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Communications to the Editor

Curable Aromatic Polyimides Containing Enaminonitrile Groups

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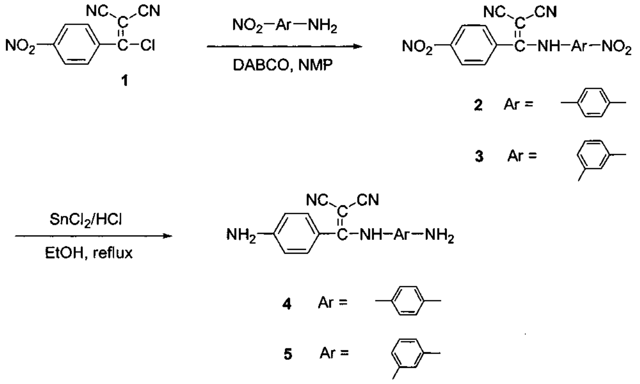
Among thermally stable polymers, aromatic polyimides find many applications in electronics and composites, because of their high glass transition temperature (T_g), outstanding chemical stability, and mechanical properties. However, their high T_g and insoluble nature in most organic solvents make them difficult to fabricate.[1] Generally, the processing of polyimides has been accomplished through the soluble poly(amic acid) precursor, which has some problems such as hydrolytic instability of the poly(amic acid)s, corrosion of copper interconnecting metal, and generation of water during the cure process.[2] To address these problems, several approaches for soluble polyimide including introduction of a flexible linkage or bulky substituents on the main chain[3] and use of noncoplanar or unsymmetrical monomers[4] have been developed. However, the approaches for soluble polyimides through structural modification are often accompanied by deterioration of some physical properties.

Poly(enaminonitrile)s (PEANs) which were synthesized by J. A. Moore show hydrolytic stability, excellent thermal properties, and good solubility in organic solvents, and can be cured thermally without evolution of volatile byproducts to the insoluble polymers.[5] Bulky enaminonitrile groups not only enhance the solubility of polymers but also increase the thermal stability, T_g and chemical resistance of polymers through curing without any volatile byproducts. Several aromatic polyamides containing enaminonitrile groups were synthesized,[6] but unsymmetrical diamines with one enaminonitrile unit have not been reported. In this communication, we describe our successful attempt to obtain a soluble polyimide by using an unsymmetrical diamine monomer containing a curable enaminonitrile unit.

Scheme 1



The diamine monomers containing one enaminonitrile unit were prepared from (chloro-4-nitrophenylmethylidene)propanedinitrile (**1**) in two steps, as shown in Scheme 1.

(Chloro-4-nitrophenylmethylidene)propanedinitrile (**1**) was prepared according to the previously reported procedure.[7] The product **1** was reacted with 4-nitroaniline in a polar aprotic solvent in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) as an acid acceptor to form the nitro compounds **2** and **3**. Complete reduction of the dinitro compounds was found to be difficult with a palladium catalyst, presumably because of the complexation of palladium with the reactant or the product.[6a] However, the nitro compounds were hydrogenated successfully with stannous chloride/HCl to give the corresponding diamine monomers **4** and **5** with 84 and 75% yields, respectively. The above result revealed

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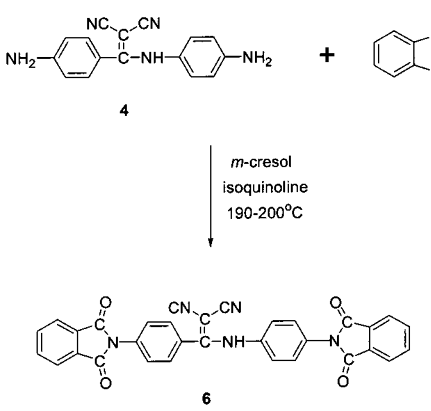
Scheme 2



Scheme 3

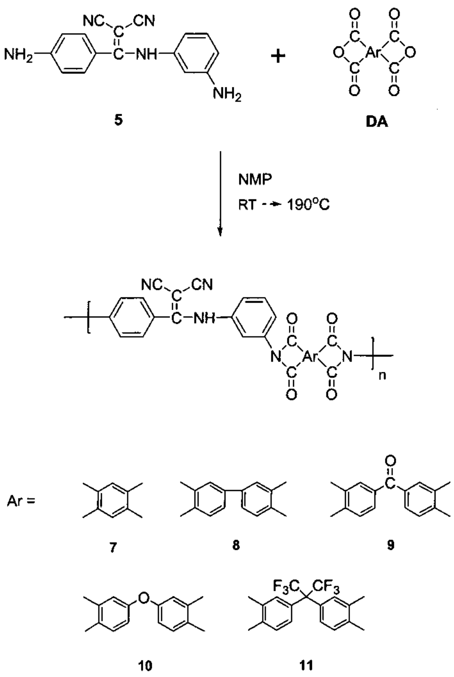


Table 1. Properties of Polyimides

polymer	$[\eta]^a$ (dL/g)	$T_{d5}{}^b$(°C) in N_2 (°C)	 in air (°C)	char yield at 800 °C (%)^c	$T_{exo}{}^d$ (°C)
7	0.54	545	493	60	387
8	0.46	572	519	67	379
9	0.45	555	507	60	376
10	0.54	548 (567)^e	514	61	373
11	0.46	524	512	52	383

[a] Intrinsic viscosity in DMAc (0.5 g/dL) at 25 °C. [b] T_{d5} (5% weight loss temperature) was measured by TGA at a heating rate of 10 °C/min. [c] Measured by TGA at a heating rate of 10 °C/min in nitrogen. [d] Measured by DSC at a heating rate of 10 °C/min in nitrogen. [e] T_{d5} (5% weight loss temperature) after curing at 450 °C was measured by TGA at a heating rate of 10 °C/min.

the hydrolytic stability of the enaminonitrile group in HCl solution. The chemical structure of the monomers were confirmed by spectral analyses.[8]

The model reaction was conducted to investigate the reactivity of the diamine monomers and to obtain a model compound as a reference material for structural analysis and curing reaction. Diamine monomer **4** was reacted with monofunctional phthalic anhydride in *m*-cresol in the presence of a catalytic amount of isoquinoline at 190 °C. The water generated during the imidization was removed by azeotropic distillation of chlorobenzene and water. Diimide model compound **6** was obtained quantitatively (Scheme 2).

The structure of model compound **6** was confirmed with IR and ^{1}H NMR analyses. FT IR spectrum of **6** shows absorption bands at 1782, 1718, 1375, and 719 cm^{-1} corresponding to the C=O imide asymmetric and symmetric stretching, C−N imide stretching, and C=O imide bending, respectively, and at 2206 cm^{-1} corresponding to the CN stretching. ^{1}H NMR spectrum of **6** shows a peak at 11.01 ppm corresponding to enaminonitrile proton ($-NH-C=C(CN)_2$). Also, thermal behavior of the diimide model compound was examined with DSC. DSC analysis showed two melting points at 358 and 442 °C, and irreversible exothermic transition between 360 and 400 °C, due to the curing of the enaminonitrile groups in the model compound **6**. It seems that upon initial melting, the compound undergoes the exothermic curing and immediately crystallizes, resulting in a second melting. The exothermic peak was completely absent, and only the second melting point was observed when the sample was cooled and rescanned.

Polymerization of the diamine monomer **4** with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) or 4,4′-oxydiphthalic anhydride (ODPA) was carried out via one-pot solution imidization method, but precipitation occurred during the imidization in both *N*-methylpyrrolidone (NMP) and *m*-cresol solvents. Polymerization of the diamine monomer **4** with ODPA in *N*,*N*-dimethylacetamide (DMAc) via chemical imidization method was also attempted, but only a low molecular weight polymer having inherent viscosity of 0.18 dL/g (DMAc, 30 °C) was obtained. However, polymerization of the diamine monomer **5** with commercially available dianhydrides, pyromellitic dianhydride (PMDA), 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA), hexafluoroisopropylidene diphthalic anhydride (6FDA), BTDA, and ODPA via the one-pot solution imidization method in NMP proceeded homogeneously, and high molecular weight polymers were obtained in quantitative yield (Scheme 3).[9] The polymers showed inherent viscosities in the range 0.45−0.54 dL/g. The weight-average molecular weight (M_w) of the polymer **11** measured by GPC was 51 000. The properties of the polymers are summarized in Table 1. The formation of polyimides was confirmed with IR and ^{1}H NMR spectroscopic analyses.

All the polymers were soluble in polar aprotic solvents such as NMP, DMAc, and *N*,*N*-dimethylformamide (DMF) and also in hot *m*-cresol. Interestingly, polymer **11** was even soluble in acetone and THF. These solubility results indicate that the enaminonitrile units in the polyimide chains effectively improve the solubility of aromatic polyimides.

Thermal behavior of these polymers was followed by DSC and TGA. DSC analysis showed a broad irreversible exothermic peak between 300 and 450 °C, depending on the dianhydride monomer employed, but the exothermic peak was completely absent when the samples were cooled and rescanned, indicating that the exothermic peak was caused by the curing of the polymers. After curing, the polymers were completely insoluble in the solvents that dissolved the uncured polymers.

The 5% weight loss temperatures of the polymers were in the range of 524−572 °C in nitrogen and 493−

519 °C in air. The above TGA results reveal that the polyimides with enaminonirile units have good thermal stability in nitrogen comparable to that of conventional polyimide like Kapton, but 5 wt % loss occurred at lower temperatures in air than in nitrogen, indicating that the polymers are somewhat susceptible to thermooxidative degradation. It seems that thermooxidative degradation of the polymer chains occurred before complete curing.

In summary, the diamine monomers containing one enaminonitrile unit were synthesized and polymerized with various aromatic dianhydrides by using the one-pot solution imidization method. While the polymerization of the diamine monomer **4** produced insoluble polymers, the polyimides from the diamine monomer **5** were soluble in polar aprotic solvents and showed excellent thermal stability. All the polymers exhibited broad irreversible exothermic transitions between 350 and 450 °C, indicating curing of enaminonitrile groups. The polymers became insoluble after curing.

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Supporting Information Available: Text giving synthetic procedures and figures showing FTIR, ^{1}H NMR, ^{13}C NMR, and HRMS spectra of monomers **4** and **5** and IR and ^{1}H NMR spectra and DSC curves of model compound **6** and polymer **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Spectral data of monomers **4** and **5**. [(*p*-Aminophenylamino)-4-aminophenylmethylidene]propanedinitrile (**4**): mp 292 °C (DSC); FT IR (KBr, cm^{-1}) 3437, 3350, 3250 (NH_2 and NH), 2213, 2190 (CN), 1606 (aromatic C═C); ^{1}H NMR (DMSO-d_6, 200 MHz) 9.96 (s, 1H, −NH-); 7.24 (s, 2H); 6.79 (s, 2H); 6.58, 6.54, 6.49, 6.45 (dd, 4H); 5.94 (s, 2H, −NH_2); 5.16(s, 2H, −NH_2); ^{13}C NMR (DMSO-d_6, 300 MHz) 167.93, 152.91, 147.19, 131.41, 127.27, 125.59, 119.03, 118.24, 116.04, 113.62, 112.74, 47.79. HRMS (*m*/*e*): calcd for $C_{16}H_{13}N_5$, 275.1172; found, 275.1172. [(*m*-Aminophenylamino)-4-aminophenylmethylidene]propanedinitrile (**5**): mp 238 °C (DSC); FT IR (KBr, cm^{-1}) 3473, 3364, 3232 (NH_2 and NH), 2207 (CN), 1602 (aromatic C═C); ^{1}H NMR (DMSO-d_6, 200 MHz) 10.08 (s, 1H, −NH−); 7.29, 7.24 (d, 2H); 6.94, 6.90, 6.86 (t, 1H); 6.58, 6.54 (d, 2H); 6.34, 6.32 (m, 2H); 6.20, 6.17 (d, 1H); 6.04 (s, 2H, −NH_2); 5.18 (s, 2H, −NH_2); ^{13}C NMR (DMSO-d_6, 300 MHz) 167.49, 153.32, 149.21, 139.67, 131.83, 129.08, 118.64, 117.45, 115.96, 112.84, 111.50, 111.18, 108.74, 49.82. HRMS (*m*/*e*): calcd for $C_{16}H_{13}N_5$, 275.1172; found, 275.1172.

(9) A typical polymerization procedure is as follows (polymer **9**): A 50 mL three-neck round-bottomed flask equipped with an argon inlet and mechanical stirrer was charged with 0.4434 g (1.6106 mmol) of diamine monomer **5** and 10 mL of NMP. To this solution was added in one portion 0.5190 g of BTDA (1.6106 mmol) at 0 °C. The solution was stirred at room temperature for 8 h and then heated gradually to 190 °C for additional 12 h. The water generated by imidization was distilled from the reaction mixture along with small amount of chlorobenzene. The product was precipitated into distilled water, filtered, washed with hot water and hot MeOH repeatedly, and dried in vacuo at 80 °C for 24 h (0.8815 g, 98%). FTIR (film, cm^{-1}): 3250 (NH); 2218 (CN); 1781, 1717 (C═O of imide); 1658 (C═O of ketone); 1600, 1513 (aromatic); 1368 (C−N stretching); 725 (C═O of bending).^{1}H NMR (DMSO-d_6, 200 MHz): 11.08 (s, 1H, −NH−); 8.27−8.16 (m, 6H); 7.87, 7.83 (d, 2H); 7.68, 7.64 (d, 2H); 7.52−7.36 (br, 4H).

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