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### Study of Polyimides Prepared from 3,3',4,4'-Benzophenonetetracarboxylic Dianhydride and 4,4'-(Alkane-1, *n*-Diyldioxy)Dianilines

M. Marek Jr.<sup>a</sup>; B. Schneider<sup>a</sup>; D. Hlavatá<sup>a</sup>; J. Labský<sup>a</sup>; M. Bleha<sup>a</sup>

<sup>a</sup> Institute of Macromolecular Chemistry Academy of Sciences of the Czech Republic, Prague, Czech Republic

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## STUDY OF POLYIMIDES PREPARED FROM 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC DIANHYDRIDE AND 4,4'-(ALKANE-1, *n*-DIYLDIOXY)DIANILINES

M. MAREK, JR.,\* B. SCHNEIDER, D. HLAVATÁ,  
J. LABSKÝ, and M. BLEHA

Institute of Macromolecular Chemistry  
Academy of Sciences of the Czech Republic  
162 06 Prague 6, Czech Republic

### ABSTRACT

Polyimides based on 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-(alkane-1,*n*-diyldioxy)dianilines were prepared via the corresponding polyamic acids and characterized by solid-state <sup>13</sup>C-NMR and IR spectroscopy. As shown by x-ray diffraction measurements, the polyimides are semicrystalline whereas the polyamic acids are entirely amorphous. Glass transition temperatures of the polyimides are lower compared with polyimides without flexible linkages. The polyimides are stable up to 400°C in nitrogen atmosphere.

### INTRODUCTION

Aromatic polyimides, which represent a very important group of high performance polymers, are widely used in microelectronics, the aerospace industry, and separation techniques [1–3]. Unfortunately, most polyimides cannot be processed in the fully cyclized state due to their high glass transition temperatures ( $T_g$ ) and insolubility in common solvents. This shortcoming is usually overcome by processing their precursors—mostly polyamic acids or their derivatives. The precursors are transformed to polyimides in the solid state by heat treatment or chemically [4].

Thermal, solid-state cyclization is associated with serious problems which might deteriorate the attractive properties of polyimides. Premature vitrification of polyamic acids during cyclization may cause a loss of chemical resistance as well as a higher water uptake due to the presence of residual *o*-carboxybenzamide groups in the polymer [5–7]. The presence of amide and COOH groups also worsens the dielectric and moisture barrier properties of polyimides [8, 9]. Moreover, evaporation of reaction water in the film leads to microvoids, and therefore the voltage breakdown threshold is low due to higher pinhole density [5, 7]. Since these problems, together with polymer shrinkage during cyclization [10], limit further application possibilities, great effort has been put forth to prepare processable and stable fully cyclized polyimides.

One of a few ways of improving the processability of polyimides is by incorporation of a short flexible chain into the polymer repeating unit. The presence of fluorocarbon [11], silicon [12, 13], and oxyalkylene [14–16] segments can decrease  $T_g$  and in some cases can even improve the solubility of polyimides. Previously, we published a study of poly(pyromellitimide)s based on 4,4'-(alkane-1,*n*-diyldioxy)dianilines [17]. Compared with highly aromatic polyimides, their  $T_g$  markedly decreased, but they were still insoluble in any convenient solvent.

In this study we extend our research to related polyimides prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The increasing importance of this monomer is manifested by a number of commercially available polyimides prepared therefrom (LARC-TPI, Syntimide, Eymide L-20, Skybond, ChemLon 601, XU 218, etc.).

## EXPERIMENTAL

### Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (Aldrich) was recrystallized from acetic anhydride. Syntheses of 4,4'-(alkane-1,*n*-diyldioxy)dianilines (DA-*n*) were described previously [17]. *N,N*-Dimethylformamide (DMF) was purified by distillation under reduced pressure.

### Syntheses of Polyamic Acids

An equimolar amount of BTDA was added to a solution of the diamine in DMF under vigorous stirring and inert atmosphere. The reaction was carried out at 25°C, and the concentration of the monomers was 15 wt%. After 24 hours the polyamic acid was precipitated into water and dried under reduced pressure. For the preparation of films, a solution of the acid in DMF (15 wt%) was poured onto glass and the solvent was evaporated at atmospheric pressure and room temperature.

### Conversion of Polyamic Acids to Polyimides

Films of the precursors were heated at reduced pressure at 100°C for 1 hour, at 200°C for 1 hour, at 250°C for 1 hour, and finally at 315°C for 10 minutes.

### Measurements

Infrared spectra were measured using a Bruker IFS 55 FTIR spectrometer. The spectra of polyamic acids were recorded in KBr pellets, while polyimides were measured as films.

$^1\text{H-NMR}$  spectroscopic measurements were carried out using a Bruker AM-400 spectrometer operating at 400 MHz at room temperature. Deuterated DMF was used as a solvent.

Solid-state  $^{13}\text{C-NMR}$  spectra were measured at 50.32 MHz with a MSL 200 (Bruker) spectrometer by the cross-polarization-magic angle spinning method (CP-MAS). For easier interpretation of spectra, nonquaternary suppression spectra (NQS) were also recorded. A more detailed explanation of these experiments has been published previously [18].

Wide-angle diffractograms were taken on a HYG4A automatic powder goniometer.  $\text{CuK}\alpha$  radiation was registered with a scintillation counter and monochromatized by a Ni filter and pulse-height analyzer. Diffractograms were performed in  $\theta/2\theta$  scan in the range of scattering angle  $2\theta = 4\text{--}40^\circ$ .

Small-angle scattering curves were measured using a Kratky camera in the region of the scattering vector  $q = 0.009\text{--}0.1 \text{ \AA}^{-1}$ . The scattering vector is defined as  $q = (4\pi/\lambda)\sin \theta$ , where  $\lambda$  is the wavelength and  $2\theta$  is the scattering angle.  $\text{CuK}\alpha$  radiation was registered using a proportional counter.

Thermogravimetric analysis (TGA) was carried out in nitrogen with a TGA Analyzer 951 (DuPont) connected with a DuPont Thermal Analyzer. The heating rate was  $10^\circ\text{C}/\text{min}$ .

Differential scanning calorimetric (DSC) experiments were carried out using a Perkin-Elmer 7 apparatus. The heating rate was  $10^\circ\text{C}/\text{min}$ .

Viscometric measurements were performed in an Ubbelohde viscometer at  $25^\circ\text{C}$  in 0.005 M solutions of LiCl in DMF.

Gas permeation properties of the films were measured using a laboratory-made apparatus described elsewhere [19].

## RESULTS AND DISCUSSION

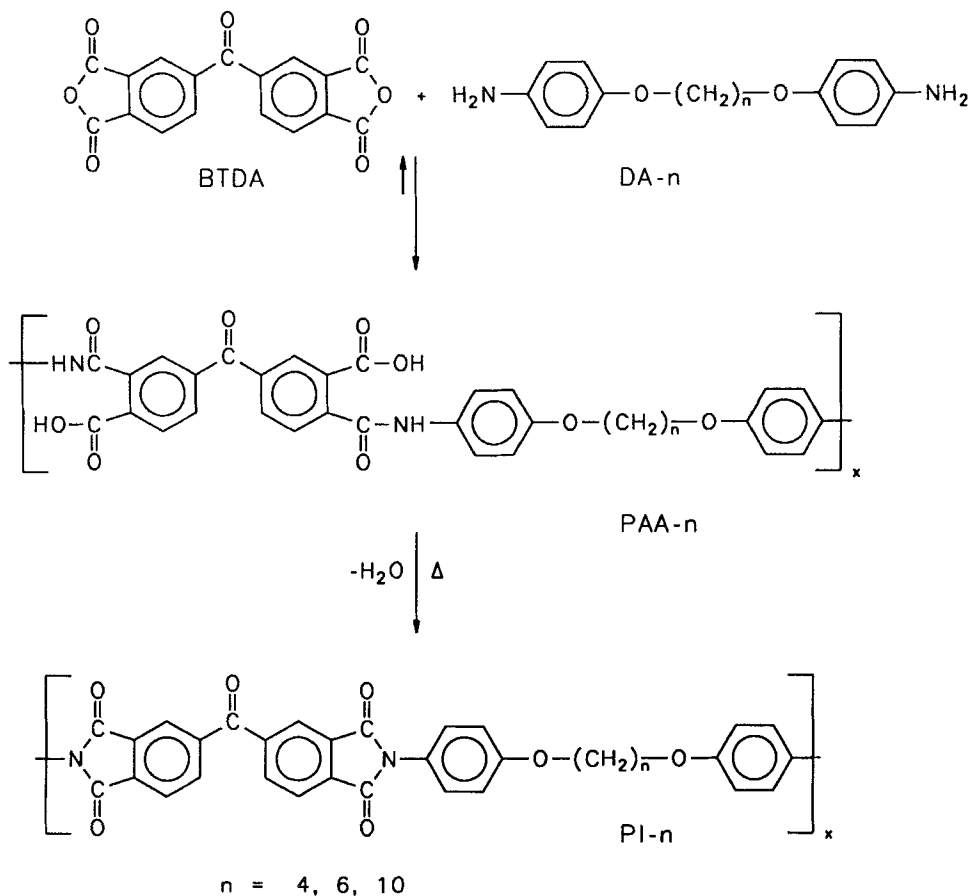
### Synthesis and Some Properties of Polyimides

Polyimides (PI-*n*) were synthesized via polyamic acids from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-(alkane-1,*n*-diyldioxy)dianilines (DA-*n*) as described in Scheme 1. The procedure was analogous to that used for the preparation of polyimides from pyromellitic dianhydride and 4,4'-(hexafluoroisopropylidene)bis(phthalanhydride) [17, 20].

Isolation of polyamic acids BTDA/DA-*n* was carried out by precipitation into water. Hydrolysis of the amide bond of polyamic acids dissolved in water-containing solutions is mentioned in the literature [21]. On the other hand, since no significant differences in molecular weight of a polyamic acid precipitated into methanol or water were observed [22], we can conclude that the extent of hydrolysis during isolation of the polyamic acid is negligible.

Reaction yields and intrinsic viscosities of precipitated polyamic acids, summarized in Table 1, are comparable with the published data on similar polymers [20, 23].

While polyamic acids BTDA/DA-*n* are soluble in polar aprotic solvents (DMF, *N*-methylpyrrolidone, dimethylsulfoxide, *N,N*-dimethylacetamide), thermally cyclized polymers BTDA/DA-*n* are insoluble in common solvents such as



SCHEME 1.

TABLE I. Yields and Intrinsic Viscosities  $[\eta]$  of Polyamic Acids PAA- $n$ , Glass Transition Temperatures  $T_g$  of Polyimides PI- $n$ , and Their 5% and 10% Weight Loss Temperatures,  $T_5$  and  $T_{10}$  (TGA)

$n$	Yield, %	$[\eta]$ , dl·g <sup>-1</sup>	$T_g$ , °C	$T_5$ , °C	$T_{10}$ , °C
4	91	0.84	248	446	464
6	90	1.21	212	427	445
10	87	0.55	Not detectable	429	447

polar aprotic solvents, as well as in *m*-cresol, alcohols, chlorinated hydrocarbons, and ethers. They are only soluble in sulfuric acid.

Glass transition temperatures of PI-4 and PI-6 are lower by 70–110°C than the  $T_g$  of highly aromatic polyimides like Kapton (see Table 1). PI-10 did not show any change in heat capacity during the DSC experiment which could be reliably taken for  $T_g$ . Neither were any endothermic peaks corresponding to the melting temperatures of the polyimides observed, indicating that their melting temperature exceeds the temperature of decomposition.

The thermal stability of polyimides was measured by TGA in a nitrogen stream. The results of TGA analyses are shown in Fig. 1 and Table 1. Temperatures of 5% weight loss are slightly higher than in the case of poly(pyromellitimide)s based on DA-*n* [17]. A comparison with the TGA results obtained for highly aromatic polyimides [24] shows that incorporation of aliphatic linkages into the polyimide main chain leads to a decrease of thermal stability (by about 120°C), but BTDA/DA-*n* polyimides are still more stable than other polyimides or other high performance polymers [25].

### Spectroscopic Characterization of Polyimides and Their Precursors

Infrared spectra of polyamic acids BTDA/DA-*n* are shown in Fig. 2. They exhibit absorption bands at 1660 and 1540  $\text{cm}^{-1}$ . These peaks have been interpreted as typical of the polyimide precursor and corresponded to the amide group [26].

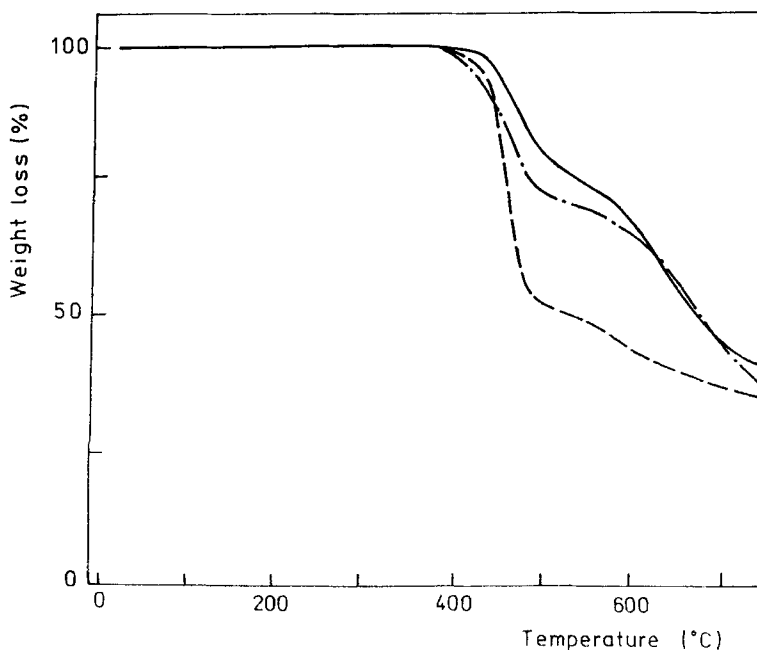


FIG. 1. Thermogravimetric measurements of polyimides PI-*n*: (—) *n* = 4, (---) *n* = 6, (-·-) *n* = 10.

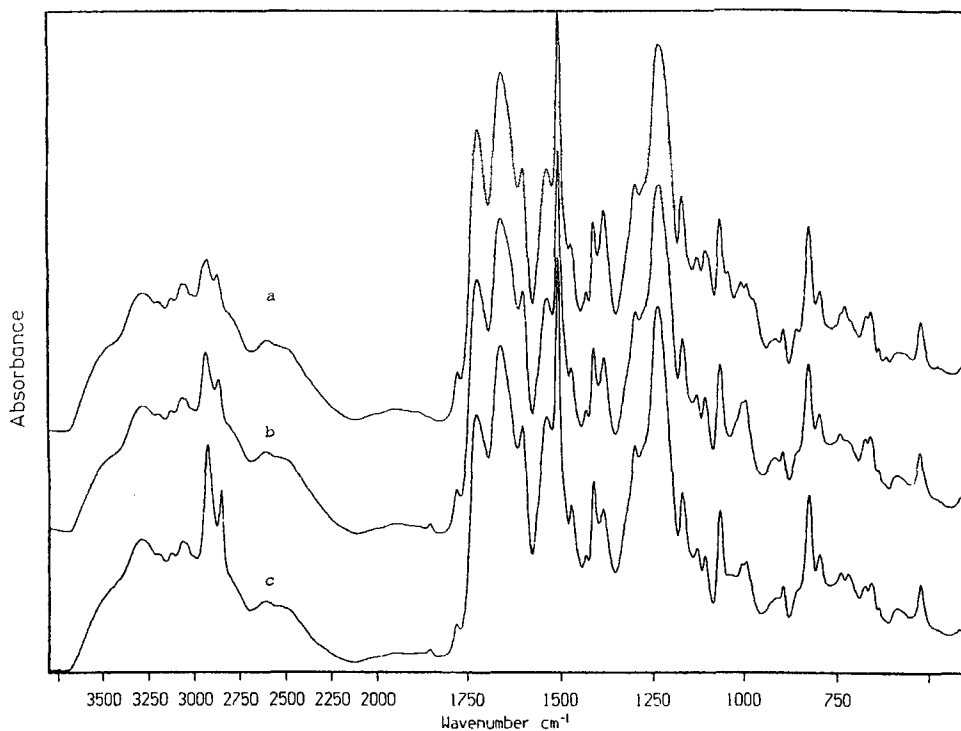


FIG. 2. Infrared spectra of polyamic acids PAA- $n$ : (a)  $n = 4$ , (b)  $n = 6$ , (c)  $n = 10$ .

Strong absorptions above  $3000\text{ cm}^{-1}$  indicate amide and carboxylic groups; typical absorption bands of carboxylic groups also appear at  $2500\text{--}2700\text{ cm}^{-1}$ . Infrared spectra of polyimides are shown in Fig. 3. After the cyclocondensation reaction (imidization), the spectra possess characteristic bands at  $1780$  and  $1730\text{ cm}^{-1}$  corresponding to the carbonyl groups of the imide ring. The wavenumbers of their maxima are the same as in corresponding poly(pyromellitimide)s [17]. The absorption peak at  $725\text{ cm}^{-1}$  is probably common to both imide and  $(\text{CH}_2)_n$  groupings of polyimides. In contrast to spectra of polyamic acids, the absence of an absorption at  $1860\text{ cm}^{-1}$  indicates negligible concentrations of anhydride end-groups. No absorption in the amide group region above  $3000\text{ cm}^{-1}$  as well as the disappearance of the peaks at  $2500\text{--}2700\text{ cm}^{-1}$  confirmed complete conversion of polyamic acids to polyimides. Since a small peak at  $1780\text{ cm}^{-1}$  can already be found in the spectra of precursors, it seems that cyclocondensation of *o*-carboxybenzamide structures also proceeds to a small extent during the reaction of dianhydride with diamine.

Because of insolubility of the polyimides, solid-state  $^{13}\text{C}$ -NMR spectroscopy was used for characterization of both polyamic acids and polyimides. The interpretation was based on our previous study of  $^{13}\text{C}$ -NMR CP-MAS and NQS spectra as well as on the interpretations of other authors [18, 27, 28]. CP-MAS spectra of PAA- $n$  show strong peaks at 193, 166, 155, 138–120, 114, 60, and 27 ppm.  $^{13}\text{C}$  CP-MAS conventional and NQS spectra of polyamic acid PAA-4 are shown in Figs. 4(a) and 4(b), respectively. All the spectra also contain peaks of complexed

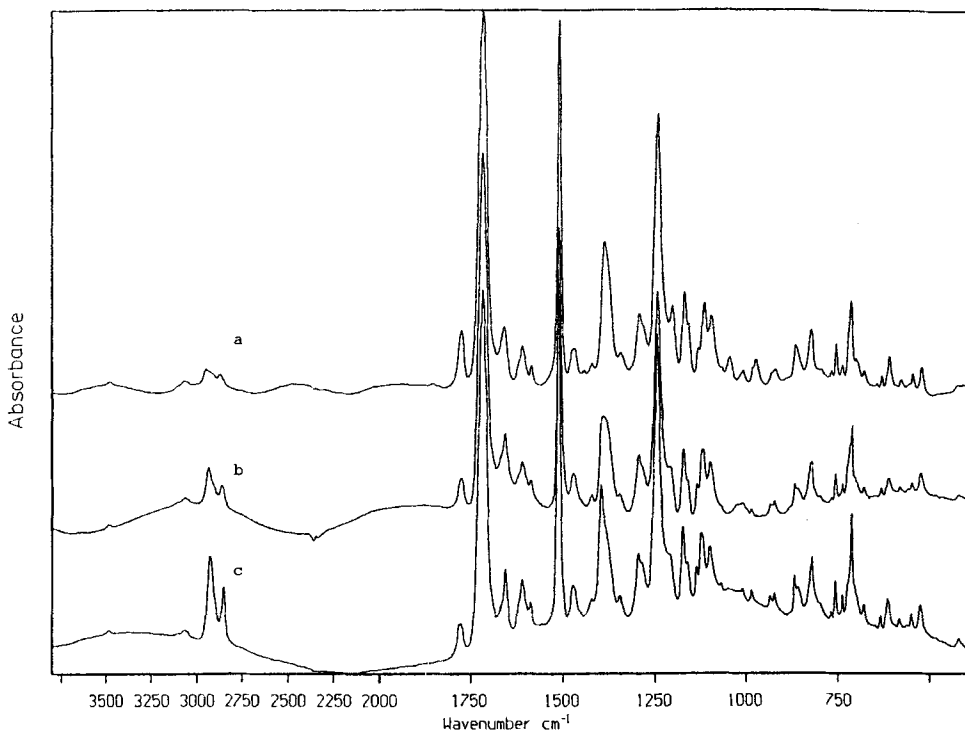


FIG. 3. Infrared spectra of polyimides PI-*n*: (a) *n* = 4, (b) *n* = 6, (c) *n* = 10.

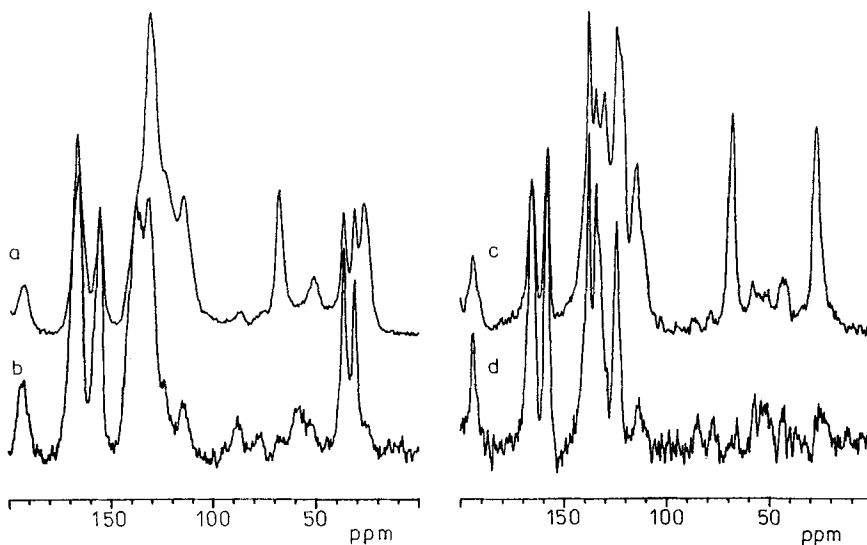


FIG. 4. <sup>13</sup>C-CP-MAS conventional (a, c) and NQS (b, d) spectra of PAA-4 (a, b) and PI-4 (c, d).



DMF [29, 30] at 36.7 and 31.4 ppm. From a comparison of both conventional CP-MAS and NQS spectra, it is evident that the peaks at 193.0, 166.3, 155.0, and 130.6 ppm correspond to quaternary carbons. The assignment of the peaks is based on previous studies [18, 27]: they belong to imide carbonyl, benzophenone carbonyl, and aromatic C—O and C—N carbons, respectively. The position of the strong peak at 139 ppm is close to the region where quaternary aromatic carbons of aromatic moieties occur [18]. C—H carbons of the dianhydride moiety of the repeating unit at 114.7 ppm and of the diamine one at 121.5 ppm disappeared in NQS spectra. Aliphatic chains are represented by two peaks at 66.0 ppm (O—CH<sub>2</sub> carbon) and 27.0 ppm (inner CH<sub>2</sub> carbons) in CP-MAS spectra.

In CP-MAS spectra of polyimides, three separated peaks were found at 193, 165, and 157 ppm, and five partly overlapping peaks lie in the region of 114–137 ppm. Aliphatic carbons are observable at the same position as in the case of the precursors. The absence of peaks between 30 and 40 ppm indicates that all DMF was removed during thermal cyclization. As follows from conventional CP-MAS and NQS spectra of PI-4 given in Figs. 4(c) and 4(d), five peaks of the CP-MAS spectrum correspond to quaternary carbons. The benzophenone carbonyl peak is located at the same frequency as in the precursor (193.0 ppm), and the position of the peak of imide C=O carbon did not change considerably (164.8 ppm) compared with the C=O group of the polyamic acid. Quaternary carbons of the dianhydride moiety are located at 137.7 and 134.5 ppm, and the peaks of C—N and C—O carbons associated with the diamine unit were found at 124.2 and 157.8 ppm. Aromatic C—H carbons of both dianhydride and diamine units are located at the same position as in the spectra of the precursor. The absence of additional peaks (except side bands) in the spectra of PI-4 indicates the absence of anomalous structures such as products of side reactions or degradation.

### X-Ray Diffraction on Polyimides and Their Precursors

Since some polyimides prepared from BTDA may be semicrystalline in nature [31], affecting mechanical and permeation properties and thermooxidative stability, we were also interested in x-ray diffraction measurements. Wide-angle x-ray diffraction (WAXD) patterns of the precursors are shown in Fig. 5. Amorphous peaks in the region  $2\theta = 13\text{--}31^\circ$  are much sharper for PAA-4 and PAA-6 than for PAA-10. No long-range order was observed in amorphous polymers, but some kind of short-range order consisting of the most probable distance between neighboring chains [32] was found. The center of the amorphous peak is therefore often taken as an average intersegmental (or interchain) spacing ( $d$ -spacing) [32–35]. In our case, the interchain spacing,  $d$ , is the same for PAA-4 and PAA-6 ( $d = 4.3 \text{ \AA}$ ), while  $d = 5.6 \text{ \AA}$  was calculated from the diffractogram of PAA-10. These results suggest a closer and more regular chain packing of precursors with a shorter aliphatic segment in the repeating unit. We believe that a short interchain spacing is responsible for the very low permeabilities of membranes prepared from the polymers under study. During our gas-permeation experiments, permeabilities to nitrogen, oxygen, and carbon dioxide were less than 0.12 barrer, i.e., below the resolution limit of our apparatus under the given experimental conditions (thickness of samples was  $30 \mu\text{m}$ ).

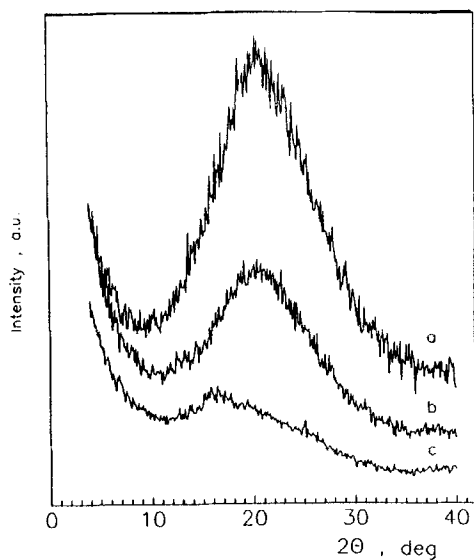


FIG. 5. Wide-angle x-ray diffractograms of polyamic acids PAA- $n$ : (a)  $n = 4$ , (b)  $n = 6$ , (c)  $n = 10$ .

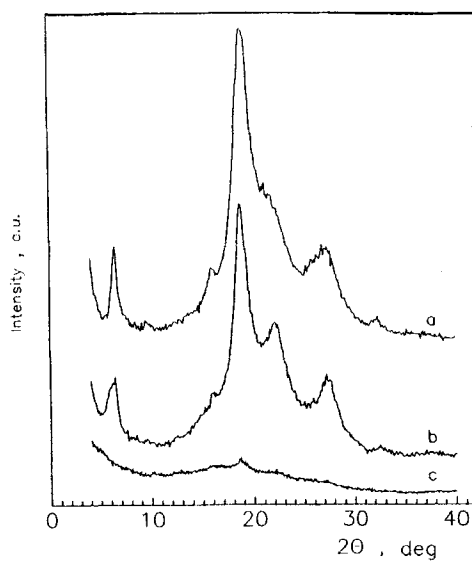


FIG. 6. Wide-angle x-ray diffractograms of polyimides PI- $n$ : (a)  $n = 4$ , (b)  $n = 6$ , (c)  $n = 10$ .

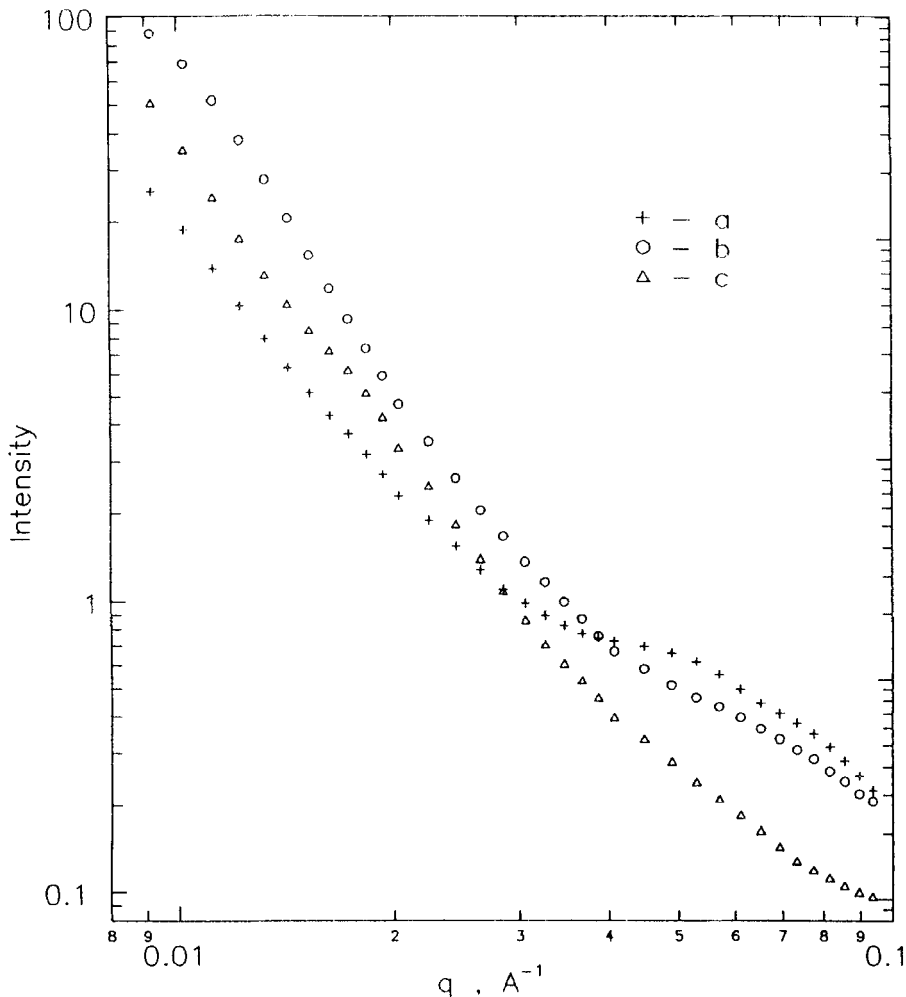


FIG. 7. Small-angle x-ray scattering of polyimides PI- $n$ : (a)  $n = 4$ , (b)  $n = 6$ , (c)  $n = 10$ .

As is apparent from Fig. 6, conversion of polyamic acids to polyimides leads to semicrystalline structures, probably due to the formation of more symmetrical macromolecules. Moreover, the repeating unit of polyamic acids occurs as three isomeric structures (due to meta or para positions of amide and benzophenone C=O groups [27]), which causes irregularities in the polymer chain. The shape and position of the amorphous halo remains unchanged after thermal cyclization for all the polymers and, compared with other polyimides [32, 33],  $d$ -spacings of PI-4 and PI-6 are considerably shorter. Crystallinity index (determined as the ratio of radiation intensity scattered by the crystalline domains to the overall scattering intensity [36]) was 0.33 for PI-4 and PI-6. Polyimide PI-10 contains only a small fraction of the ordered phase, estimated to amount to about 5%. This fact indicates that

incorporation of a longer aliphatic chain leads to an increase in the amorphous phase content. Diffractograms of polyimides display three main reflections corresponding to the spacings  $d = 4.4, 4.0,$  and  $3.3 \text{ \AA}$ . Since the reflections were also observed in samples of polyimide LARC-TPI (Mitsui Toatsu) and  $N,N'$ -diphenyl-3,3',4,4'-benzophenonetetracarboxylic diimide (model compound), we believe that they belong to the intersegmental distance of BTDA-related structures [37]. In addition, another peak at low diffraction angles appears for PI-4 and PI-6, corresponding to the projected length of the repeating unit ordered along the chain axis. The long spacing seems to increase with the number of methylene groups  $n$  in the repeating unit.  $d$ -spacings of 13.6 and 15.0  $\text{\AA}$  were found for PI-4 and PI-6, respectively. The absence of the first reflection in PI-10 can be explained by an overlap of strong small-angle x-ray scattering intensity in the region of  $2\theta$  where this reflection is supposed to be observed.

In the small-angle region, periodic alternation of the crystalline and amorphous phases gives rise to an interference maximum, corresponding to the long period. SAXS curves of polyimides are shown in Fig. 7. It is evident that with semicrystalline PI-4 and PI-6, SAXS curves exhibit broad, ill-developed interference maxima, the positions of which were estimated from Lorentz-corrected scattering curves ( $Iq^2$  vs  $q$ ) to be 0.06 and 0.07  $\text{\AA}$ , respectively. Consequently, the values of the long period are somewhat lower compared with other polyimides [31, 38], 105  $\text{\AA}$  for PI-4 and 90  $\text{\AA}$  for PI-6. No interference maxima were observed on SAXS curves of polyamic acids and polyimide PI-10. The semicrystalline nature of polyimides should lead to a further decrease of gas permeability; indeed, polyimide films were not permeable under the experimental conditions used.

### ACKNOWLEDGMENTS

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