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Synthesis and characterization of polyimides from 1,4-bis[4-(*n*-alkyloxy)phenyloxy]pyromellitic dianhydrides and 4,4'-oxydianiline

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Summary

New pyromellitic dianhydrides having (n-alkyloxy)phenyloxy (-O-Ph-O-n-C_mH_{2m+1}, m=1,4,8,12) side chains were synthesized and polymerized with 4,4'-oxydianiline (ODA) in NMP at room temperature. Imidization was carried out using triethylamine and acetic anhydride. The synthesized polyimides (C_m-OPIs) were characterized and their properties were measured and discussed in respect to the effects of side chains. Inherent viscosities of the polymers were in the 0.46 - 0.68 dL/g range. All the polymers were highly soluble in N-methylpyrrolidinone (NMP) and slightly soluble in DMSO, m-cresol, DMF and concentrated H_2SO_4 at room temperature. TGA pyrograms showed two-step degradation. In DSC thermograms the polymers exhibited T_g's between 219 °C and 305 °C and melting points near 350 °C were observed in C_8- and C_{12}-OPIs. Wide-angle X-ray diffractometry for as-polymerized samples revealed very low crystallinities and layered structures which were better developed in the polymers with longer side chains.

Introduction

Wholly aromatic polyimides are widely used in many applications because of their outstanding thermal, mechanical and electrical properties and excellent chemical resistance(1,2). However, in most cases their applications are restricted by a poor processability naturally resulting from their highly rigid main chain structure. Without doubt, poly(pyromellitimide)s belong to the most distinctive examples simultaneously showing these two extreme behaviors.

In recent years, structural modifications of the aromatic polyimides have been successfully conducted to improve their solubility and fusibility by incorporating flexible main-chain linkages or attaching flexible side chains(3~8) or bulky pendant groups(9~12). The method of affixing long and flexible side chains have recently drawn particular interests, and n-alkyl(4), n-alkyloxy(5), poly(ethyleneoxy)(6), or (n-alkyloxy)methyl groups(7,8) have been studied(6~8) in modifying a lot of rigid-rod polymers. However, in poly(pyromellitimide)s introduction of such side chains was made mostly not onto pyromellitic anhydride units but only onto diamine units, because the synthesis of pyromellitic dianhydrides having such side chains is certainly more difficult than that of diamines having the same sorts. To our best knowledge, no example of such poly(pyromellitimide)s has been reported yet.

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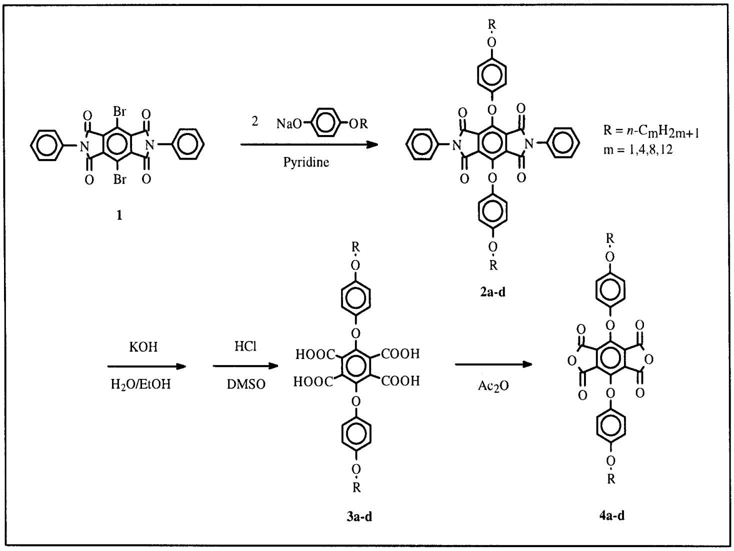
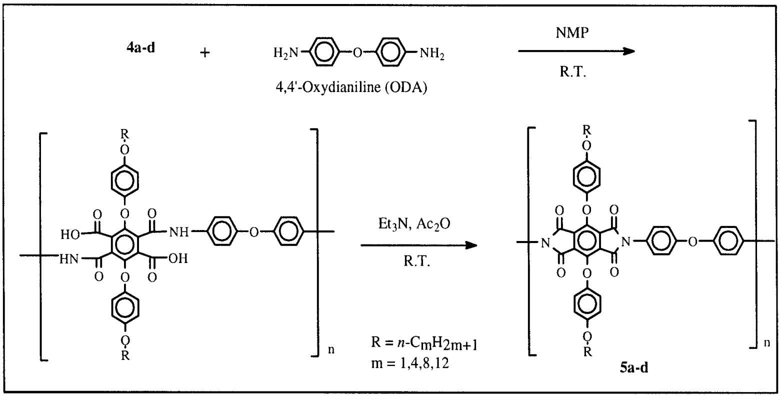
In this study, we report a series of new poly(pyromellitimide)s having (n-alkyloxy)phenyloxy groups in their side chains. These new polyimides were synthesized from 3,6-bis[(n-alkyloxy)phenyloxy]pyromellitic dianhydrides. These dianhydride monomers had been prepared from 3,6-dibromo-N,N'-diphenylpyromellitimide by nucleophilic substitution of the two bromine atoms by sodium (n-alkyloxy)phenoxides, as shown in Scheme 1. As their polymerization counterpart 4,4'-oxydianiline was chosen and the polymerizations were carried out in NMP at room temperature. The precursors thereby formed were chemically imidized using triethylamine and acetic anhydride(11, 13).



Scheme 1. Synthetic route to monomers.



Scheme 2. Polymerization reaction.

Experimental

Chemicals and Equipments : NMP, triethylamine, pyridine and acetic anhydride were purified by vacuum distillation. Durene, bromine, potassium permanganate, aniline and other reagents were used as received. 4,4'-Oxydianiline was purified by sublimation.

IR-spectra of synthesized compounds were recorded on Shimadzu FTIR-4300 spectrometer and ^{1}H-NMR spectra on Brucker Fourier Transform DPX 300 (300 MHz) spectrometer. DSC measurements were performed on a Perkin-Elmer DSC7 calorimeter and TGA thermograms were taken from a Perkin-Elmer TGA7 analyzer, both at a heating rate of 20 °C/min. under N_2. Elemental analyses were made by an Elementar Vario EL microanalyzer. Inherent viscosities of the polymers were measured in NMP with an Ubbelode viscometer at 25 °C. Wide-angle X-ray diffractograms were taken in reflection and transmission mode using Ni-filtered CuKα radiation on a Rigaku Geiger Flex D-Max.

*Synthesis of 3,6-dibromo-N,N'-diphenylpyromellitimide(**1**)* : This was obtained in 82 % yield by the reaction of 3,6-dibromopyromellitic dianhydride[m.p.: 274 ~ 276 °C; Lit.(15): 270 ~ 275] with aniline in NMP followed by dehydration using toluene azeotrope. This dianhydride was prepared from durene by sequential reactions of bromination(14), oxidation with $KMnO_4$(10, 12) and cyclization with AC_2O(total yield 53%). M.p.: >450 (dec.)

*Synthesis of 3,6-bis[4-(n-alkyloxy)phenyloxyl-N,N'-diphenylpyromellitimides(**2**)* : In a thoroughly dried 250 mL round-bottomed flask equipped with a drying tube, a distillation head and a gas inlet tube 0.46g (19.9 mmol) of sodium were dissolved in 20 mL of anhydrous methanol in N_2 atmosphere and then 19.9 mmol of n-alkyloxyphenols were added and stirred for 30 min at room temperature. After methanol and the water formed were completely distilled out, 70 mL of anhydrous pyridine were added and cooled to 0 °C. To this solution 5.26 g (10 mmol) of **1** dissolved in 20 mL pyridine were dropped in over a period of 20 min under rapid stirring and the mixture was stirred further at 0 °C for 12 hrs. Then the reaction mixture was poured into large excess of cold water to precipitate. The precipitates were filtered, washed with water and dried in *vacuo.* They were purified by recrystallization from ethyl acetate.

2a) Yield: 94.2%, m.p.: 381 °C(DSC), IR(KBr, cm^{-1}): 1774 & 1726 (imide I), 1596 & 1508 (aromatic), 1396 (imide II), 1255 & 1193 (C-O-C). ^{1}H-NMR (DMSO-d_6, ppm) : 3.70 (s, 6H,-C$\underline{H}_3$), 6.85, 6.88,7.06,7.09 (dd, 8H, aromatic), 7.36 ~ 7.51 (m, 10H, aromatic).

2b) Yield: 91.3%, m.p.: 332~334 °C, IR(KBr, cm^{-1}): 2960 ~ 2880 (CH, aliphatic), 1779 & 1733 (imide I), 1596 & 1506 (aromatic), 1394 (imide II), 1244 & 1188 (C-O-C). ^{1}H-NMR ($CDCl_3$, ppm): 0.92 ~ 0.97 (t, 6H, -C$\underline{H}_3$), 1.42 ~ 1.49 (sext, 4H, -C$\underline{H}_2$-CH_3) 1.70 ~ 1.75 (quint, 4H, -O-CH_2-C$\underline{H}_2$-), 3.87 ~ 3.91 (t, 4H, -O-C$\underline{H}_2$-), 6.81, 6.84, 6.96, 6.99 (dd, 8H, aromatic), 7.34 ~ 7.46 (m, 10H, aromatic).

2c) Yield: 98%, m.p.: 262~263 °C, IR(KBr, cm^{-1}): 2950 ~ 2880 (CH, aliphatic), 1776 & 1731 (imide I), 1596 & 1506 (aromatic), 1394 (imide II), 1244 & 1188 (C-O-C). ^{1}H-NMR ($CDCl_3$, ppm): 0.85 ~ 0.89 (t, 6H, -C$\underline{H}_3$), 1.27 ~ 1.41 (br m, 20H, -(C$\underline{H}_2$)$_5$-CH_3) 1.68 ~ 1.78 (quint, 4H, -O-CH_2-C$\underline{H}_2$-), 3.86 ~ 3.90 (t, 4H, -O-C$\underline{H}_2$-), 6.81, 6.84, 6.97, 7.00 (dd, 8H, aromatic), 7.34 ~ 7.46 (m, 10H, aromatic).

2d) Yield: 97.5%, m.p.: 236~238 °C, IR(KBr, cm^{-1}): 2920 ~ 2880 (CH, aliphatic), 1776 & 1731 (imide I), 1596 & 1506 (aromatic), 1396 (imide II), 1244 & 1188 (C-O-C). ^{1}H-NMR ($CDCl_3$, ppm) : 0.85 ~ 0.89 (t, 6H, C$\underline{H}_3$), 1.25 ~ 1.41 (br m, 36H, -(C$\underline{H}_2$)9-CH_3) 1.68 ~ 1.75 (quint, 4H, -O-CH_2-C$\underline{H}_2$-), 3.85 ~ 3.90 (t, 4H, -O-C$\underline{H}_2$-), 6.80, 6.83, 6.96, 6.99 (dd, 8H, aromatic), 7.34 ~ 7.46 (m, 10H, aromatic).

*Synthesis of 3,6-bis[4-(n-alkyloxy)phenyloxy]pyromellitic acids(**3**)* : In 250 mL round-bottomed flasks with condensers and stirrers 2~3 g of **2a~d** were dissolved with 10% NaOH solution (EtOH/water mixture). These mixtures were refluxed for 12 hrs, cooled to room temperature and acidified with cone. HCl solution to precipitate. The precipitates were collected and added to the stirred solution of 40 mL of conc. HCl and 150 mL of

DMSO. These solutions were stirred at 80 °C for 2~6 days, cooled to room temperature and poured into cold water. The crude products were obtained by extraction with ether (**3a**) or filtration (**3b~d**) and purified by recrystallization in EtOH/H_2O(**3a**) or hexane/ethyl acetate mixture(**3b~d**). Yield: 55~67 %. M.p.: These acid were dehydrated before their melting.

*Synthesis of 3,6-bis[4-(n-alkyloxy)phenyloxy]pyromellitic dianhydrides(**4**)* : In 100 mL round-bottomed flasks with reflux condensers, drying tubes and gas inlet tubes 2~3 g of **3a~d** were dissolved in 20 mL of acetic anhydride. After refluxing for 6 hrs the reaction mixtures were evacuated to remove acetic anhydride. The remained residues were collected and recrystallized from toluene.

4a) Yield: 85%, m.p.: 294~296 °C, IR(KBr, cm^{-1}): 1851, 1830, 1780 (C=O), 1600 & 1510 (aromatic), 1257 & 1190 (C-O-C). ^{1}H-NMR (Acetone-d_6, ppm): 3.77 (s, 6H,-$C\underline{H}_3$) 6.87, 6.90, 7.08, 7.11 (dd, 8H, aromatic). Analysis calc. for $C_{24}H_{14}O_{10}$ in wt. % : C 62.35, H 3.05 and found: C 62.52, H 2.75.

4b) Yield: 88%, m.p.: 262~264 °C, IR(KBr, cm^{-1}): 2976 ~ 2872 (CH, aliphatic), 1857 & 1799 (C=O), 1600 & 1506 (aromatic), 1247 & 1193 (C-O-C). ^{1}H-NMR (Acetone-d_6, ppm): 0.93 ~ 0.97 (t, 6H, -$C\underline{H}_3$), 1.44 ~ 1.51 (sext, 4H, -$C\underline{H}_2$-CH_3), 1.68 ~ 1.75 (quint, 4H, -O-CH_2-$C\underline{H}_2$-), 3.93 ~ 3.98 (t, 4H, -O-$C\underline{H}_2$-), 6.86, 6.89, 7.06, 7.09 (dd, 8H, aromatic). Analysis calc. for $C_{30}H_{26}O_{10}$ in wt. % : C 65.93, H 4.80 and found: C 66.10, H 4.32.

4c) Yield: 87%, m.p.: 233~235 °C, IR(KBr, cm^{-1}): 2976 ~ 2848 (CH, aliphatic), 1853, 1830, 1784 (C=O), 1600 & 1504 (aromatic), 1249 & 1191 (C-O-C). ^{1}H-NMR (Acetone-d_6, PPM) : 0.86 ~ 0.90 (t, 6H, -$C\underline{H}_3$), 1.30 ~ 1.46 (br m, 20H, -$(C\underline{H}_2)_5$-CH_3), 1.72 ~ 1.77 (quint, 4H, -O-CH_2-$C\underline{H}_2$-), 3.93 ~ 3.97 (t, 4H, -O-$C\underline{H}_2$-), 6.86, 6.89, 7.06, 7.09 (dd, 8H, aromatic). Analysis calc. for $C_{38}H_{42}O_{10}$ in wt. % : C 69.29, H 6.42 and found: C 68.99, H 6.08.

4d) Yield: 89%, m.p.: 218-220 °C, IR(KBr, cm^{-1}): 2976 ~ 2850 (CH, aliphatic), 1849, 1811, 1774 (C=O), 1598 & 1506 (aromatic), 1249 & 1184 (C-O-C). ^{1}H-NMR (Acetone-d_6, ppm): 0.85 ~ 0.90 (t, 6H, -$C\underline{H}_3$), 1.41 ~ 1.46 (br m, 36H, -$(C\underline{H}_2)_9$-CH_3) 1.72 ~ 1.77 (quint, 4H, -O-CH_2-$C\underline{H}_2$-), 3.93 ~ 3.97 (t, 4H, -O-$C\underline{H}_2$-), 6.86, 6.89, 7.06, 7.09 (dd, 8H, aromatic). Analysis calc. for $C_{46}H_{58}O_{10}$ in wt. % : C 71.67, H 7.58 and found : C 71.26, H 7.40.

Polymerization : 0.5 mmol of the dianhydrides thus obtained were added to stirred solutions of 0.5 mmol of ODA in anhydrous NMP (solid content 9~10% w/w) under N_2 at room temperature. After the solutions were stirred for 48 hrs, 1.1 mmol of triethylamine and 1.1 mmol of acetic anhydride were added. After these solutions were stirred for 24hrs, they were diluted with 5 ml of NMP and then poured into 500 mL of EtOH. The polymers precipitated were collected by filtration, washed thoroughly with EtOH and dried at 120 °C in vacuum oven. Yields were nearly quantitative in all polymerizations.

5a) (**C_1-OPI**) IR(KBr, cm^{-1}): 1778 & 1726 (imide I), 1596 & 1500 (aromatic), 1392 (imide II), 1242 & 1184 (C-O-C). Analysis calc. for $C_{36}H_{22}O_9N_2$ in wt. % : C 69.01, H 3.54, N 4.47 and found : C 67.00, H 3.59, N 4.86.

5b) (**C_4-OPI**) IR(KBr, cm^{-1}): 2960 ~ 2830 (CH, aliphatic), 1778 & 1728 (imide I), 1596 & 1502 (aromatic), 1392 (imide II), 1244 & 1186 (C-O-C). Analysis calc. for $C_{42}H_{34}O_9N_2$ in wt. % : C 70.98, H 4.82, N 3.94 and found: C 70.42, H 4.70, N 3.94.

5c) (**C_8-OPI**) IR(KBr, cm^{-1}): 2960 ~ 2830 (CH, aliphatic), 1778 & 1730 (imide I), 1598 & 1502 (aromatic), 1392 (imide II), 1242 & 1186 (C-O-C). Analysis calc. for $C_{50}H_{50}O_9N_2$ in wt. %: C 72.98, H 6.12, N 3.40 and found : C 71.41, H 6.04, N 3.76

5d) (**C_{12}-OPI**) IR(KBr, cm^{-1}): 2960 ~ 2830 (CH, aliphatic), 1780 & 1730 (imide I), 1598

& 1500 (aromatic), 1392 (imide II), 1242 & 1186 (C-O-C). Analysis calc. for $C_{58}H_{66}O9N_2$ in wt. % : C 74.49, H 7.11, N 3.00 and found : C 73.32, H 6.51, N 3.29.

Results and discussion

Monomer Synthesis : The two (n-alkyloxy)phenyloxy side chains were successfully introduced to pyromellitic dianhydride by nucleophilic substitution reaction of bromine atoms by (n-alkyloxy)phenoxide anions in pyridine at 0 °C followed by hydrolysis of the imide groups. To proceed this substitution reaction successfully, the dianhydride had to be blocked to diimide using aniline. In spite of repeated attempts no monosubstituted diimide compounds could be isolated.

3,6-Bis(n-alkyloxy)phenyloxy-N,N'-diphenylpyromellitimides were hydrolyzed to obtain corresponding tetracarboxylic acids. This hydrolysis was undertaken by two-step reaction. Although imide groups could be easily converted to amic acid groups in 10 % NaOH solution, amic acid groups of these compounds were found to be highly resistant against the basic hydrolysis. Even 50 % NaOH solutions were not able to hydrolyze the amic acids, and the amic acid compounds completely recovered. Therefore, they had to be treated with conc. HCl in DMSO. This acid hydrolysis was able to convert amic acids to tetracarboxylic acids. The tetraacids(**3a~d**) were dehydrated by treating with acetic anhydride. Independent of side chain length, all the dianhydride monomers (**4a~d**) could be purified to polymerization grade by recrystallization from a single solvent toluene.

Polymerization : The polymerization reactions were carried out in two steps, as shown in Scheme 2. Poly(amic acid)s were first prepared from reaction with dianhydride monomers (**4a~d**) with ODA in NMP and subsequently cyclized with triethylamine and acetic anhydride at room temperature. In later spectroscopic characterizations it could be confirmed that the cyclization reactions proceeded completely even at room temperature. In both steps the reaction systems remained homogeneous in NMF, implying that attachment of the side groups greatly enhances solubility of the resulting polymers in the solvent.

Characterization : To characterize chemical structures of the obtained polyimides having bis[4-(n-alkyloxy)phenyloxy] side groups by IR spectroscopy, their IR spectra were compared to those of 3,6-bis[4-(n-alkyloxy)phenyloxy] -N,N'-diphenylpyromellitimides (**2a~d**). These compounds had already been prepared as intermediates for the dianhydride monomers. They were used as model compounds helping to characterize imide structures of the poyimides. In Figure 1 is reproduced the spectrum of C_8-OPI as compared with that of **2c**. Both spectra clearly show the

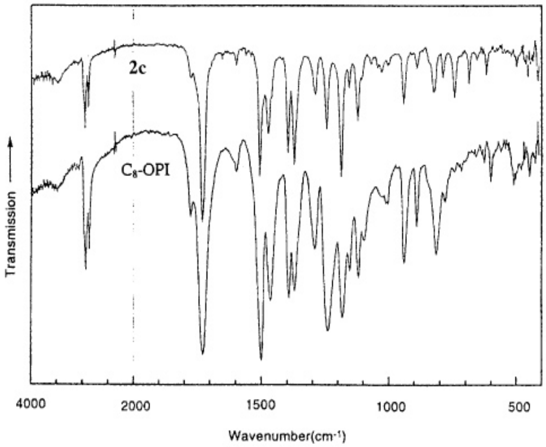


Figure 1. IR spectra of C_8-OPI and **2c**.

characteristic imide I, II bands at 1776, 1731 and 1394 cm^{-1} and C-H stretching vibrations of aliphatic groups in 2940 ~ 2840 cm^{-1}. In the other polymers C_1-, C_4-, and C_{12}-OPIs analogous IR-spectroscopic characterizations could be made by comparison to the same characteristic imide peaks of **2a**, **2b** and **2d**, respectively.

The elemental analysis data measured for C, H and N of the polyimide samples are given in the experimental part. It is to see that the data measured are well coincident with those theoretically calculated, indicating that chemical structure of the polyimides prepared coincide well with those given in Scheme 2.

Solution Properties : The solution properties of C_m-OPIs are summarized in Table 1. The polymers are highly soluble in NMP even at room temperature, but only slightly soluble in the other polar solvents such as m-cresol, DMAc, concentrated sulfuric acid and HMPA. It is quite surprising that there is a great solubility difference between NMP and other highly polar aprotic or protic solvents. Inherent viscosities of the polymers measured from NMP are in the range of 0.46 ~ 0.68 dL/g, indicating that they have relatively high molecular weights.

Table 1. Solution properties of C_m-OPIs.

Polymer Code	$\eta_{inh.}$ [a] (dL/g)	Solubility [b]				
		NMP	m-Cresol	DMAc	HMPA	H_2SO_4
C_1-OPI	0.51	++	+	+	+	+
C_4-OPI	0.68	++	+	+	+	+
C_8-OPI	0.66	++	+	+	+	+
C_{12}-OPI	0.46	++	+	+	+	+

[a] Determined at 25 ℃ in NMP (0.2 g/dL).

[b] + Slightly soluble, ++ soluble at room temperature.

Thermal Resistance : Thermal resistances were studied by TGA in N_2 at 20 °C/min scan rate and the TGA pyrograms are reproduced in Figure 2. As Figure 2 shows, all C_m-OPIs show two-step pyrolysis behavior with increasing temperature. This behavior may reasonably be presumed(7) to arise from the fact that side chains are degraded in the lower-temperature range and the main chains in the higher-temperature range. To see which part of side chains splits away in the lower-temperature range, we calculated wt. %'s of n-alkyloxy group (Ws(A)) and those of (n-alkyloxy)phenyloxy group (Ws(B)) and compared with the measured wt. % values (Ws(C)) decreased in the first step, as summarized in Table 2. As it shows, the observed Ws(C)

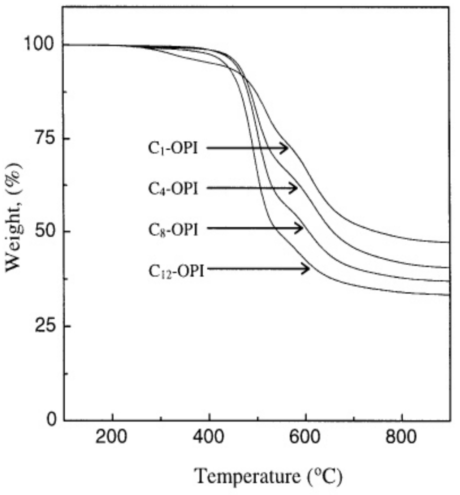


Figure 2. Thermal pyrograms of C_m-OPIs in N_2.

values lie in between the two Ws(A) and Ws(B) values. This fact means only that no single side group selectively degrades away in the low-temperature range. At this stage it can not also be said if main chain degradation takes place to some degree or not. To obtain more exact understanding of the thermal pyrolysis behaviors, more detailed studies are required.

From Table 2 it is also to see that with increasing side chain length the onset temperatures of lower-temperature degradation decrease greatly, indicating that thermal stability of the polyimides is greatly affected by the presence of the side chains, whereas those of higher-temperature degradation change only slightly, suggesting that fairly entire side chains have already degraded away in the lower-temperature range.

Table 2. Thermal behavior of C_m-OPIs in N_2.

Polymer code	1st T_i [a] (℃)	2nd T_i [a] (℃)	WR_{900} [b] (wt%)	Ws [c] in wt% Calculated (A)		Observed (C)
				Calculated (A)	(B)	Observed (C)
C_1-OPI	478	584	47	10	39	26
C_4-OPI	463	591	41	21	47	33
C_8-OPI	464	582	37	31	54	43
C_{12}-OPI	457	577	33	40	59	51

[a] T_i : Onset temperature of degradation.
[b] WR_{900} : Weight remained at 900 ℃.
[c] Ws(A) : Wt.% of n-alkyloxy groups contained.
Ws(B) : Wt.% of (n-alkyloxy)phenyloxy groups contained.

Phase Behaviors : *DSC* thermograms were used to study the phase behaviors of the polyimides. They were obtained from first and third heating scans of as-polymerized C_m-OPIs powder samples at of 20 °C/min heating rate and they are represented in Figure 3. The upper four curves were obtained from the first scans and the lower four from third scans. DSC curves obtained from first scans of C_8- and C_{12}-OPI clearly show a melting endotherm at 345 and 350 °C, respectively, indicating that both have some crystallinity. Presence of these crystallinities could be confirmed by WAXS. The curves obtained from first scans of C_1- and C_4-OPI do not exhibit any clear melting endotherm. All the polymer samples heated twice to 370 °C and cooled to ambient temperature show no endothermic peaks, meaning that these samples are completely amorphous. The disappearance of the crystallinity in C_8- and C_{12}-OPI by the heat treatment indicates that on cooling to ambient temperature they have been quenched. The glass transition temperatures (T_g's) of C_1-, C_4-, C_8-, and C_{12}-OPIs are detectable at 305, 260, 231, and 219 °C, respectively. The observation that T_g decreases with increasing side chain length demonstrates that the flexible side chains exert an attractive interaction with the rigid main chain at high temperatures, as already

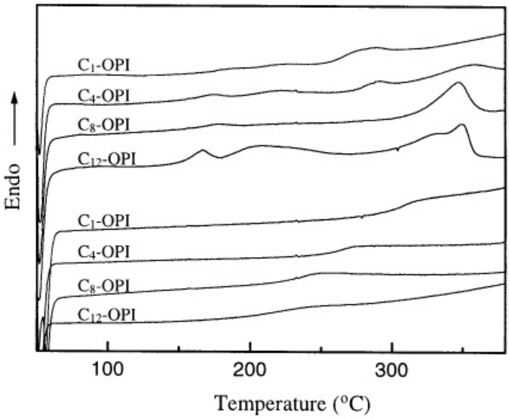


Figure 3. DSC thermograms of C_m-OPIs 1st (upper curves) and 3rd (lower curves) heatings.

observed in many rigid-rod polymers with flexible side chains(3-8).

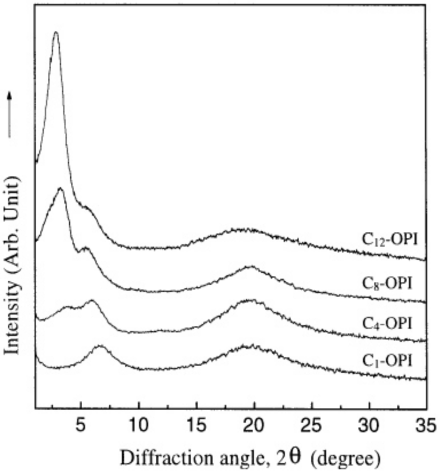


Figure 4. Wide-angle X-ray diffractograms of as-polymerized C_m-OPIs.

Crystal Structure : From Wide-angle X-ray diffractograms of the C_m-OPIs crystalline structure was studied. The diffractograms were obtained from as-polymerized samples and reproduced in Figure 4. At wider angles they show only broad reflections originated from their very low crystallinities. The peaks in smaller angle region are characteristic of typical layered crystalline structure whch usually develops more tightly with increasing side chain length(3, 7), and in C_1- and C_4-OPI no crystallinity was detectable by DSC while C_8- and C_{12}-OPI reveal melting endotherm. Detailed studies on crystalline structure is in progress now and these results will be published later.

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