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A novel low colored and transparent shape memory copolyimide and its durability in space thermal cycling environments

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HIGHLIGHTS

- A novel low colored and transparent shape memory copolyimide (SMcoPI) with good optical transmittance was synthesized.
- The high optical transmittance of SMcoPI is the results of the reduction of the charge transfer complex interactions.
- SMcoPIs exhibit excellent low and high temperature resistance in the ground-simulated space thermal cycling environments.

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ABSTRACT

Recently, shape memory polymers (SMPs) with high optical transmittance have been paid great attentions to endow the flexible optoelectronics with shape memory functions. Herein, a low colored and transparent shape memory copolyimide (SMcoPI) is obtained by suppressing the charge transfer complex interactions. The optical transmittance of the synthesized SMcoPI film could reach at ~86% at the wavelength of 450 nm, far higher than the nearly zero optical transmittance of yellow and brown Kapton H. The better optical transparency could be attributed to the loose molecular chain arrangements induced by the *meta*-substituted groups and flexible ether linkages. The glass transition temperature (T_g) range of the synthesized SMcoPI films is from 179 °C to 220 °C, which is higher than that of reported optically transparent SMPs. The effective decomposition temperature at the weight loss of 5 wt% is 517 °C, showing excellent thermal stability. The SMcoPI also demonstrated good shape memory behaviors with high shape recovery ratio (R_r, > 96%) and shape fixity ratio (R_f, > 97%). In addition, the SMcoPI could maintain high optical transmittance, good thermostability and excellent shape memory behaviors after the ground-stimulated space thermal cycling test for 250 h. The synthesized SMcoPI has application potentials in high temperature areas or optoelectronic devices.

1. Introduction

Among engineering polymers, aromatic polyimides (PIs) have been widely applied in heat insulators [1–3], fuel cells [4–7], gas separation [8–10], heaters [11,12], sensors [13,14], etc., due to their excellent mechanical properties and thermal and chemical stabilities. However, wholly aromatic PIs has poor solubility in common organic solvents due to the rigid molecular chains and strong interchain interactions, thus making the processing inconvenient and expensive [15–19]. The applications of fully aromatic PIs are also severely restricted in some fields where high optical transparency is basically required due to their deep color and poor optical transparency [20–25], which could be attributed to the strong intra-/inter-molecular charge transfer complex (CTC) interactions in the highly conjugated molecular structures [22,26–29]. Therefore, the studies on soluble and transparent PIs have attracted many attentions by researchers in past few decades. To improve the processability and optical transparency of PIs, many investigations has been carried out in modifying the molecular structures of PIs, including introduction of bulky pendant groups [18,30], high fluoride and sulfone structures [17,30–32], unsymmetrical and noncoplanar structures [16,32] or flexible linkages [33] into polyimide chains to suppress CTC interactions. These fabricated colorless and transparent PIs have been used as the substrates for displays [34,35], transistors [36], solar cells [37], and heaters [38,39].

Integrating shape memory functions with the optical transparency will enormously expand the applications of PIs. Using optically

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transparent shape memory PIs as the substrates for flexible electronics will meet the requirements of high temperature applications that traditional transparent shape memory polymers are not available [40–45]. In past ten years, shape memory polyimides (SMPIs) and their composite materials with adjustable T_g ranging of 140–323 °C have been well developed and the shape memory functions have been also investigated trough bending, stretching and twisting methods [46–53]. Those SMPIs will have attractive high temperature applications where active shape change is required [47,54]. However, most SMPIs have deep color and poor optical transparency besides the only optically transparent SMPI that fabricated by Xiao et al. [55] in 2016. The optical transparency of the reported SMPI is achieved by reducing the molar ratio of the diamine to dianhydride, which will lead to poor mechanical properties.

In this paper, SMcoPI films were fabricated while keeping constant molar ratio of diamine ((1,3-bis(3-aminophenoxy)benzene (BAB)/(4,4′-(1,1′-biphenyl-4,4′-diyldioxy)dianiline (BAPB)) to dianhydride (bis phenol A dianhydride (BPADA)) of 1:1 and solid content of 15 wt%. The SMcoPI films have high optical transparency, excellent thermo-mechanical properties, thermal stabilities, excellent shape memory performances and good thermal cycling resistant properties. The T_g range of the SMcoPI is 179 °C–220 °C and could be tuned through adjusting the molar ratio of BAB to BAPB. The basic performances of SMcoPI films were characterized and the possible mechanism of the high transmittance of SMcoPI film was discussed, which could be a reference for the development of other transparent SMPs. Moreover, the durability of the high transmittance of SMcoPI film in the simulated space thermal cycling environments was investigated.

2. Experimental

2.1. Synthesis of the low colored and transparent shape memory copolyimide films

The two-step polycondensation process is demonstrated in Scheme 1, and the synthetic procedures are described as follows (as illustrated in Fig. S1). Firstly, the BAB (Tokyo Chemical Industry Co. Ltd., Japan) and BAPB (Aladdin Industrial Co. Ltd., China) were fed into DMAc (Aladdin Industrial Co. Ltd., China) solvent successively and stirred at 20 °C until completely dissolved. Then, BPADA (Sigma-Aldrich Co. Ltd., USA) was added into the above solution and stirred for one day at 20 °C, thus a poly(amic acid) with high viscosity (PAA) was formed successfully. The above polycondensation procedure was finished under the protection of dry nitrogen. Lastly, PAA was degassed on vacuum dry chamber at 40 °C for 3 h and then cast onto the supporting plates and the imidization occurs inside the oven where the temperature was successively kept at 80 °C, 110 °C, 180 °C, 200 °C and 250 °C for 2 h each. The samples were peeled off glass substrates in warm water, and dried at 100 °C in the vacuum dry chamber for 30 min. SMcoPI film samples named A1, A2, A3 and A4 were synthesized with different molar ratio of BAB to BAPB. The basic properties of these samples were characterized and the characterization methods could be found in Supplementary Information. The molar ratio, molecular weights (M_n), polydispersities (PDI), densities (ρ) and T_g of those samples are summarized in Table 1.

2.2. Ground-simulated space thermal cycling experiments

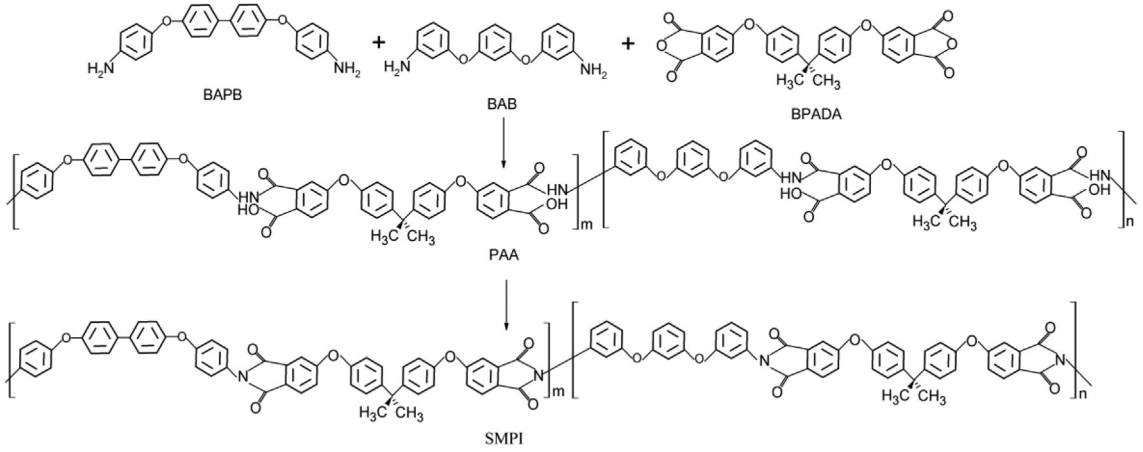
The simulated thermal cycling experiments were carried out in the BZ11 thermal cycling chamber with a vacuum pressure $\leq 6.65 \times 10^{-3}$ Pa. The operating temperature ranged from +88 °C to −117 °C at a heating/cooling temperature gradient of 3 °C/min. Each thermal cycle lasted for about 13.4 h, including 5 h at constant +88 °C and −117 °C, respectively. The total number of thermal cycling was 18.5 and the whole test period was about 250 h.

3. Results and discussion

3.1. Chemical structures and molecular chain structures

ATR-FTIR spectra of the samples are illustrated in Fig. 1. There are three typical peaks of PIs, i.e., the stretching vibration of C—N—C at 1368 cm^{-1}, symmetric stretching of C═O at 1715 cm^{-1} and asymmetric stretching of C═O at 1782 cm^{-1}. Meanwhile, we cannot find the traces of carbonyl (C═O) peaks of isoimides at 1795-1820 cm^{-1} or 920-935 cm^{-1}, and cannot observe the carbonyl (C═O) stretching peaks of inter-chain imides at around 1675 cm^{-1} neither [53–56]. Hence, the samples were all fully imidized after the second polycondensation process.

Judging from M_n and the structural unit (as illustrated in Scheme 1), the copolyimide chain of A2 comprises 120 structural units (m = 48, n = 72), where the repeat units are 24. Sample A2 has the larger structural unit number and higher distortion of copolyimide chains, since it has the highest M_n and PDI according to Table 1. The XRD patterns of the samples are shown in Fig. 2. The broad peaks of samples indicate that these samples are non-crystalline structures since the diffraction of intermolecular packing has some regularity combined with amorphous halo [22,55]. The amorphous nature of these SMPIs could be due to the introduction of the ether linkages and isopropylidene groups of BPADA and the *meta*-substituted ether linkages of BAB and BAPB. The broad peaks centered 2θ = 17.3°, 16.7°, 17.2° and 17.6°, for A1, A2, A3, A4, respectively, and the calculated interchain distances (d-spacing) were 5.1 Å, 5.3 Å, 5.1 Å, 4.9 Å. The larger interchain distance indicates that A2 might have looser polymer chain



Scheme 1. The two-step polycondensation process of SMcoPI films.