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A New Strategy To Prepare Rodlike/Flexible Polyimide Blends through Poly(amic acid) Amine Salt Precursors

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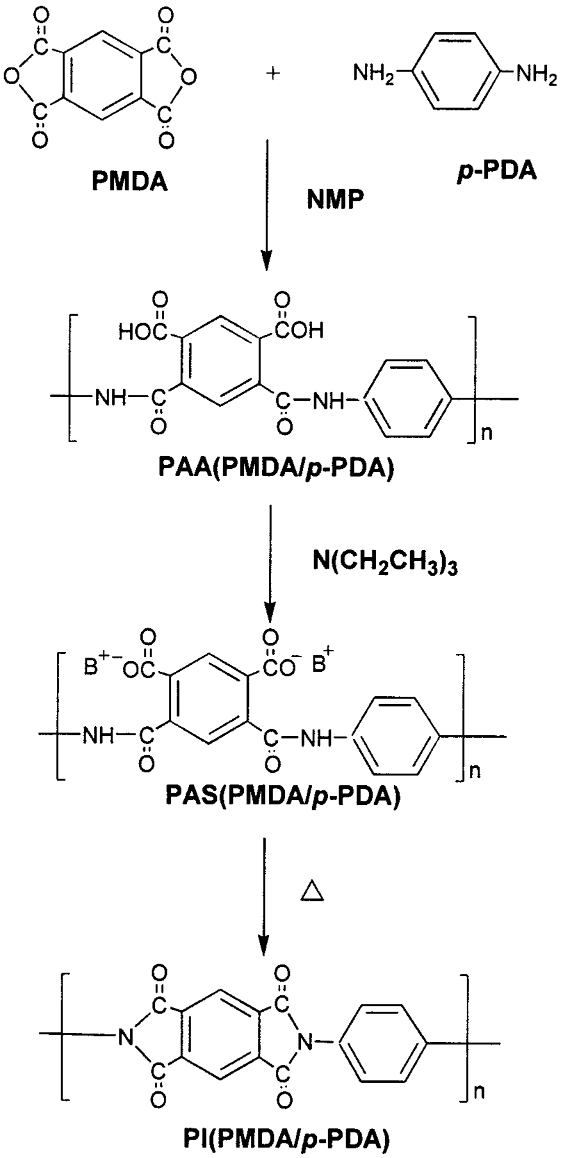
Introduction. Polyimides (PIs) are extensively used in microelectronics and aerospace industries owing to their excellent thermal, mechanical, and dielectric properties.[1,2] A variety of PIs have been molecularly designed on the basis of knowledge acquired on the structure−property relationships to satisfy the specific requirements for optimal performance in specialty applications. Blending, especially rodlike and flexible pair, provides an alternative and economical route for producing new PI materials.[3−10] Miscibility is crucial to the performance of the resulted blends, e.g., molecular composites, where rigid and flexible components are miscible which enables to enhance simultaneously conflicting properties such as modulus and toughness. Thus, study on the miscibility of rodlike/flexible PI blends is very important.

Unlike traditional polymers, which may be blended by mixing polymer solutions or melts, polyimides preclude such an approach since the majority of polyimides of practical importance are insoluble and infusible. Thus, PI blends are best approached via mixing of the soluble polyimide precursors, followed by either thermal or chemical imidization to the final polymides. Poly(amic acid)s are the most common precursors to polyimides and are thus considered as the precursors in blending.[3,4] However, studies by Ree et al. showed that mixtures of poly(amic acid)s could lead to the formation of segmented copolymers via transamidation exchange reactions rather than molecularly mixed blends of two homopolymers.[4] Unlike poly(amic acid)s, poly(amic ester)s in a solvent are not in equilibrium with their constituent monomers, and the lack of transamidation makes it possible to prepare polyimide blends by solution blending of respective poly(amic ester)s.[5−8]

Poly(amic acid) amine salts, which are the derivatives of poly(amic acid)s obtained by neutralizing the protons at the carboxylic groups using amines such as triethylamine, can also act as precursors for PIs. Exchange reactions do not prevail in poly(amic acid) amine salts, too.[11,12] However, compared to poly(amic ester)s, the preparation of poly(amic acid) amine salts is much more straightforward and easier. In addition, poly(amic acid) amine salts as PI precursors are used more and more in practice. For instance, the ionic photosensitive precursors of polyimides have found wide use in the microelectronic field.[2,13,14] This paper presents a new approach to obtain miscible rodlike/flexible polyimide blends through poly(amic acid) amine salt precursors.

Scheme 1



Experimental Section. Pyromellitic dianhydride (PMDA), biphenyltetracarboxylic dianhydride (BPDA), 2,2′-bis(3,4-dicarboxy)phenylhexafluoropropane (6FDA), 1,4-phenylenediamine (*p*-PDA), and 2,2′-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) were available commercially. All the dianhydrides and diamines were purified by vacuum sublimation or recrystallization just before use in polymerization. Anhydrous grade *N*-methyl-2-pyrrolidinone (NMP) and triethylamine (TEA) were purified by drying with 4 Å molecular sieves for about 1 week followed by distillation under a nitrogen atmosphere.

Poly(amic acid) amine salts were prepared as shown in Schemes 1−3. Typically, a mixture of a dianhydride and a respective diamine in NMP was stirred for 6 h at room temperature under nitrogen, and an appropriate amount of TEA was added to the above poly(amic acid) solution to neutralize all the carboxylic acid groups. The weight-average molecular weights of PMDA-*p*-PDA PAA, BPDA- *p*-PDA PAA, and 6FDA-BAPP PAA precursors measured by GPC were 308 350, 310 870, and

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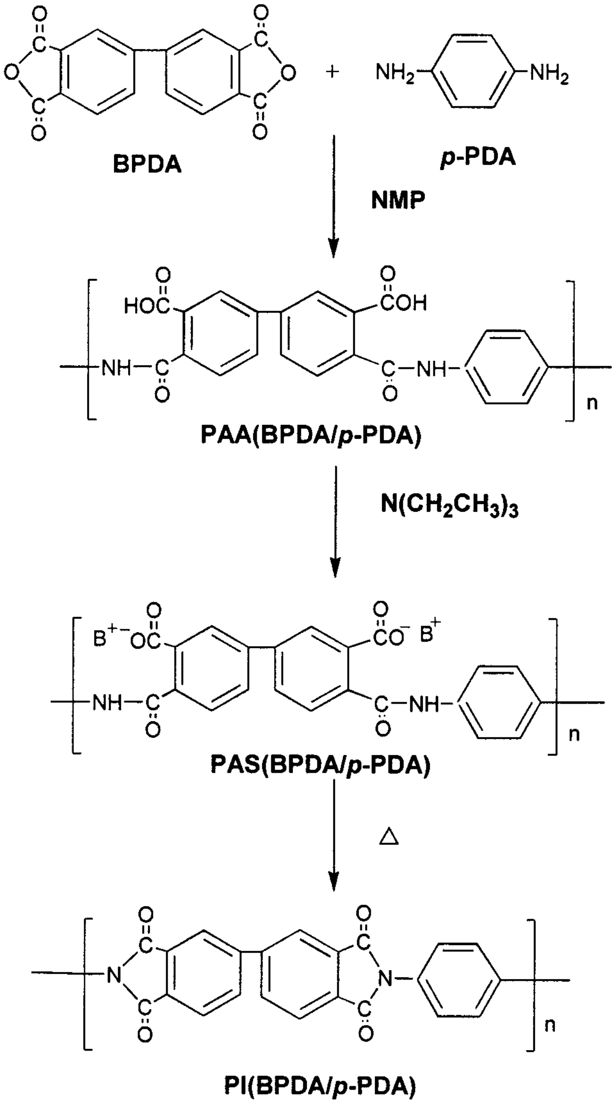
Scheme 2

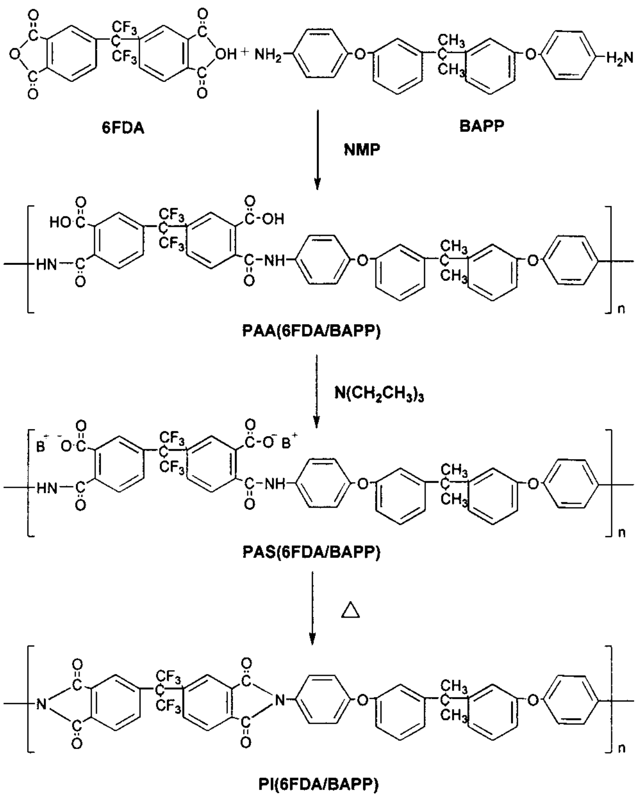


302 930 Da, respectively. GPC measurements were performed on a Waters GPC system containing a Waters 2690 separation module and a Waters 2487 UV detector. Polystyrene samples were used as a calibration standard, and the mobile phase used was THF:DMF (1:1) containing 0.06 M LiBr and 0.06 M H_3PO_4. Three numbers of Gelpack GL-S300MDT-5 column of size 8 mm × 300 mm were used.

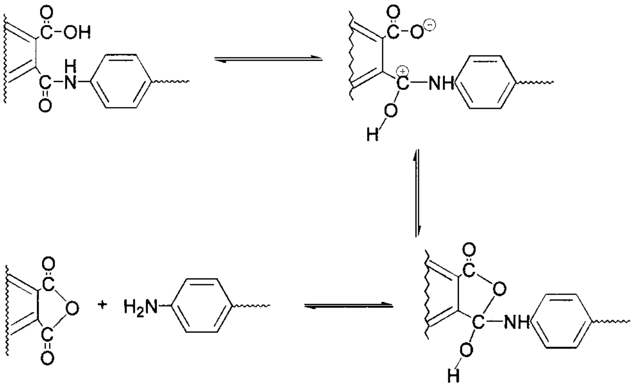
The NMP solutions of poly(amic acid) amine salts were blended at various compositions (100/0, 75/25, 50/50, 25/75, and 0/100 in w/w) for 24 h on a roller mixer. The resulting solutions at a concentration of 6−10 wt % were cast onto glass plates or silicon wafers, followed by soft baking at 100 °C for 60 min. The films were then thermally cured in an oven with nitrogen flow by step curing at 200 °C for 1 h, 250 °C for 1 h, and finally 320 °C for 1 h with a heating rate of 10.0 °C/min.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elemer Pyris 1 DSC. The instrument was calibrated with an indium standard, and a heating rate of 20 °C/min was used. Dynamic mechanical analysis (DMA) measurements were performed using a TA Instruments DMA 2980. A heating rate of 3 °C/min and a frequency of 1 Hz were employed. Thermomechanical analysis (TMA) was performed using a TA Instruments TMA 2940 at a heating rate of 5 °C/min. All the thermal analysis experiments were conducted in an inert nitrogen atmosphere.

Scheme 3



Scheme 4



Results and Discussion. The exchange reaction in poly(amic acid) solutions may due to a reverse reaction to anhydride and amine as shown in Scheme 4. The main cause for the chain scission may be attributed to the neighboring hydroxyl of the carboxylic group.[1,11,12] If proton transfer can be prevented, then the potential for the amic acid reverse reaction might be eliminated. The formation of poly(amic acid) amine salts by neutralizing with a tertiary amine is the simplest way to prevent proton transfer.

The blend solutions of PMDA-*p*-PDA/6FDA-BAPP amic acid amine salts were inhomogeneous and had no obvious change even after 10 days stirring, indicative of immiscibility of this pair. The fully imidized PMDA-*p*-PDA/6FDA-BAPP blend films showed obvious macrophase separation. Figure 1 shows DSC curves of the fully imidized flexible PI 6FDA-BAPP and its 50/50 (w/w) blend with PMDA-*p*-PDA stirred for 1 and 10 days in solution state before thermal imidization. The glass

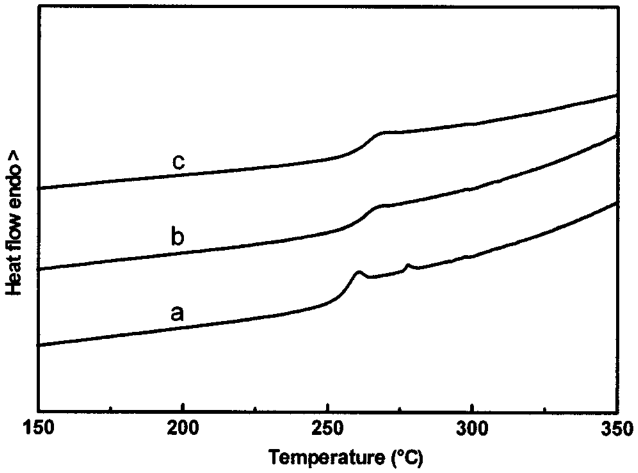


Figure 1. DSC curves of 6FDA-BAPP (a) and 50/50 PMDA-*p*-PDA/6FDA-BAPP blends: mixing time in the precursor solution was (b) 1 day and (c) 10 days.

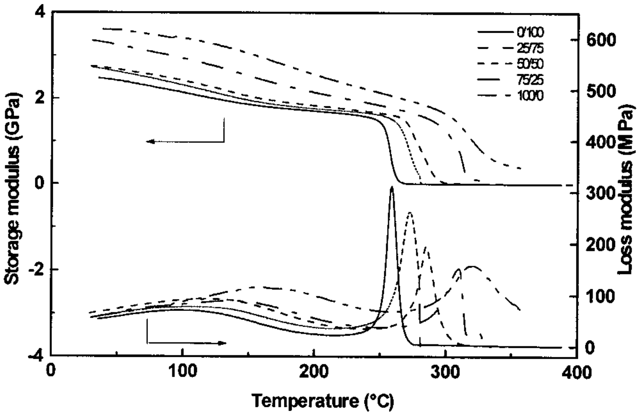


Figure 2. Dynamic mechanical relaxation behaviors of BPDA-*p*-PDA/6FDA-BAPP blends of different feed ratios.

transition temperature (T_g) of the rigid PI PMDA-*p*-PDA is too high to be detectable by DSC. The blend showed a T_g very close to the flexible one, demonstrating the immiscibility of the blend. The T_g showed no apparent change even after 10 days stirring, precluding the existence of intermolecular exchange reactions for the blends of poly(amic acid) amine salts.

The NMP blend solutions of BPDA-*p*-PDA/6FDA-BAPP of various feed ratios were optically clear, indicative of the formation of miscible solutions. The cast and the fully thermally imidized BPDA-*p*-PDA/6FDA-BAPP blend films of various feed ratios were transparent. The dynamic mechanical curves of the fully imidized blends of different feed ratios are shown in Figure 2. The rodlike PI BPDA-*p*-PDA shows a broad β transition at around 160 °C, which is due to the motion of aromatic moieties on the backbone, and a T_g around 325 °C. The flexible one showed its β and T_g's at 100 and 259 °C, respectively. Each BPDA-*p*-PDA/6FDA-BAPP blend was found to exhibit a single and composition-dependent T_g, which can be correlated by the Kwei equation:[15]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2$$

where T_g, T_{g1}, and T_{g2} are respectively the glass transition temperatures of the blend, polymer 1, and polymer 2; w_1 and w_2 are the corresponding weight fractions, and k and q are fitting constants. As shown in Figure 3, the T_g–composition curve for BPDA-*p*-PDA/6FDA-BAPP blends can be fitted using $k = 0.8$ and $q = 0$. It is worth noting that the values of storage modulus of the blends were located between the values of two components.

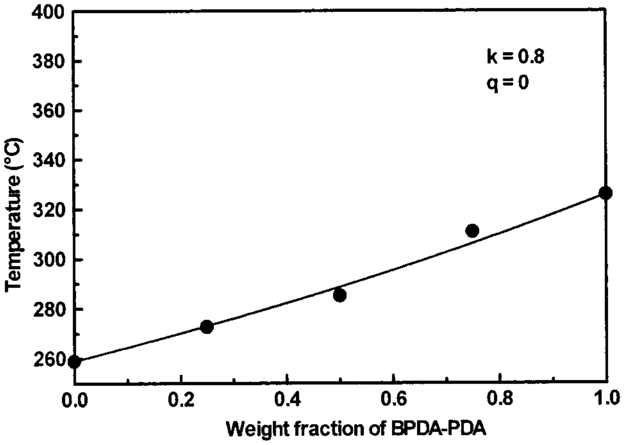


Figure 3. T_g–composition curve for BPDA-*p*-PDA/6FDA-BAPP blends fitted by the Kwei equation.

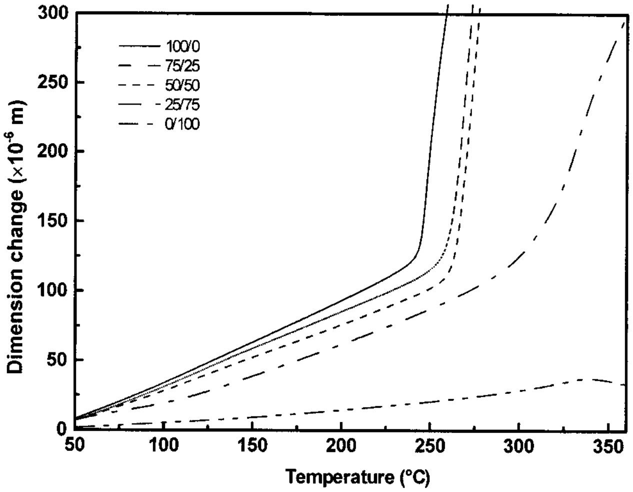


Figure 4. TMA curves of BPDA-*p*-PDA/6FDA-BAPP blends of different feed ratios.

Table 1. T_g's and CTE of BPDA-*p*-PDA, 6FDA-BPAA, and Their Blends of Different Feed Ratios

BPDA-*p*-PDA/6FDA-BPAA	0/100	25/75	50/50	75/25	100/0
T_g (DMA) (°C)	259.0	272.9	285.2	310.8	325.0
T_g (TMA) (°C)	243.1	261.5	264.5	313.6	338.0
CTE (ppm/m °C)	68.5	63.5	57.2	54.8	14.8

Figure 4 shows the thermomechanical curves for BPDA-*p*-PDA/6FDA-BAPP blends. A single T_g is also evident at the abrupt change in dimension change. The coefficients of thermal expansion of pure polymers and their blends are listed in Table 1. The flexible PI 6FDA-BAPP possesses a relatively high thermal expansion coefficient, and the thermal expansion coefficients of the blends decrease gradually as the rigid component increased.

Conclusion. The preparation of rodlike/flexible polyimide blends is feasible by utilizing poly(amic acid) amine salt precursors, which are free from the intermolecular transamidation reaction. Miscibility of a rodlike/flexible blend, BPDA-*p*-PDA/6FDA-BAPP, was demonstrated using various thermal analyses.

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