of 10°C min^{-1}. The specimens were vacuum dried for 24 h before being sealed in a nitrogen atmosphere.

RESULTS AND DISCUSSION

To ensure the copolymerization, rather than blending, of designated composition, maximum solubility of the reactants must be maintained throughout the polymerization process in order to obtain high-molecular-weight, tough film samples. The monomer addition procedure is crucial because PSX comes as a viscous solution and thus affects the dissolving of reactants. Therefore, it is better to add other monomers (except PMDA) before PSX. PMDA is added to the solution last because it has to be simultaneously reacted with the other three reactants, condensing into copolymer. During out study, the above procedure was purposely altered and the resulting solution became an inhomogeneous mixture separated into two parts and a non-uniform film resulted. The present molar ratio is chosen because in our last report[7] a composition of 4PMDA:3ODA:0.6PSX gave the highest ionic conductivity. The final chemical struc-

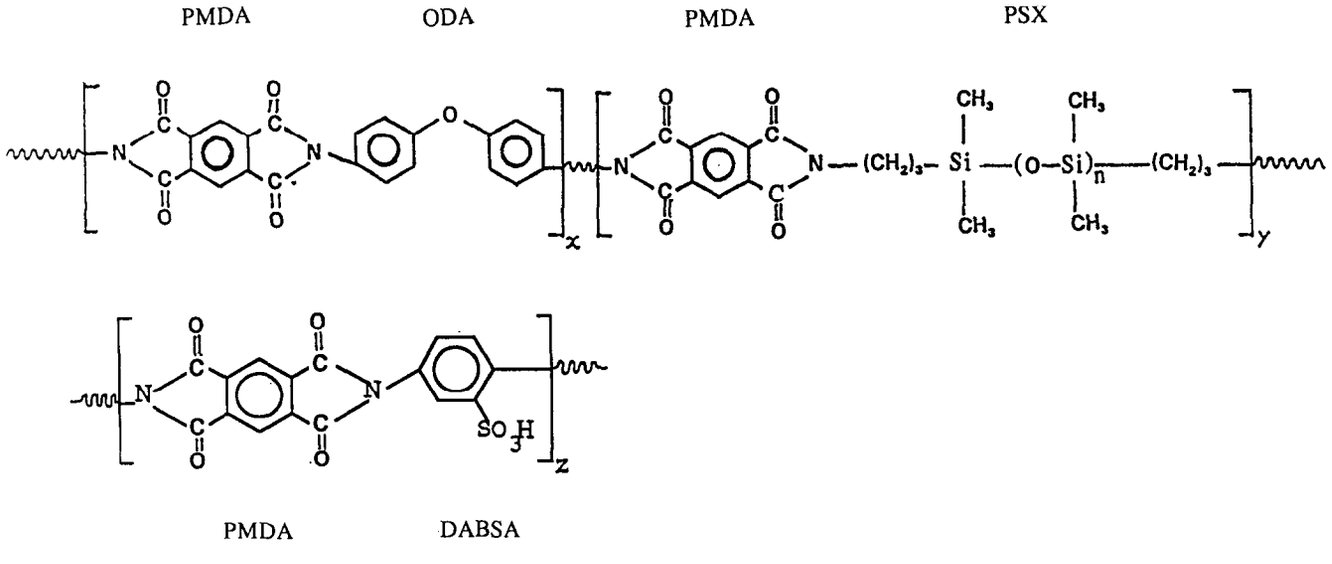

Figure 1 Chemical structure of PMDA–ODA–PSX–DABSA copolymer (molar ratio of $x:y:z = 3.0:0.6:0.4$)

ture of the copolymer is shown in *Figure 1*. Although the addition of 0.4 moles DABSA to the composition makes the mole number of PMDA equal to the mole numbers of (ODA + PSX + DABSA), the balance between organic acid and base may still not be perfect because PSX is a polymer itself, with an average molecular weight.

In the synthesis of the copolymer, it was found that PSX was sometimes floated in the solution, indicating that PSX had not been incorporated to become a copolymer and a non-homogeneous film was subsequently obtained. When a clear solution and a uniform film were produced, we believe that PSX had already been reacted into PMDA–ODA-PSX–DABSA copolymer. This can be verified by the thermal analysis of the shift of T_g. To characterize the copolymer, the i.r. spectrum of the PMDA–ODA–PSX–DABSA sample was measured and is shown in *Figure 2*. The wide band at 704–881 cm^{-1} can be attributed to Si–C absorbance and that at 1030–1170 cm^{-1} to those of Si–O–Si, Si–O and C–N. The peak at 1500 cm^{-1} is assigned to the aromatic carbon–carbon stretching vibration and both patterns at 1770 and 1735 cm^{-1} represent the cyclic imide structure. The sharp line at 2969 cm^{-1} is related to the characteristic line of hydrocarbon (methyl) groups within the PSX. The presence of water in the copolymer can be seen in the hydrogen–oxygen stretching vibrational regions near 3400 cm^{-1}.

The d.s.c. measurement carried out for the sample of 4PMDA:3ODA:0.6PSX:0.4DABSA is shown in *Figure 3*. A kink at ca. 120°C found on the thermogram is attributed to the glass transition temperature (T_g) of the

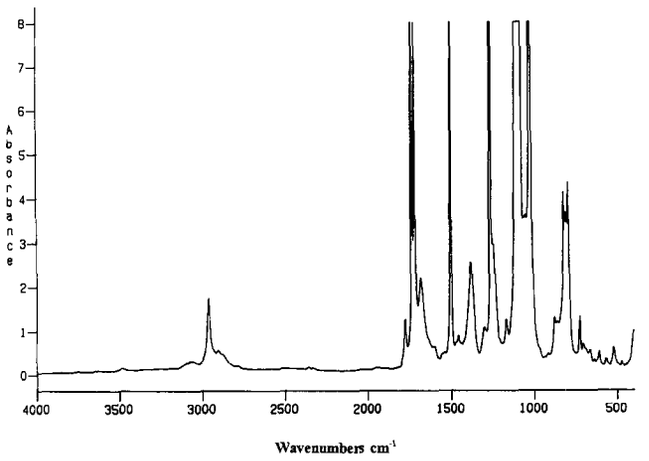

Figure 2 I.r. spectrum of PMDA–ODA–PSX–DABSA copolymer

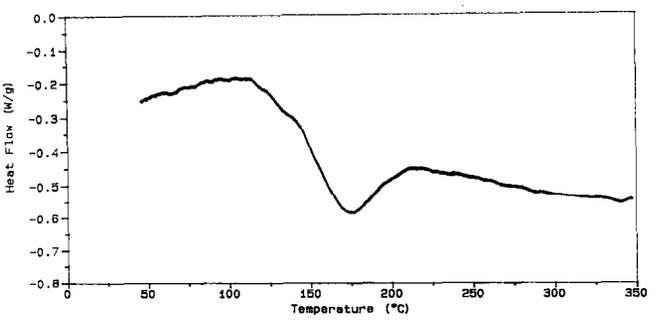

Figure 3 Differential scanning calorimetry thermogram of PMDA–ODA–PSX–DABSA copolymer

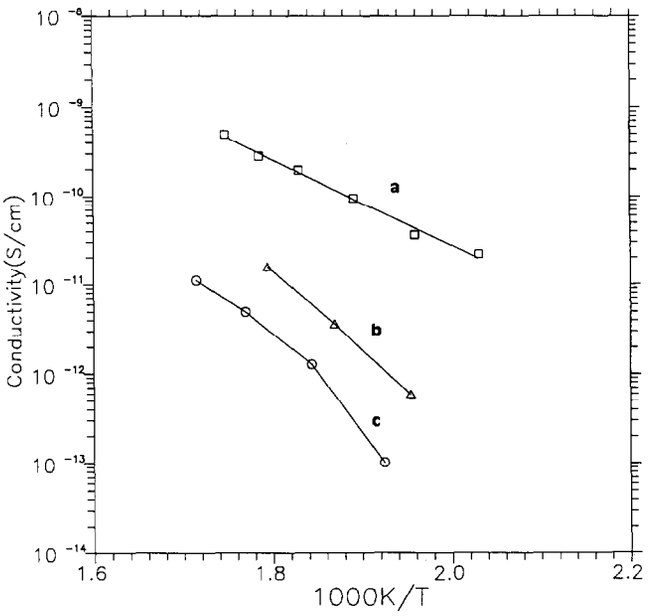

Figure 4 Logarithmic conductivity *versus* reciprocal temperature for three samples (curve a, 4PMDA:30DA:0.6PSX:0.4DABSA; curve b, 4PMDA:30DA:1DABSA; curve c, 4PMDA:3ODA:0.6PSX)

copolymer. It drops by more than 200°C from the T_g of PMDA–ODA–DABSA copolymer (347°C)[1]. This further supports our claim to have a copolymer of PMDA–ODA–PSX–DABSA, because PSX is a rubbery polymer whose incorporation lowers the T_g of the overall copolymer structure. This is also desirable because the chain flexibility of the copolymer is then increased by a large amount to assist the ionic motion. However, the film itself is thermally stable at 300°C.

The conductivity of pure PMDA–ODA–PSX–DABSA copolymer (shown in *Figure 4*, curve a), measured by the a.c. impedance method, was found to reach 10^{-9} S cm^{-1} at 300°C (ca. 10^{-10} S cm^{-1} at 250°C). Compared with that of pure polyimide (PMDA–ODA, 10^{-14}–10^{-16} S cm^{-1} at the same temperature range), five orders of magnitude enhancement has been achieved. This enhancement is also compared with those of the two polyimide-containing copolymers reported earlier[2,7], which are also listed in *Figure 4*. The conductivity was at 10^{-12} S cm^{-1} for PMDA–ODA–DABSA copolymer (4PMDA:3ODA:1DABSA, curve b in *Figure 4*) and 10^{-13} S cm^{-1} for PMDA–ODA–PSX copolymer (4PMDA:3ODA:0.6PSX, curve c) around 300°C, i.e. three and two orders of magnitude improvement from that of pure polyimide, respectively. As was discussed before[1,2], the conductivity improvement in PMDA–ODA–DABSA was caused by the immobilized anionic groups (SO_3^-) incorporated into polyimide, which increases mobile cation concentration and hence the ionic conductivity. The cation jumping via activation can be proved by the Arrhenius relation found in its logarithmic conductivity *versus* reciprocal temperature plot (curve b, *Figure 4*). On the other hand, the enhancement by PSX incorporated into polyimide is caused by the introduction of chain flexibility, thus increasing the ionic conductivity via chain motion assistance[7], which is supported by the Bent–Arrhenius relation of logarithmic conductivity *versus* reciprocal temperature (VTF)[8–10]. Since both PSX and DABSA are

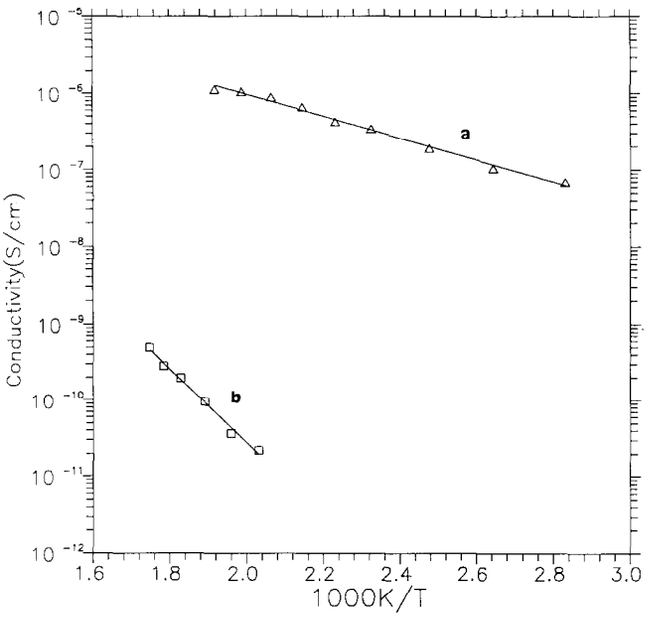

Figure 5 Logarithmic conductivity *versus* reciprocal temperature for PMDA–ODA–PSX–DABSA copolymers (curve a, 4PMDA:3ODA: 0.6PSX:0.4DABSA:2$LiCF_3SO_3$; curve b, 4PMDA:3ODA:0.6PSX: 0.4DABSA)

incorporated in the new copolymer, the combination of the above two mechanisms, i.e. of fixed anion group SO_3^- and of flexible chain motion assistance, enables us to get a multiple ionic conductivity enhancement up to five orders of magnitude from the pure polyimide, almost the product of the two (2 + 3) enhancement factors of each function. The Arrhenius relation found for this new PMDA–ODA–PSX–DABSA copolymer indicates that the cation jumping is still the dominating mechanism, although there is a combination of two effects. In addition, the electronic conductivity of this quaternary copolymer was found to be much less than 5% of the total, confirming the ionic nature of conduction.

To further increase the ionic conductivity, lithium triflate was doped into the copolymer with a molar ratio of 4PMDA:3ODA:0.6PSX:0.4DABSA:2$LiCF_3SO_3$. The resulting logarithmic conductivity is plotted *versus* reciprocal temperature in *Figure 5* (curve a). The conductivity of the lithium-doped copolymer reaches 10^{-6} s cm^{-1} at 250°C, which is another four orders of magnitude higher than that of pure PMDA–ODA–PSX–DABSA copolymer (also shown in *Figure 6*, curve b). The logarithmic conductivity *versus* reciprocal temperature of this copolymer is still a straight line showing Arrhenius behaviour. The activation energy is found to be 0.24 eV, which has dropped sharply from 0.89 eV of undoped PMDA– ODA–PSX–DABSA samples. This is obviously caused by the cation concentration increase via doping. Since the doped anions ($CF_3SO_3^-$) serve also as available sites for cations and act as (besides SO_3^- sites) intermediate sites for the cation jump, the average distance for a cation jump is greatly shortened, hence cation motion is easily accomplished and the conductivity is increased. Moreover, lithium ions may be coordinated by adjacent ether oxygens to form ionic complexes within the copolymer although the details remain to be explored. It should be noted that all our conductivity data are obtained under the stable condition, and the measurements are repeatable. Normally, these conductivities are not affected by moisture for temperatures above 120°C. In addition, the electronic conductivity is again found to be less than 5% of the total, indicating that our lithium triflate-doped PMDA–ODA–PSX–DABSA copolymer is indeed a cation conductor.

CONCLUSIONS

PMDA–ODA–PSX–DABSA copolymers with or without doped lithium triflate ($LiCF_3SO_3$) have been prepared. It was found that the addition procedure of the monomer was crucial in synthesizing the copolymer formed by three monomers plus PSX. The large conductivity improvement of this quaternary copolymer was achieved by the combined effect of fixed anionic groups (SO_3^-), which increase mobile cation concentration, and PSX, which introduces chain flexibility. The conductivity of 4PMDA: 3ODA:0.6PSX:0.4DABSA:2$LiCF_3SO_3$ reaches 10^{-6} s cm^{-1} at 250°C, which is four orders of magnitude higher than that of 4PMDA:3ODA:1DABSA:1$LiCF_3SO_3$ and two orders of magnitude higher than that of 4PMDA:3ODA:0.6PSX:2$LiCF_3SO_3$ copolymers reported previously by this group. Moreover, the electronic conductivity of our new copolymer is found to be less than 5% of the total, indicating that the conductivity is essentially ionic.

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