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ORIGINAL CONTRIBUTION

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Synthesis and properties of poly(amide–imide)s containing a *N*-methylcarbazole group

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Abstract A new dicarboxylic acid monomer containing the *N*-methylcarbazole and imide structures, 3,6-bis(trimellitimido)-*N*-methylcarbazole (**I**), was prepared from the condensation of 3,6-diamino-*N*-methylcarbazole (**c**) and trimellitic anhydride. The diamine **c** was synthesized in three steps starting from the methylation of carbazole, followed by nitration and catalytic hydrazine reduction. A series of *N*-methylcarbazole-containing poly(amide–imide)s were synthesized by direct polycondensation from the diimide–diacid **I** with various aromatic diamines. These poly(amide–imide)s had inherent viscosities of 0.66–1.47 dl/g and were readily soluble in a variety of organic solvents, including *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylacetamide (DMAc). Transparent, flexible, and tough films of these polymers could be cast from DMAc solutions, and these films exhibited excellent mechanical strength. The glass-transition temperatures of these poly(amide–imide)s were in the range 317–362 °C. All the poly(amide–imide) did not degrade noticeably below 480 °C in nitrogen, and the 10% weight loss temperatures and char yields at 800 °C were above 520 °C and 60% in nitrogen, respectively, indicating high thermal stability.

Key words Poly(amide–imide) · 3,6-Bis(trimellitimido)-*N*-methylcarbazole · 3,6-Diamino-*N*-methylcarbazole · Thermal stability

Introduction

Many studies of new polymer syntheses have been carried out to prepare high-performance polymers. In general, high performance means high thermal stability, good chemical resistance, and excellent mechanical properties. However, tractability is more important for polymer material, so the search for new polymers with better processability, while maintaining their outstanding properties, should bring new materials with better applications. It is generally known that the incorporation of rigid segments in the polymer chain, specially in polyamide and polyimide, is an effective method to enhance the thermal stability. Although polyimides have higher thermal stability, they are generally insoluble and infusible after conversion from their poly(amic acid) precursors [1, 2]. Thermal resistance of polyamides is lower than that of polyimides, but polyamides have better solubility and processability than polyimides. Poly(amide–imide)s were developed from high-performance polymers which combine the advantages of high-temperature stability and processability. A notable example is Torlon (Amoco Chemicals), a commercial poly(amide–imide) obtained from trimellitic anhydride chloride and 4,4′-methylenedianiline (**II$_c$**) [3]. Much research has been done on the methods for synthesizing poly(amide–imide)s [4–10].

In addition, carbazole-containing polymer synthesized mainly from vinyl carbazole is a conducting polymer; however, monomers having a carbazole group are little used in polycondensation, and it has been reported that carbazole-containing polypyromellitimide has been synthesized and shows dark coloration, is insoluble in organic solvents, has brittle tensile property, and has acceptable thermal resistance [11]. Because copolymerization can improve the solubility of polymers and incorporation of a rigid carbazole segment in the polymer chain may enhance the thermal stability, poly(amide–imide)s containing the *N*-methylcarbazole group were synthesized and characterized in the present study.

High-molecular-weight poly(amide–imide)s are synthesized successfully utilizing triphenyl phosphite (TPP) and pyridine as condensing agents in the presence of $CaCl_2$ or LiCl in *N*-methyl-2-pyrrolidone (NMP) [12–15]. In this study, a new family of poly(amide–imide)s derived from the *N*-methylcarbazole-based bis(trimellitimide) has been synthesized. Also, the organic solubility, tensile properties, and the thermal properties of the poly(amide–imide)s were examined.

Experimental

Materials

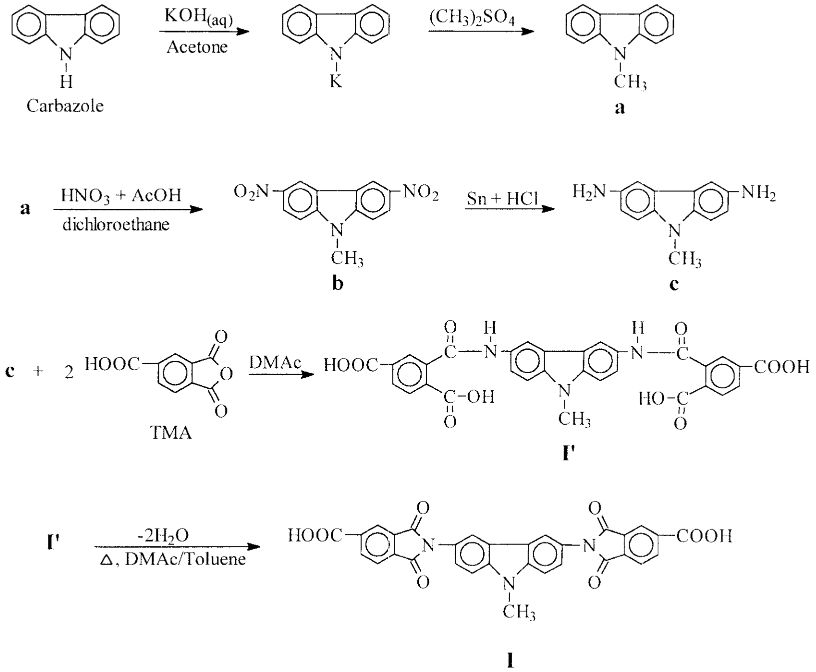
Carbazole (from TCI) was purified by recrystallization from ethanol. Dimethyl sulfate (from TCI) was used as received. Aromatic diamine *m*-phenylendediamine (**II**$_a$ from TCI) was vacuum-distilled before use. All other diamines, such as 2,4-tolylenediamine (**II**$_b$ from TCI), **II**$_c$ (from TCI), 4,4′-thiodianiline (**II**$_d$ from TCI), 4,4′-oxydianiline (**II**$_e$ from TCI), 3,4′-oxydianiline (**II**$_f$ from Teijin), 4,4′-(1,4-phenylenedioxy)dianiline (**II**$_g$ from TCI), 4,4′-(1,3-phenylenedioxy)dianiline (**II**$_h$ from Chriskev), 4,4′-[sulfonylbis(1,4-phenyleneoxy]dianiline (**II**$_j$ from Chriskev), 4,4′-[isopropylidenebis(1,4-phenyleneoxy)]dianiline (**II**$_k$ from Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**II**$_l$ from TCI), were used without further purification. Bis[4-(4-aminophenoxy)phenyl]ether (**II**$_i$), 1,1′-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**II**$_m$), and 2,7-bis(4-aminophenoxy)naphthalene (**II**$_n$) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction of the dinitro compounds with hydrazine/Pd-C [16–18]. The cardo bis(ether amine), 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene (**II**$_o$) was prepared according to the method reported in a previous article [19]. Trimellitic anhydride (TMA from Wako) and TPP (from TCI) were used as supplied. NMP (from Fluka), *N*,*N*-dimethylacetamide (DMAc from Fluka), and pyridine (from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Commercially available ($CaCl_2$) was dried under vacuum at 180 °C for 10 h.

Monomer synthesis

3,6-Diamino-N-methylcarbazole

In a 500-ml flask, 0.09 mol (15.0 g) of carbazole was dissolved in acetone (200 ml) and then potassium hydroxide solution (15 g KOH dissolved in 7.5 ml distilled water) was added. After 30 min of stirring, 0.24 mol (30.0 ml) dimethyl sulfate was added dropwise to the reaction mixture. Stirring was continued for another 1 h, and the resulting solution was filtered. Then, the solution was heated and dropped into hot water and crystals *N*-methylcarbazole (**a**) were produced, filtered off and dried (94% yield); m.p, 85 °C(lit. 84 °C [11]).

N-Methylcarbozole (15.0 g, 0.084 mol) was dissolved in 200 ml 1,2-dichloroethane followed by addition of glacial acetic acid (75 ml). A nitrating mixture (nitric acid/glacial acetic acid = 75 ml/75 ml) was added dropwise at room temperature with continuous stirring. After all the mixture had been added, the solution was stirred at 70 °C of 5 h. On cooling, the product mixture was stirred overnight. The resulting solution was poured into 500 ml ethanol and the precipitate was collected by filtration,



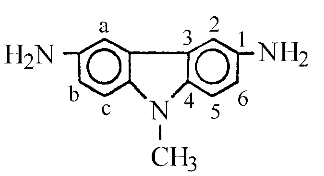
washed thoroughly with ethanol, and dried. The yield of 3,6-dinitro-*N*-methylcarbazole (**b**) was 80%; m.p. above 300 °C.

The dinitro compound **b** (18.0 g, 0.06 mol) obtained was heated at reflux in concentrated HCl in the presence of tin (0.30 g, 0.25 mol) for 3 h. A white solid separated out, and the resulting solution was cooled and poured into 1500 ml distilled water. The compound dissolved in water and the solution was neutralized to pH 8–9 by 10% aqueous NaOH. The crude product separated out and was filtered, washed thoroughly with distilled water, and dried in a vacuum. The precipitate and moderate decolorizing carbon were added into 500 ml toluene, and the mixture was refluxed for 30 min and filtered to remove the carbon. Upon cooling, light-yellow needle shaped crystals 3,6-diamino-*N*-methylcarbazole (**c**) precipitated (70% yield); m.p. 206–207 °C (lit. 174–175 °C [11]).

The IR spectrum (KBr) exhibited absorptions at 3402, 3269 (N–H), and 1315 cm^{-1} (N–C).

^{1}HNMR (dimethyl sulfoxide, DMSO-d_6, δ): 7.15 (d, H$_c$, 2H), 7.12 (s, H$_a$, 2H), 6.76 (d, H$_b$, 2H), 4.64 (s, -NH$_2$, 4H), 3.63 ppm (s, -CH$_3$, 3H).

^{13}CNMR (DMSO-d_6, δ): 141.90 (C^1), 135.91 (C^4), 123.41 (C^3), 115.74 (C^6), 109.92 (C^5), 104.91 (C^2), 28.81 (-CH$_3$).



$(C_{13}H_{13}H_3)$ (211.27) Calculated: C, 73.91%; H, 6.20%; N, 19.89% Found: C, 73.43%; H, 6.44%; N, 19.56%.

3,6-Bis(trimellitimido)-N-methylcarbazole

The diamine **c** (0.027 mol, 5.7 g) was dissolved in 50 ml dried DMAc, and then TMA (0.059 mol, 11.4 g) was added in one portion. The mixture was stirred at 20–60 °C until the solution was transparent. Stirring was continued for another 30 min, then toluene (20 ml) was added. The solution was heated (about 140 °C) using a Dean–Stark trap to remove the water (1.08 ml) azeotropically for 4 h. After cooling, the insoluble red precipitate was isolated by filtration, washed with hot methanol, and dried in a vacuum to give 14.2 g 3.6-bis(trimellitimide)-*N*-methylcarbazole (**I**) (95% yield); m.p. 423 °C (by Differential Scanning Calorimetry, DSC), The diimide–acid **I** was insoluble in NMP, DMAc, *N, N*-dimethylformamide (DMF), and DMSO.

$(C_{31}H_{17}O_8N_3)$ (559.49). Calculated: C, 66.55%; H, 3.06%; N, 7.51%. Found: C, 66.53%; H, 3.21%; N, 7.47%.

Polymer synthesis

Synthesis of poly(amide–imide) **III**$_\mathbf{g}$ is described as a typical procedure. A mixture of 0.350 g (0.625 mmol) diacid **I**, 0.183 g (0.625 mmol) **II**$_\mathbf{g}$, 0.2 g CaCl$_2$ 0.7 ml pyridine, 0.4 ml TPP, and 3.0 ml NMP was heated to 100 °C while being stirred. After the monomers had dissolved completely to give a transparent solution, stirring was continued for another 3 h. The viscosity of the reaction solution increased during the polymerization, and an additional 3.5 ml NMP was added to the reaction mixture. At the end of the reaction, the reaction mixture was poured slowly into 300 ml stirred methanol, giving rise to a fiberlike precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried under vacuum at 100 °C. The yield was 0.532 g (100% yield). The inherent viscosity of the poly(amide–imide) **III**$_\mathbf{g}$ was 1.09 dl/g, as measured at a concentration of 0.5 g/dl in DMAc at 30 °C.

Other poly(amide–imide)s were synthesized in an analogous manner. The synthesis conditions and the inherent viscosities of the polymers obtained are summarized in Table 1.

Measurements

Melting points were measured in capillaries with a Yamato melting point apparatus (model MP-21) without correction. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-400 NMR spectrometer operated at 30 °C with tetramethylsilane as the internal standard and DMSO-d_6 as the solvent, respectively. Elemental analyses were run on a Perkin-Elmer model 2400 CHN analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform IR spectrometer using KBr disks or solution-cast films. The inherent viscosities of all the polymers were measured at a concentration of 0.5 g/dl with a Cannon–Fenske

Table 1 The preparation of poly(amide–imide)s. In each polymerization, the amount of triphenyl phosphite and pyridine was dependent on the monomers used, i.e., 0.625 mmol diacid **I** uses 0.4 ml triphenyl phosphite and 0.7–0.8 ml pyridine. Reaction temperature = 100 °C; reaction time = 3 h; *NMP* = *N*-methyl-2-pyrrolidone

Code	Amount of reagents used			Time need to become transparent solution (min)	η_{inh}^a (dl/g)	Coloration	
	NMP (ml)	Additional NMP (ml)	CaCl$_2$ (g)			Stringy polymer	Film
I						Bright red	
III$_\mathbf{a}$	2.7		0.2	100	1.47	Yellow	Dark yellow
III$_\mathbf{b}$	3.0	1.5	0.2	120	0.92	Yellow	Red-brown
III$_\mathbf{c}$	3.0		0.2	60	0.66	Yellow	Red-brown
III$_\mathbf{d}$	3.5		0.4	90	1.24	Yellow	Dark yellow
III$_\mathbf{e}$	4.0	3.5	0.4	55	0.81	Yellow	Dark yellow
III$_\mathbf{f}$	3.0	1.0	0.2	45	0.82	Yellow	Dark yellow
III$_\mathbf{g}$	3.0	3.5	0.2	60	1.09	Yellow	Dark yellow
III$_\mathbf{h}$	3.0	1.0	0.2	60	0.98	Yellow	Red-brown
III$_\mathbf{i}$	3.0		0.2	65	1.02	Yellow	Dark yellow
III$_\mathbf{j}$	4.0	2.0	0.4	45	0.86	Yellow	Dark yellow
III$_\mathbf{k}$	4.0	1.0	0.4	40	0.88	Yellow	Dark yellow
III$_\mathbf{l}$	4.0	2.0	0.4	60	0.90	Yellow	Dark yellow
III$_\mathbf{m}$	4.0		0.4	60	0.95	Yellow	Dark yellow
III$_\mathbf{n}$	4.0		0.4	70	0.95	Yellow	Dark yellow
III$_\mathbf{o}$	4.0		0.4	60	1.02	Yellow	Dark yellow

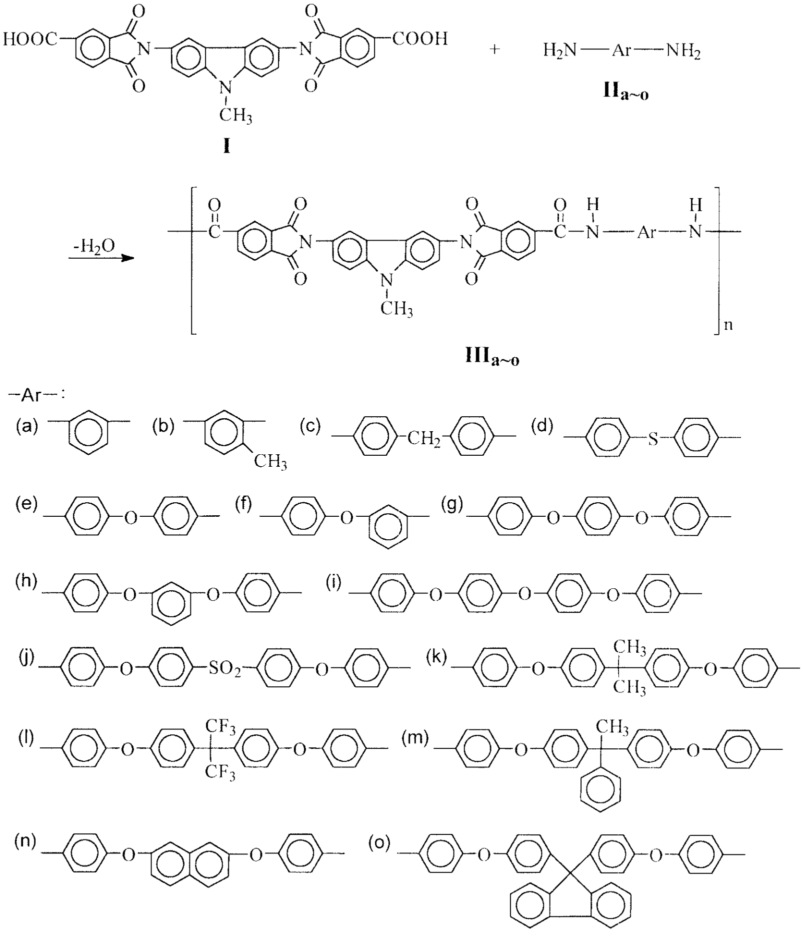
^{a} Measured at 30 °C at a concentration of 0.5 g/dl in *N*-*N*-dimethylacetamide viscometer at 30 °C. Solubilities were determined at 1% (w/w) concentration. The DSC analyses were performed on a Dupont 910 differential scanning calorimeter coupled to a Dupont 1090 thermal analyzer in flowing nitrogen (30 cm^3/min) at a heating rate of 15 °C/min. Thermogravimetric analysis (TGA) was done with a Dupont 951 coupled to a Dupont 1090 thermal analyzer. Measurement were performed with 10 ± 2 mg samples in flowing air or nitrogen (50 cm^3/min) at a heating rate of 20 °C/min. An Instron universal tester (model 1130) with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and an extension rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick); an average of at least five individual determinations was used.

Results and discussion

Monomer synthesis

The *N*-methylcarbazole-containing diamine was prepared from the methylation of carbazole, nitrated to form intermediate dinitro compound, then reduced with tin in concentrated HCl to produce **c**, as shown in Scheme 1. However, the discrepancy between the resulting melting point of **c** and the literature value was significant [11], so the structure of **c** was confirmed by elemental analysis, IR Spectroscopy and ^{1}H NMR and ^{13}C NMR spectroscopy (Fig. 1). The results were in good agreement with the expected characteristics. The higher melting point of **c** may be due to the difference in the purification between the product reported in the literature and our experiment, and we obtained a purer product in this study.

The *N*-methylcarbazole-containing diimide–diacid **I** was synthesized from diamine **c** with TMA in a 1:2 molar ratio. Because the direct heating of the mixture of **c** and TMA might cause the reaction to be incomplete and a low yield to be obtained, the diamine **c** was first dissolved in an amide-type solvent (such as DMF or DMAc), and TMA was added at room temperature to form an intermediate product **I'** by ring-opening addition. A moderate amount of toluene was then added, and the mixture was heated under a nitrogen atmosphere to remove the water azeotropically and thermal cyclodehydration proceeded to give high-purity **I**. The toluene in the solution allowed imidization to be carried out at a lower reaction temperature (140–150 °C), and the toluene vapor in the reactor also prevented the reactants from coming into contact with air and thus reduced the



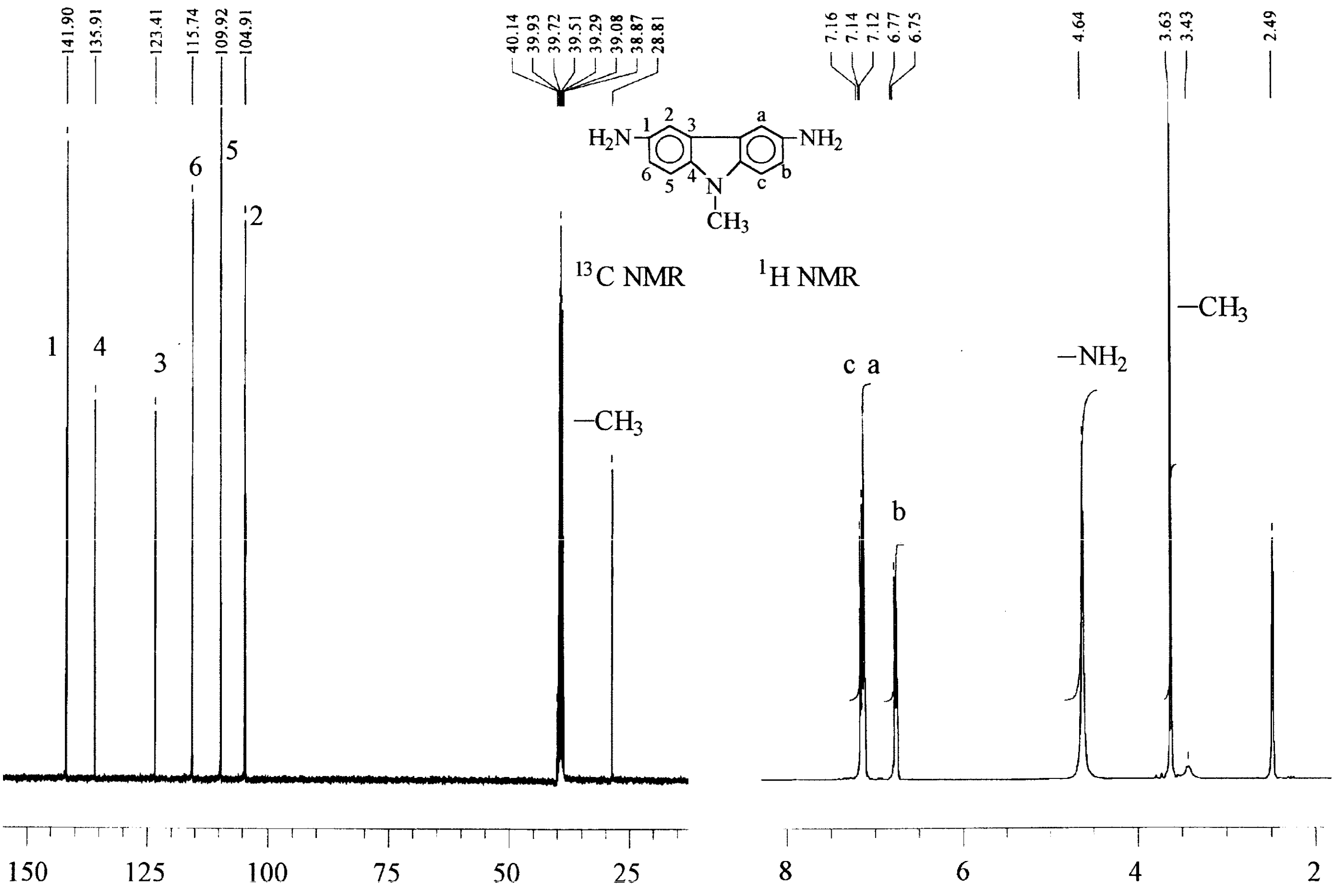


Fig. 1 ^{1}H NMR and ^{13}C NMR Spectra of the diamine 3, 6-diamino-*N*-methylcarbazole (DMSO-d_6)

oxidation of the product. Diimide–diacid **I** is bright red and is different from other diimide–diacids. This may be attributed to the extent of conjugation at the five-membered imide ring with the *N*-methylcarbazole moiety, which should lead to a deep coloration [20]. The IR spectrum of **I** (Fig. 2) exhibited characteristic absorptions at 3456 cm^{-1}, due to carboxylic acid -OH, and at 1773 and 1729 cm^{-1}, peculiar to the coupled carbonyl stretching vibrations of imide rings. The DSC trace of **I** showed a sharp endotherm peak at 423 °C, and the solubility of **I** was poor in NMP, DMAc, DMF, and DMSO at room temperature. Because the solubility of **I** was limited, its NMR spectrum could not be obtained.

Polymer synthesis

A series of novel poly(amide–imide)s **III**$_{a-o}$ containing *N*-methylcarbazole moieties were synthesized from diimide–diacid **I** and various diamines by a phosphorylation reaction using TPP as a promoter in NMP in the presence of pyridine and CaCl$_2$ (Scheme 2). Specially, the monomers were insoluble during the initial period of reaction (45–120 min), and the viscosity of the reaction solution increased after the solution has become transparent. Numerous experiments in which the solvent, the amount of CaCl$_2$ added, the reactant concentration, the temperature, etc., were varied convinced us that the conditions listed in Table 1 are optimal. To obtain a high molecular weight, although the reaction conditions required might be different due to the different kinds of monomers used, the optimum polymerization conditions seem to depend upon two main factors. The first is the amount of solvent during the initial period of reaction and the second is the amount of salt used. Higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of a swollen gel. The inherent viscosities of these polymers were in the range 0.66–1.47 dl/g.

The structures of the polymers were confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polymers are listed in Table 2. In all cases, the values found for carbon and nitrogen were lower than those calculated for the proposed structures, but the hydrogen values were found to be higher. This may be due to the hygroscopic nature of the amide group. The moisture uptakes for these poly(amide–

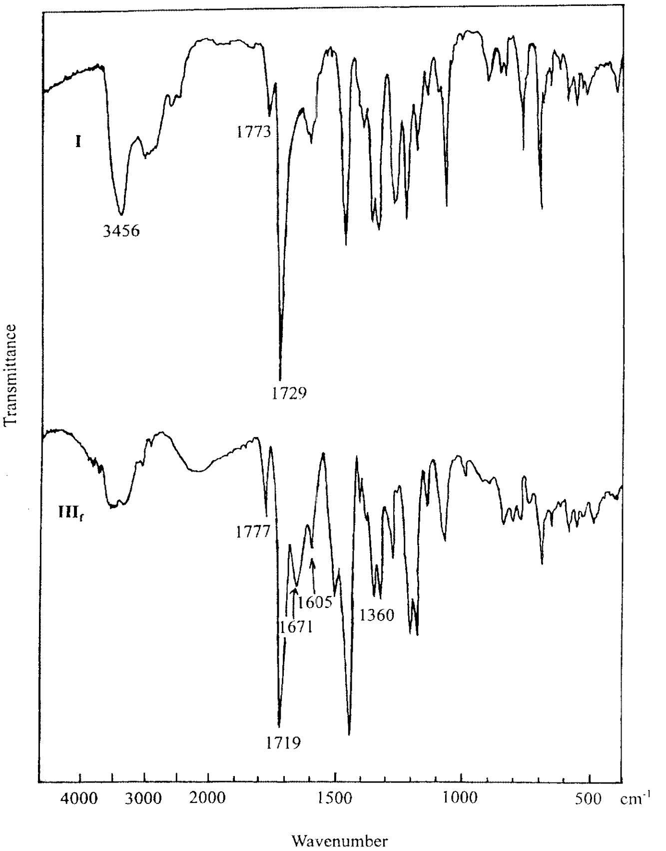


Fig. 2 IR spectra of 3-6-bis (trimellitimido)-*N*-methylcarbazole (I) and poly(amide-imide)**III$_f$**

imide)s were in the range 1.65–3.68% at room temperature and normal pressure in our laboratory. The corrected values were in good agreement with the calculated ones after deducting the amount of moisture uptake. The IR spectra of all the poly(amide–imide)s are very similar between 1350–4000 cm^{-1}, and a typical spectrum of poly(amide–imide) **III$_f$** is shown in Fig. 2. The spectrum shows characteristic absorptions for the imide ring at 1777 and 1719 cm^{-1} and for the amide group at 1671 and 1605 cm^{-1}. Also, the N–C aromatic stretching for N–CH_3 of the *N*-methylcarbazole unit exhibits characteristic absorption near 1360 cm^{-1}.

Properties of polymers

The solubility of all the poly(amide–imide)s was tested qualitatively using various solvents and the results are summarized in Table 3. Poly(amide–imide)s **III$_{a-o}$** containing *N*-methylcarbazole repeating units had good solubility in NMP and DMAc, even in *m*-cresol and *o*-chlorophenol. In general, polymers that are easily soluble in DMAc are soluble in DMF and DMSO; however, most of the poly(amide–imide)s in this study were insoluble in DMF and were soluble in hot DMSO, but they were soluble in *m*-cresol and *o*-chlorophenol. The results of the solubility are different from other series of poly(amide–imide)s. This may be attributable to the structure of diimide–diacid **I** having a tertiary amine (> N-CH_3). The solubility was also affected by using diamine in the polymerization, so **III$_{i-o}$** containing more flexible groups and bulky units in the polymer backbone showed better solubilities than **III$_{a-h}$**. From the data in Table 3, the diimide-diacid **I** with a *N*-methylcarbazole group is a useful monomer to synthesize rigid but easily soluble polymers.

Polymer films were prepared by slow evaporation of their DMAc solutions at 60–80 °C for 12 h, followed by sequential vacuum heating at 100–160 °C for 6 h. Flexible and tough films of most polymers could be obtained, and these films showed considerable coloration from dark yellow to red-brown (Table 1). This may be because the *N*-methylcarbazole group in the diimide–diacid **I** is effective in increasing the charge-transfer complex formation [21, 22], so the films are dark. Several series of compounds have been synthesized and characterised in previous work [23, 24] to study the coloration of polymer films, but this is not discussed here. The tensile properties of the poly(amide–imide) films are summarized in Table 4. Except for films **III$_{b,c,h}$**, which where too brittle to evaluate, the other films had tensile strengths of 81–118 MPa, elongations at break of 9–27%, and initial moduli of 1.8–2.6 GPa. Flexible polymer films derived from diamines **II$_{f,g,i,k,l,n,o}$** exhibited yield points on their stress–strain curves, especially polymer **III$_o$** which had the highest value. The displaced linkage (-Ar-) of diamine **II$_i$** contained more phenylether chains, so it had a larger elongation at break but a smaller tensile strength and initial modulus than the other polymers. As a whole, most of the polymers listed in Table 4 behave as duticle materials with good tensile strengths and moderate elongations at break.

The thermal properties of all the poly(amide–imide)s were evaluated by TGA and DSC. The thermal behavior data of all polymers are listed in Table 5. Almost all the poly(amide–imide)s showed similar decomposition behavior and did not degrade noticeably below 480 °C in nitrogen, but the polymers decomposed fast between 500–650 °C. The 10% weight loss temperature (T_ds) of the polymers stayed in the range 521–572 °C in nitrogen and 501–564 °C in air, depending on the diamine used. Their char yields at 800 °C in nitrogen were in the range 60–71%, indicating high thermal stability. Polymer **III$_o$** showed the highest thermal stability and this might be accounted for by its high aromaticity. Because the methyl group in the *N*-methylcarbazole moiety is easily decomposed, it may affect the initial decomposition temperature of polymers with lower T_d values; however, the T_ds and char yields of all the polymers were found to be high owing to incorporation of biphenyl groups into

Table 2 Elemental analysis of poly(amide–imide)s

Polymer	Formula (Molecular weight)		Elemental analysis[a] (%)			Moisture uptake[b] (%)
			C	H	N	
$\mathbf{III_a}$	$(C_{37}H_{21}N_5O_6)_n$	Calc.	70.35	3.35	11.09	
	$(631.60)_n$	Found	68.83	3.45	10.53	2.16
		Corrected	70.32	3.38	10.76	
$\mathbf{III_b}$	$(C_{38}H_{23}N_5O_6)_n$	Calc.	70.68	3.59	10.85	
	$(645.63)_n$	Found	68.50	3.71	10.56	3.08
		Corrected	70.61	3.60	10.89	
$\mathbf{III_c}$	$(C_{44}H_{27}N_5O_6)_n$	Calc.	73.22	3.77	9.70	
	$(721.73)_n$	Found	71.64	3.91	9.63	2.16
		Corrected	73.19	3.83	9.84	
$\mathbf{III_d}$	$(C_{43}H_{25}N_5O_6S)_n$	Calc.	69.82	3.41	9.47	
	$(739.76)_n$	Found	67.25	3.61	9.29	3.68
		Corrected	69.72	3.48	9.63	
$\mathbf{III_e}$	$(C_{43}H_{25}N_5O_7)_n$	Calc.	71.37	3.48	9.68	
	$(723.70)_n$	Found	69.24	3.58	9.49	2.98
		Corrected	71.30	3.47	9.77	
$\mathbf{III_f}$	$(C_{43}H_{25}N_5O_7)_n$	Calc.	71.37	3.48	9.68	
	$(723.70)_n$	Found	69.88	3.51	9.58	2.09
		Corrected	71.34	3.44	9.78	
$\mathbf{III_g}$	$(C_{49}H_{29}N_5O_8)_n$	Calc.	72.14	3.58	8.58	
	$(815.80)_n$	Found	69.99	3.60	8.40	2.98
		Corrected	72.08	3.49	8.65	
$\mathbf{III_h}$	$(C_{49}H_{29}N_5O_8)_n$	Calc.	72.14	3.58	8.58	
	$(815.80)_n$	Found	70.64	3.72	8.43	2.08
		Corrected	72.11	3.64	8.61	
$\mathbf{III_i}$	$(C_{54}H_{33}N_5O_9)_n$	Calc.	72.40	3.71	7.82	
	$(895.88)_n$	Found	70.56	3.85	7.71	2.54
		Corrected	72.35	3.75	7.91	
$\mathbf{III_j}$	$(C_{55}H_{33}N_5O_{10}S)_n$	Calc.	69.10	3.48	7.33	
	$(955.95)_n$	Found	66.99	3.68	7.26	3.05
		Corrected	69.03	3.57	7.48	
$\mathbf{III_k}$	$(C_{58}H_{39}N_5O_8)_n$	Calc.	74.59	4.21	7.50	
	$(933.98)_n$	Found	72.77	4.47	7.31	2.44
		Corrected	74.55	4.36	7.49	
$\mathbf{III_l}$	$(C_{58}H_{33}N_5O_8F_6)_n$	Calc.	66.86	3.19	6.72	
	$(1041.92)_n$	Found	64.72	3.31	6.64	3.20
		Corrected	66.79	3.20	6.85	
$\mathbf{III_m}$	$(C_{63}H_{41}N_5O_8)_n$	Calc.	75.97	4.15	7.03	
	$(996.05)_n$	Found	73.84	4.29	6.87	2.80
		Corrected	75.91	4.17	7.06	
$\mathbf{III_n}$	$(C_{53}H_{31}N_5O_8)_n$	Calc.	73.52	3.61	8.09	
	$(865.86)_n$	Found	71.35	3.84	7.88	2.95
		Corrected	73.45	3.73	8.11	
$\mathbf{III_o}$	$(C_{67}H_{41}N_5O_8)_n$	Calc.	77.08	3.96	6.71	
	$(1044.09)_n$	Found	75.81	4.11	6.55	1.65
		Corrected	77.06	4.04	6.66	

[a] For C and N: corrected value = found value × (100% + moisture uptake%). For H: corrected value = found value × (100% − moisture uptake%)

[b] Moisture uptake (%) = $(W - W_0)/W_0 \times 100\%$, where W is the weight of the polymer sample after standing at room temperature for 3 days and W_0 is the weight of the polymer sample after being dried in a vacuum at 100 °C for 10 h

the main chain, which leads to polymers with outstanding thermal stability.

The thermal transition data of the poly(amide–imide)s could be detected by DSC. Since the residual water or solvent and the history of thermal annealing may sometimes influence the first run of the DSC, experiment quenching from elevated temperatures (400 °C) to room temperature in air yields more

Table 3 Solubility of poly(amide–imide)s in various solvents: *NMP*, *N*,*N*-dimethylacetamide (*DMAc*), dimethyl sulfoxide (*DMSO*), *N*,*N*-dimethylformamide (*DMF*), *m*-cresol, *o*-chlorophenol, and H_2SO_4

Polymer	Solvent						
	NMP	DMAc	DMSO	DMF	*m*-Cresol	*o*-Chlorophenol	H_2SO_4
$\mathbf{III_a}$	+	+	+h	–	+h	–	+
$\mathbf{III_b}$	+	+	+	+	+	+	+
$\mathbf{III_c}$	+	+	+h	–	+	+	+
$\mathbf{III_d}$	+	+	+h	–	+	+	+
$\mathbf{III_e}$	+	+	+h	–	+	+	+
$\mathbf{III_f}$	+	+	+h	–	+	–	+
$\mathbf{III_g}$	+	+	+h	–	+	+	+
$\mathbf{III_h}$	+	+	+h	–	+	+	+
$\mathbf{III_i}$	+	+	+h	+h	+	+	+
$\mathbf{III_j}$	+	+	+	+	+	+	+
$\mathbf{III_k}$	+	+	+h	–	+	+	+
$\mathbf{III_l}$	+	+	+h	+h	+	+	+
$\mathbf{III_m}$	+	+	+h	+h	+	+	+
$\mathbf{III_n}$	+	+	+h	–	+	+	+
$\mathbf{III_o}$	+	+	+h	+h	+	+	+

+ indicates soluble at room temperature, +*h* indicates soluble on heating, and – indicates insoluble

Table 4 Tensile properties of poly(amide–imide) films. Films were cast from slow evaporation of the polymer solutions in DMAc

Polymer	Yield strength (MPa)	Break strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
$\mathbf{III_a}$	–	100	15	2.3
$\mathbf{III_d}$	–	105	10	2.4
$\mathbf{III_e}$	–	90	17	2.2
$\mathbf{III_f}$	104	97	19	2.4
$\mathbf{III_g}$	95	93	27	2.3
$\mathbf{III_i}$	82	81	25	1.8
$\mathbf{III_j}$	–	91	9	2.2
$\mathbf{III_k}$	104	100	15	2.3
$\mathbf{III_l}$	103	98	17	2.1
$\mathbf{III_m}$	–	110	12	2.6
$\mathbf{III_n}$	102	92	23	2.5
$\mathbf{III_o}$	118	118	11	2.3

Table 5 Thermal behavior data of poly(amide–imide)s

Polymer	Differential scanning calorimetry	Thermogravimetric analysis		
		Decomposition temperature[b] (°C)		Char yield[c] (%)
	T_g[a] (°C)	In air	In nitrogen	
$\mathbf{III_a}$	–	510	572	63
$\mathbf{III_b}$	–	515	552	64
$\mathbf{III_c}$	–	501	535	63
$\mathbf{III_d}$	–	512	566	67
$\mathbf{III_e}$	–	508	569	65
$\mathbf{III_f}$	362	545	565	63
$\mathbf{III_g}$	349	547	563	64
$\mathbf{III_h}$	324	540	567	68
$\mathbf{III_i}$	339	537	558	66
$\mathbf{III_j}$	–	516	544	60
$\mathbf{III_k}$	322	541	540	66
$\mathbf{III_l}$	337	547	555	60
$\mathbf{III_m}$	323	545	540	66
$\mathbf{III_n}$	317	510	521	68
$\mathbf{III_o}$	–	564	572	71

[a] From the second heating differential scanning calorimetry trace conducted at a heating rate of 15 °C/min in nitrogen

[b] Temperature at which a 10% weight loss was recorded by thermogravimetric analysis at a heating rate of 20 °C/min

[c] Char yield from thermogravimetric analysis at 800 °C under a nitrogen atmosphere

amorphous samples, so in most cases the glass-transition temperatures (T_gs) could be easily measured in the second heating. The results are also tabulated in Table 5. Due to the stiffness of *N*-methylcarbazole in the polymer backbone, chain rotation of polymers is difficult, and no discernible T_g was observed for some poly(amide–imide)s. The other polymers $\mathbf{III_{f-i}}$ and $\mathbf{III_{k-n}}$ showed clear glass transitions between 317 and 362 °C, which may be attributed to the effect of flexible ether linkages in the diamine. The more phenyl–ether chains the polymers have, the easier the T_gs can be detected at low temperatures; however, the T_gs were still high enough in this series and this may be attributed to the rigid nature of the polymers, so their macromolecular backbones rotated at higher temperature. $\mathbf{III_j}$ and $\mathbf{III_o}$ containing polar sulfonyl groups and bulky pendent groups along the main chain had increased intermolecular forces and steric hindrances, respectively, and these reasons may be why their T_gs could not be detected up to 400 °C.

Conclusion

A novel *N*-methylcarbazole-containing diimide–diacid I was successfully prepared. Poly(amide–imide)s with moderate-to-high molecular weight were synthesized based on the diacid in good yields. These polymers generally showed good thermal stability and outstanding solubility in NMP and DMAc, and the cast films exhibited excellent tensile properties. Thus, the present poly(amide–imide)s are considered as new candidates for processable high-performance polymeric materials.

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