New Poly(bisbenzoylamine imide) Series: Synthesis and Characterization

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SYNOPSIS

Three new series of poly(bisbenzoylamine imide)s, incorporating different aromatic diamines, have been synthesized. The polymers, obtained by the two-step procedure, have been characterized by DSC, TGA, X-ray, FTIR, and ^{1}H–NMR methods. Thermal analysis showed glass transition temperatures in the range of 200°–250°C and decomposition at 430°–495°C. Most DSC runs displayed an exothermic event above T_g that was due to cold crystallization of the polymer molecules. A melting point was not observed. The new polymers, even before annealing, showed sharp X-ray diffraction patterns, evidence of semicrystallinity. The polymers, soluble in polar solvents, were analyzed by NMR in solution. Typical chemical shifts for the bisbenzoylamine protons were reported; FTIR spectra showed the characteristic imide peaks. Due to a near overlap of the carbonyl vibration of the imide group with the bisbenzoylamine carbonyl, the latter vibration was detected in only one series. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The synthesis and characterization of new polymeric materials have always been important for furthering our understanding of the chemical structure–physical properties relationship. The goal of investigations of high-performance polyimides (PIs) is to improve processibility while maintaining useful mechanical, thermal, and electrical properties. Thus, it is useful to know how glass transition temperature (T_g), thermal stability, and molecular orientation depend on the chemical structure, synthesis, and solvent/mechanical history of the polymers.

It has been shown that partial flexibilization of the rigid polyimide backbone reduces thermal stability but increases processibility.[1] Ester, ketone, and ether units are widely described in the literature as units that provide semiflexible linkages. Because of their applications, polyimides containing such groups have been the subject of numerous publications dealing with structure–property relationships.[2-5] Nitrogen-containing semiflexible groups also have been introduced into the polyimide main chain and have improved processibility.[6,7] In four previous articles we described the synthesis of polymers containing the bisbenzoylamine unit and the thermal properties of the resulting poly(bisbenzoylamine imide)s.[8-11] We have also studied the changes in thermal behavior and solubility that result from introducing the bisbenzoylamine group step by step into a fully rigid material.[11]

In this contribution, we describe new poly(bisbenzoylamine imide)s and thermal, infrared (IR), and molecular orientation studies of these compounds. For convenience, we have named the polymers according to their chemical structure, starting with the dianhydride. The designation SA always denotes the bisbenzoylamine unit; the specification preceding it denotes the side-group connected to the central nitrogen of the SA group (e.g., Me-SA denotes an *N*-methyl bisbenzoylamine unit). The abbreviation of the appropriate diamine completes the designation of the entire structure (see Fig. 1).

EXPERIMENTAL

Materials

Nitrogen-substituted bisbenzoylamine-3,3',4,4'-tetracarboxylic acid dianhydrides were synthesized

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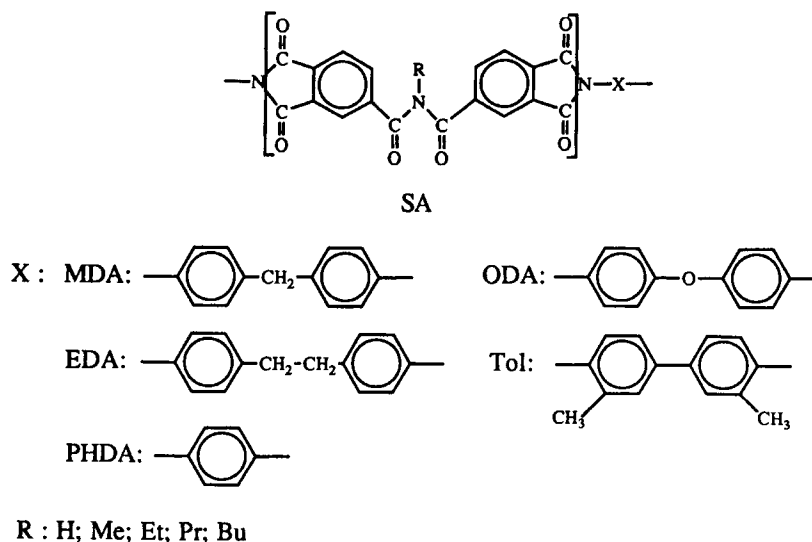* To whom correspondence should be addressed.

Figure 1 Structure of poly(bisbenzoylamine imide)s. MDA, 4,4'-diaminophenyl methane; EDA, 4,4'-diaminodiphenyl ethane; PHDA, phenylene-1,4-diamine; ODA, 4,4'-diamino-diphenyl ether; Tol, 3,3'-dimethyl-4,4'-diamino biphenyl; Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl.

and purified according to the method reported in our previous publication, using bistrimethylsilylated amines and trimellitic anhydride chloride.[8]

Phenylene-1,4-diamine (PHDA) was recrystallized from water in the presence of carbon black and was dried at 100°C in a vacuum oven for 24 h. The 4,4'-diaminodiphenyl ethane (EDA), 3,3'-dimethyl-4,4'-diaminobiphenyl (*o*-tolidine) (Tol), 4,4'-diaminodiphenyl ether (ODA), and 4,4'-diaminodiphenyl methane (MDA) were recrystallized from an ethanol–water mixture and were dried at 50°C in a vacuum oven for 24 h. All reactants were stored in a desiccator until used.

N,N-Dimethylacetamide (DMAc), anhydrous, 99[+]% (Aldrich Chemical Co.), was used without further purification. We also obtained polyimide samples PI 2080 (Dow Co.), XU 218 (Ciba–Geigy Co.), and Ultem 1000 (General Electric Co.) from the manufacturers for certain comparison measurements. These commercial polymers were dried in a vacuum oven at 200°C for 24 h before use.

Polymerization

For the polycondensation, 0.005 mol dianhydride and 0.005 mol diamine were mixed as powders in a 50-mL, three-necked flask, equipped with a stirrer, a gas inlet tube, and a reflux condenser. The apparatus was purged with dry nitrogen for 5 min, then 30 mL dry DMAc was added. The mixture was stirred to dissolve the reactants. To avoid the intro-

duction of moisture, the solvent was added with a syringe. The reaction mixture was stirred at 40°C for 5 h under a slow nitrogen flow. Acetic anhydride (0.04 mol, 4.18 g) was added to the resulting polyamic acid (PAA) solution, and the cyclization was carried out, with stirring, at the boiling temperature of the system for 1 h. At the end of the reaction, the mixture was poured into a large excess of methanol (500 mL), was stirred for 1 h, and was filtered. The imidization was completed by drying the samples at 250°C in a vacuum oven for 24 h.

Measurements

Differential scanning calorimetry (DSC) analyses were carried out on sample pellets (approximately 10 mg) sealed in an aluminum pan. The measurements were made on a DSC-7 system (Perkin–Elmer) purged with dry nitrogen; the heating rate was 10 K/min. Each sample was annealed at 300°C for 3 min before the run.

Temperatures of decomposition (T_{dec}) were determined with the thermogravimetric analyzer TGA-7 (Perkin–Elmer) in air; the sample size used for this analysis was 15–20 mg of the polymer. A 20 K/min heating rate was applied over the entire range of 25°–750°C. The temperature at which the sample had lost 5% of its original weight was arbitrarily taken to be the temperature of decomposition.

Elemental composition data were obtained with

the C,H,N elemental analyzer model 240 XA (Control Equipment Corp.).

Nuclear magnetic resonance (NMR) spectra were obtained with a XL-300 spectrometer (Varian Co.). The concentration of the polymer (dissolved in DMSO-d_6) was approximately 10% by weight.

Crystallographic data were obtained with a Nicolet X-ray generator, equipped with a flat plate camera. The graphite monochromated, pinhole-collimated Cu — K_α beam was scattered by the finely ground polymers, which filled a glass capillary 1.5 mm in diameter. Distance calibration was carried out by using cholesteryl nonanoate with 2θ parameters of 6.0°, 17.5°, and 19.0°.

RESULTS AND DISCUSSION

In this work, we used the well-known two-step method for polyimide preparation.[12-14] A publication by Grenier–Loustalot et al.[15] shows that this reaction of diamines with dianhydrides is very complex. The first step—a polyaddition yielding PAA—has been shown to be of critical importance for achieving a high yield of high-mol wt products. Reactant concentrations of 10–15% and reaction temperatures no higher than 40°C have been found to be optimal. It is well known that the second step—the cleavage of water from the PAA—may decrease mol wts and broaden mol wt distribution if the water being produced is not removed properly. To assure the binding of water at the molecular level, we used acetic anhydride in a molar ratio of 2:1 as a dehydrating agent. However, the use of dehydrating agents to remove water from PAA can lead to isoimide formation; fortunately, these thermally unstable materials will then convert to imide at higher temper-

atures.[1] Therefore, we annealed the samples at 250°C in vacuum for 24 h. This thermal treatment completed the imidization, converted any isoimide present, and dried the polymers. The curing temperature was chosen in the context of the studies of isothermal imidization by Hasegawa et al.[16] Their results showed an increase in the rate of ring closure in the range of 230°–270°C in the solid state. An additional factor was the fact that polyimides containing aliphatic side groups tended to crosslink at elevated temperatures.[2] Even partial crosslinking decreases the solubility of polymers; therefore, the poly(bisbenzoylamine imide)s were not exposed to temperatures greater than 250°C.

Elemental analysis data, presented in Table I, show good correlation of calculated and experimental values for the elemental composition.

As described in previous papers,[8-11] several poly(bisbenzoylamine imide)s are soluble in polar solvents such as DMAc, N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO). To estimate the absolute mol wts of our polymers, light scattering experiments on selected samples were attempted. However, persistent aggregation prevented meaningful measurements by this or related solution techniques.

The glass transition temperature of polymers provides valuable information about the rigidity of the polymer main chain. For high persistence length macromolecules, such as fully aromatic polyimides, T_gs above 280°C are common.[17] Polyimides with more flexible backbones tend to have a T_g that is somewhat lower. Because greater chain mobility improves processibility but decreases thermal stability, the goal is to find the optimum balance. Typically, polyimides that display a T_g around 250°C are processible by molding.

Table I   Results of Elemental Analysis

Polyimide[a]	Calculated			Experimental		
	%C	%H	%N	%C	%H	%N
H–SA–EDA	70.98	3.51	7.76	70.45	3.79	7.39
Me–SA–EDA	71.35	3.78	7.57	70.97	3.50	7.07
Et–SA–EDA	71.71	4.04	7.38	71.44	3.93	6.97
Pr–SA–EDA	72.04	4.29	7.20	71.54	4.02	7.33
Bu–SA–EDA	72.36	4.52	7.04	71.33	4.65	6.78
H–SA–Tol	70.98	3.51	7.76	71.15	3.79	8.03
Me–SA–Tol	71.35	3.78	7.57	70.65	3.89	7.36
Et–SA–Tol	71.71	4.04	7.38	71.47	4.10	7.04
Pr–SA–Tol	72.04	4.29	7.20	71.92	4.29	7.07

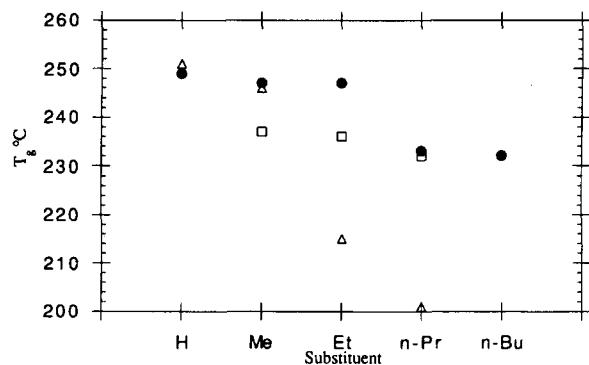[a] See Figure 1 for meaning of abbreviations.

Figure 2   Glass transition temperatures for poly(bis-benzoylamine imide)s showing the dependence on the chain length of side group. (●) EDA, (□) PHDA, (△) Tol.

The poly(bisbenzoylamine imide)s described in this contribution showed T_gs in the range of 200°–250°C, depending on the diamine component and the side group used. All the new polymers had T_gs in the same range, although a decrease in T_g weakly dependent on the length of the aliphatic side groups was observed. As the length of the aliphatic group increased, conjugation over the bisbenzoylamine unit seemed to become less effective, thus allowing the backbone to attain mobility at a lower temperature. However, this dependence was significant only when the diamine was o-tolidine (see Fig. 2).

Despite the relatively low T_gs, no melting points were found up to 350°C. However, most samples displayed an exothermic transition above the T_g (Fig. 3). Because the TGA curves also did not show a change at the exothermic transition temperatures

for the particular sample, we assumed that this peak was due to a cold crystallization process in the amorphous phase.

In the TGA studies, no sample showed significant weight loss up to the expected temperature of decomposition. This finding is an important proof of completed imidization and it supports the use of our method of cyclization. Figure 4 shows a typical TGA result. The differences of T_{dec} within a given series of N-substituted poly(bisbenzoylamine imide)s were not significant. Although T_{dec} decreased slightly as the length of the aliphatic side chain increased, the influence of the side group on the thermal stability was not as great as expected. Figure 5 shows the temperatures of decomposition for the synthesized materials.

The value of T_{dec} when phenylenediamine was used as the diamine component was unexpected. It is known that a polymer containing aliphatic groups has a lower T_{dec} than a comparable polymer containing aromatic units. Because PHDA does not have an alkyl group attached to its aromatic rings, we anticipated a greater thermal stability for these samples. The decomposition temperatures, however, were approximately 20° lower than the comparable values for the o-tolidine (Tol) series. The temperatures of decomposition for the EDA polymers were 20 or more degrees higher than those of the o-tolidine series, but this shift can be attributed to the location of the aliphatic unit. The ethylene group of EDA within the polymer main chain seemed to be more protected against thermooxidative attack than were the side chain methylene groups of Tol. These observations contradict our prediction[9] that thermal decomposition of the new polymers would be most
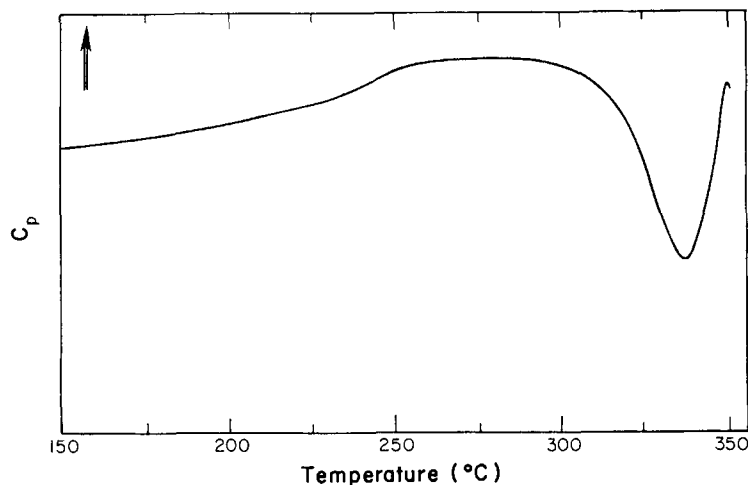

Figure 3   Typical DCS data showing an exotherm above the T_g. The sample was poly(N-methyl-bisbenzoylamine-3,3'-dimethyl biphenyl-4,4'-imide) (Me–SA–Tol).
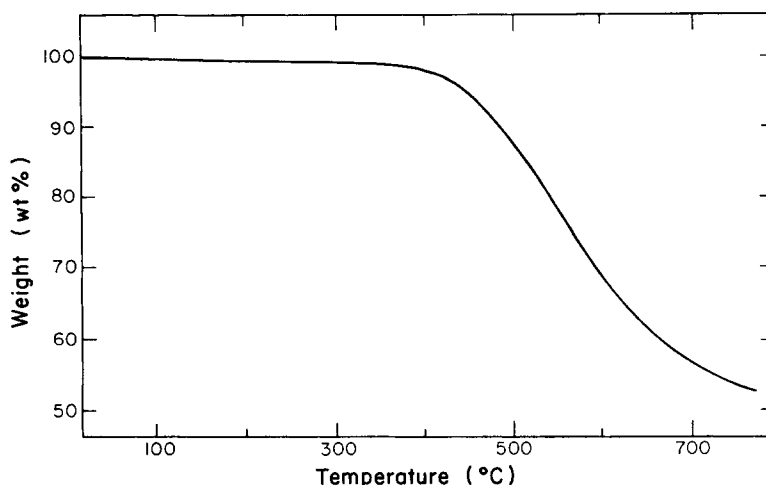
Figure 4   TGA data showing absence of weight loss below the temperature of decomposition.

dependent on the stability of the bisbenzoylamine group. It is more likely that the thermal stability of these poly(bisbenzoylamine imide)s is strongly influenced, not only by the flexible unit, but also by the diamine component. Although more data are needed, electron-donating aliphatic groups, attached to the diamine portion of the macromolecule, seem to increase the thermal stability of these materials.

Polyimides as a class of engineering materials are known to be mostly amorphous. However, several publications describe the crystalline behavior of certain polyimide systems.[18,19] A recent study deals with the crystallinity of fully aromatic polyimides containing ether and ketone groups as their flexible units. These polymers show semicrystalline properties, depending on the arylene structure. Furthermore, it has been suggested that the crystallinity is also related to the presence of the diaryl ketone unit. In these X-ray studies, in addition to diffuse halos, sharp peaks were found in the range of 2θ = 15°–30°.[3]

In the present work, we used a flat plate camera at a constant distance from the sample and set perpendicular to the beam to obtain diffractograms. We examined powder samples, thus generating one or more isotropic halos on the film.

Figure 6 shows typical X-ray patterns for three of our semicrystalline materials and, for comparison, the diffuse pattern produced by Ultem 1000. Table II lists the 2θ values of the characteristic sharp reflections for the poly(bisbenzoylamine imide)s. As anticipated, most of the new polyimides showed some crystallinity. Poly(bisbenzoylamine imide)s having MDA and ODA in the backbone were synthesized previously, but have not yet been charac-

terized with respect to their crystallinity.[8–11] Compared with the MDA and ODA polymers, the materials in the three other series were more crystalline. Because of possible hydrogen bonding, which facilitates chain orientation, we also conducted an X-ray study of H–SA–MDA and H–SA–ODA polymers, described earlier.[20] H–SA–ODA displayed two weak reflections, but H–SA–MDA showed only a diffuse halo with no maxima. The same diffuse patterns were found for Ultem 1000 (Fig. 6), Dow 2080, and XU-218.

Polymers in the PHDA series showed weak but sharp reflections. Furthermore, the scattering angle did not vary with side group chain length. This effect can be attributed to the backbone rigidity of the system. In fact, the DSC data, with respect to the almost invariant T_g, support that conclusion. The backbone flexibility did not vary with side group
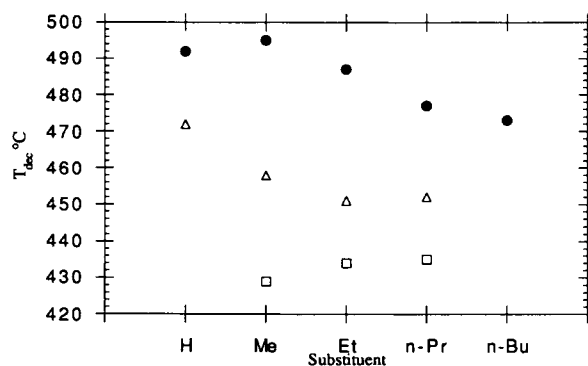

Figure 5   Temperatures of decomposition of aromatic poly(bisbenzoylamine imide)s as a function of the side group: H, proton; Me, methyl; Et, ethyl; n-Pr, propyl; n-Bu, butyl. (●) EDA, (□) PHDA, (△) Tol.
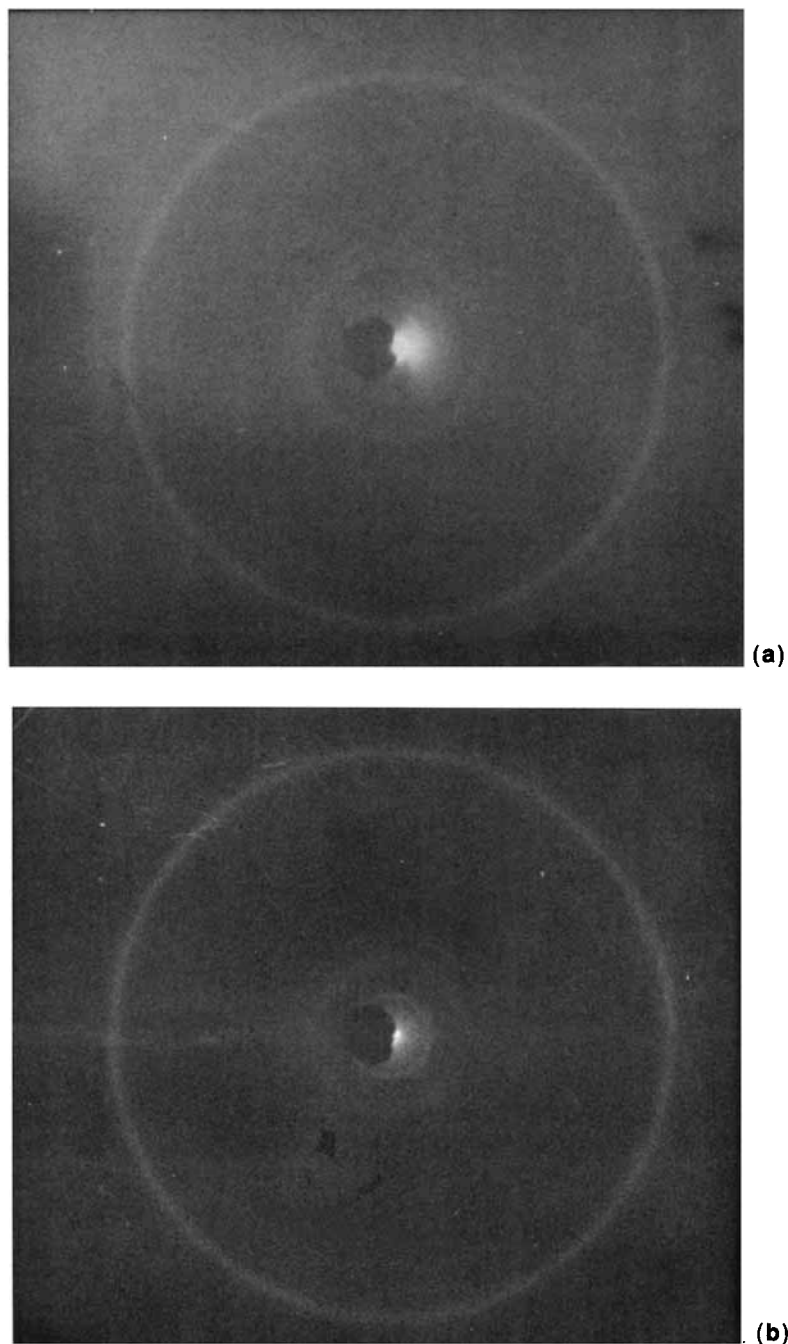
Figure 6   X-ray diffraction patterns showing typical semicrystalline halos: (a) H–SA–EDA, (b) Bu–SA–EDA, (c) H–SA–Tol, (d) Ultem 1000.

length, a result implying that the crystallinity is controlled by the main chain only. In other words, crystallinity and the distance between segments remained the same despite the changes in the length of the side group. Because we used similar conditions for all the measurements, we may use the strength of the reflections to compare qualitatively the

amounts of the crystalline phase in these materials. The PHDA polymers had reflections of lowest intensity, and we concluded that the degree of crystallinity in the PHDA polymers was lower than that of all the other polymer systems under investigation.

A greater number of reflections appeared in the patterns of poly(bisbenzoylamine imide)s contain-
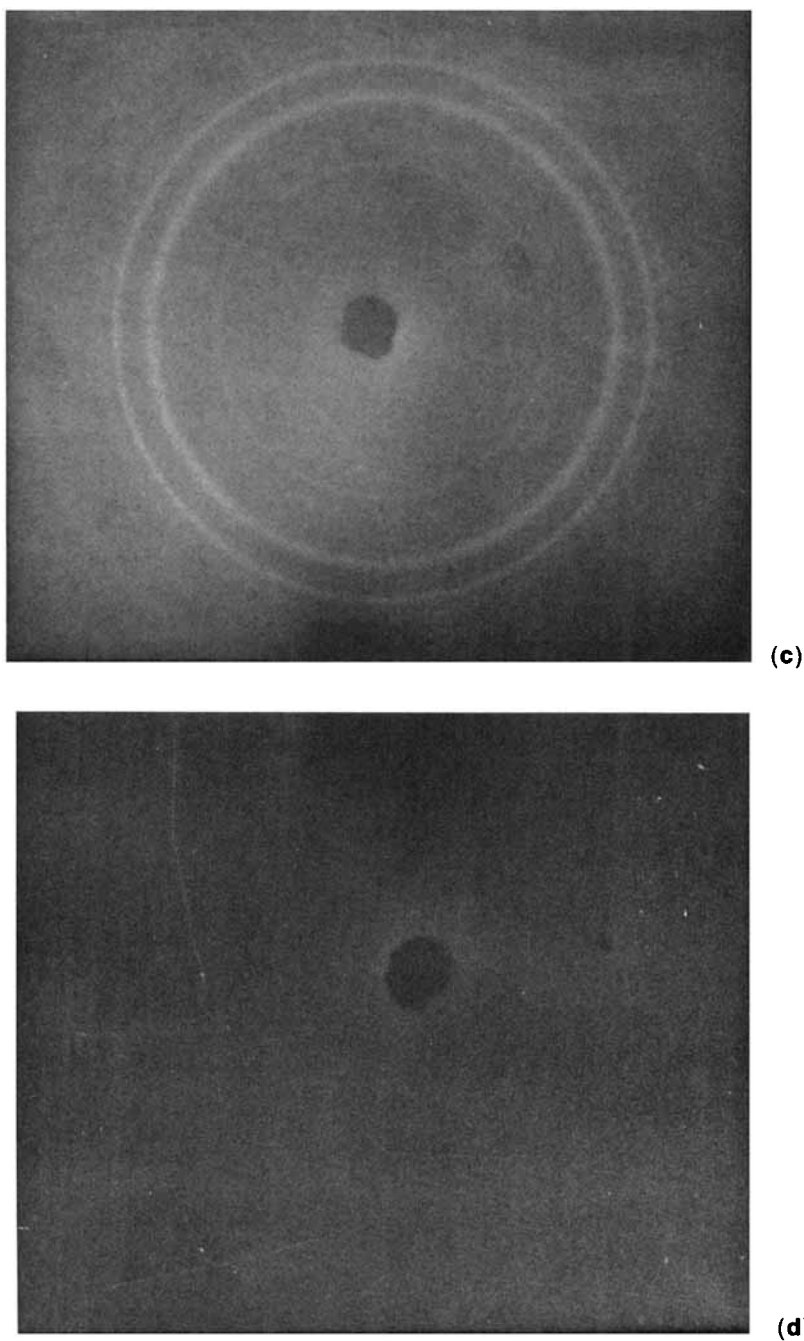
(c)

(d)

Figure 6   (continued from the previous page)

ing o-tolidine. In all cases, except for the methyl-substituted material, the most intense reflection was at $2\theta = 19°$. Similar behavior can be found for the EDA polymers. The most intensive reflection in this series was at $2\theta = 20°$; the methyl-substituted material, however, had the most intensive ring pattern at 16.8°. The origin of this phenomenon is not yet known and is the subject of further investigations.

A comparison of the intensities showed that the EDA series showed the highest degree of crystallinity, a property attributed to its stretched structure.

We also obtained FTIR spectra; a typical spectrum (H–SA–Tol in KBr) is shown in Figure 7. Table III lists characteristic vibrations for our materials. Note that the PHDA polymers display a broadening of the asymmetrical carbonyl stretching

Table II Diffraction Maxima (2Θ) of Poly(bisbenzoylamine imide)s

Amine Unit	Diffraction Angle (degrees)[a]				
	H–SA	Me–SA	Et–SA	Pr–SA	Bu–SA
PHDA	—	21.5 w	21.9 w	21.9 w	—
		19.6 w	19.2 w	19.2 w	
ODA	13.7 vw	nm	nm	nm	nm
	7.9 vw				
MDA	nm	nm	nm	nm	nm
EDA	22.2 d	21.5 w	28.1 w	28.3 w	20.6 vs
	10.2 vs	16.8 s	22.2 d	20.6 vs	7.9 w
	7.1 i	11.2 w	19.6 vs	6.0 w	6.4 d
			6.4 w		3.4 w
Tol	28.9 w	20.2 w	19.2 s	18.9 s	—
	25.3 w	15.8 s		14.7 w	
	20.2 w				
	19.2 vs				
	16.8 vs				
	12.2 w				

[a] (d) diffuse, (s) strong, (vs) very strong, (w) weak, (vw) very weak.
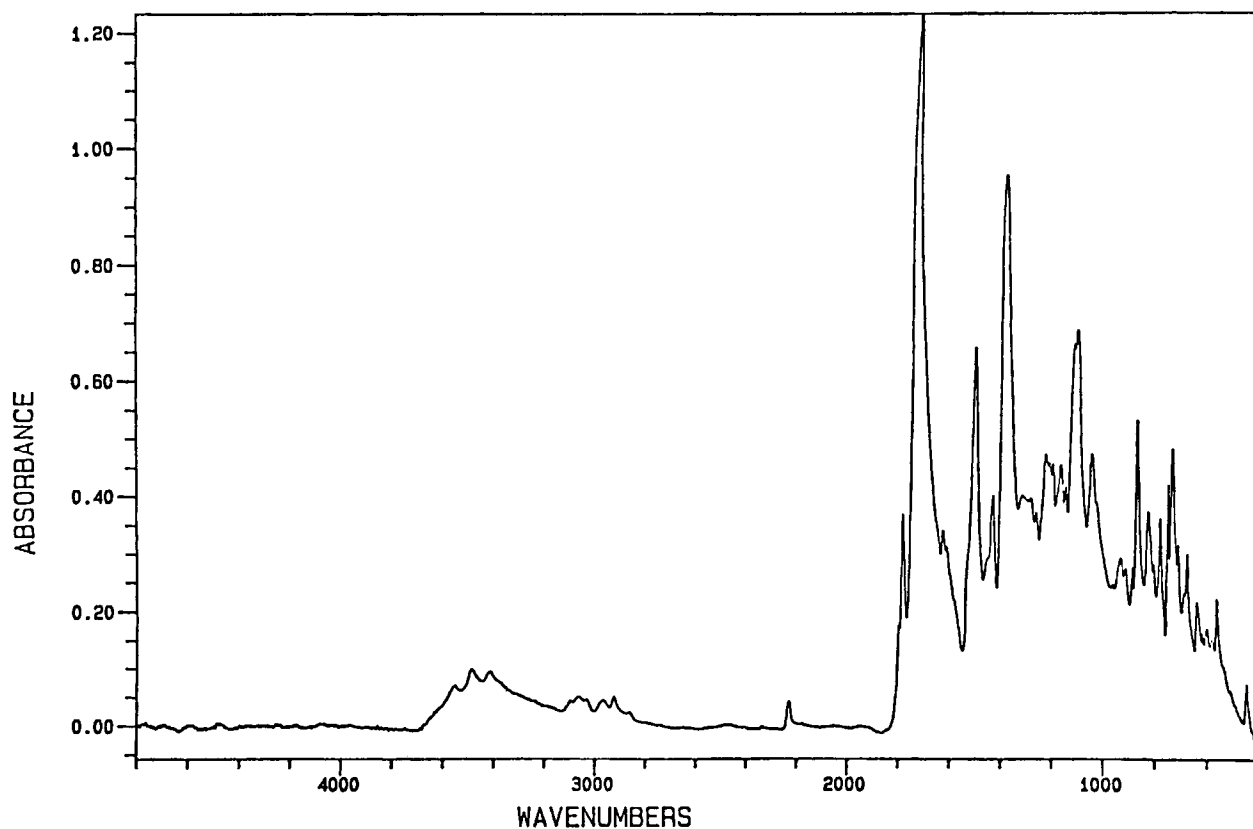[b] (nm) no maxima.

Figure 7 FTIR spectrum of poly(bisbenzoylamine-3,3'-dimethyl biphenyl-4,4'-imide) (H–SA–Tol) in a potassium bromide pellet.

Table III   Characteristic IR Maxima

Wavelength (cm⁻¹)	Explanation
1778–1784	Symmetrical carbonyl stretching
1718–1724	Symmetrical carbonyl stretching
1705	Symmetrical carbonyl stretching, PHDA polymers only
1495–1510	C–N
1370–1390	Imide ring stretching

frequency at 1720 cm^{-1}. This broadening is due to the similarity of the absorptions of the different carbonyl units in the material. The peak contains two vibrations with maxima at 1725 and 1705 cm^{-1} (see Fig. 8). For samples of the other poly(bisbenzoylamine imide) series, this expected difference was not large enough to be detected. In these polymers, all carbonyl groups absorbed at 1720 cm^{-1} only.

No significant absorption at 1550 cm^{-1}, generally characteristic of PAA, was seen. Therefore, we concluded that the imidization was quantitative.

The solubility of the materials in DMSO permitted us to obtain solution NMR spectra. In the ^{1}H–NMR study, the three protons connected to the trimellitic benzene ring showed a characteristic AB–X spectrum. The strong electron withdrawing effect of the three carbonyl groups caused a shift to higher fields. Typical chemical shifts for this multiplet signal were 8.2, 8.4, and 8.55 ppm. The proton attached to the bisbenzoylamine nitrogen was found at 3.35 ppm. Figure 9 shows the ^{1}H–NMR spectrum of the H–SA–Tol polymer in DMSO-d_6.

CONCLUSION

Aromatic poly(bisbenzoylamine imide)s, with and without alkyl side groups, have been synthesized. The semiflexible bisbenzoylamine unit reduced the rigidity of the backbone. This phenomenon was evident from the T_g of 200–250°C, a range lower than those reported for rigid aromatic polyimides. The flexibilization of the polyimide backbone led to more versatile processibility, because the new polymers could be dissolved and can be processed from solution.
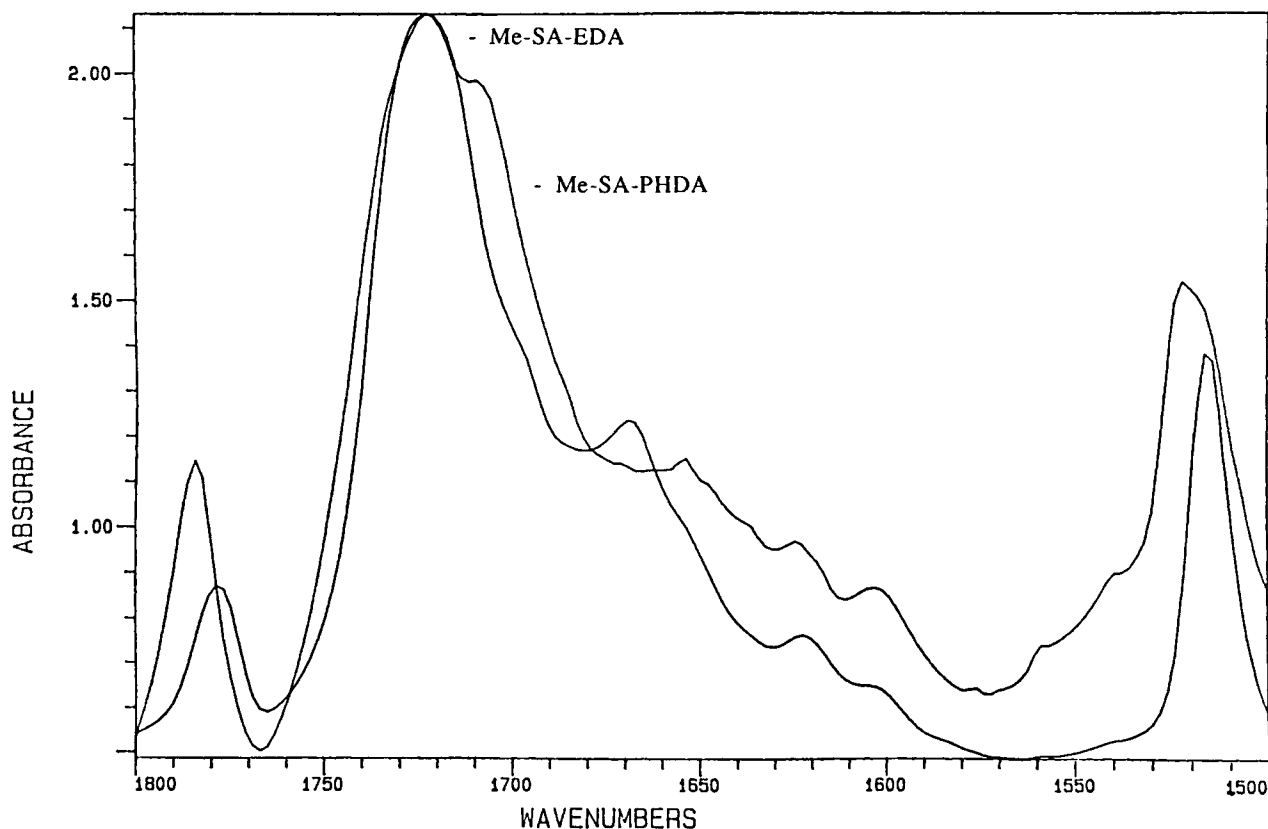

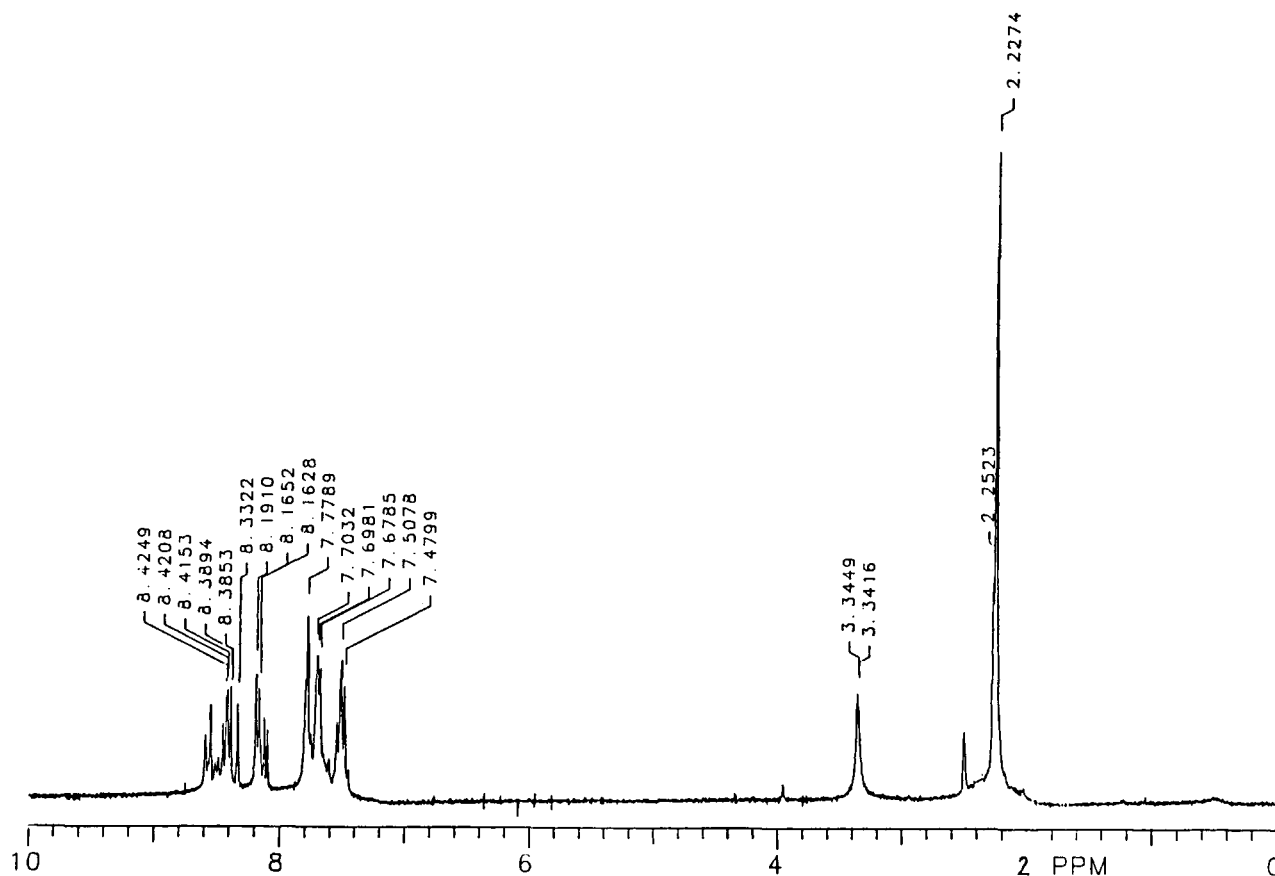**Figure 8**   FTIR spectra of poly(bisbenzoylamine imide)s with differing diamine units.

Figure 9 Typical ¹H–NMR spectrum for poly(bisbenzoylamine-3,3'-dimethyl biphenyl-4,4'-imide) (H–SA–Tol).

The temperature of decomposition decreased to the range 430–495°C. Nevertheless, the thermal stability of these materials was still sufficient to allow the new polymers to be used at high temperatures.

As a result of the greater mobility of the backbone, the aromatic poly(bisbenzoylamine imide)s displayed semicrystallinity. Of the five series, EDA polymers produced the sharpest and most intense reflections in the X-ray diffraction studies. Thus, EDA in the main chain supported crystallinity the most.

Light scattering showed that the dissolved polymer formed aggregates. This phenomenon did not affect the NMR spectroscopy; thus, NMR spectra could be obtained in the solution. As expected—and as was found for the monomers—the aromatic protons of the bisbenzoylamine unit showed a multiplet. The characteristic AB–X spectrum was shifted to higher fields as a result of the electron attraction in the carbonyl groups. Typical shifts were in the range of 8.2–8.55 ppm.

The FTIR spectroscopic data indicated that the ring closure, effected by a combined chemical/thermal imidization, was quantitative in these new polyimides.

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