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Synthesis and characterization of polyimides from 9,10-dialkyloxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic-2,3:6,7-dianhydrides and 4,4'-oxydianiline

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Summary

New dianhydrides having alkyloxy side chains were synthesized and polymerized with 4,4'-oxydianiline in NMP. Chemically cyclized polyimides were obtained with inherent viscosities of 0.30~0.84 dL/g range. All the polymers were highly soluble in polar solvent such as NMP at room temperature. TGA pyrograms showed two-step degradation and in DSC thermograms the polymers exhibited T_gs between 124°C and 259°C. Wide-angle X-ray diffractograms revealed very low crystallinity and layered structure, which was better developed in the polymers with longer side chains

Introduction

Wholly aromatic polyimides are an important classes of high performance polymers exhibiting not only excellent high-temperature stability, which makes them suitable for continuous high-temperature but also good mechanical and electrical properties [1,2]. However, most of these materials cannot be molded as polyimides but must first be prepared as a soluble precursor poly(amic acid) and then processed into final form by thermal or chemical methods.

In the past decades, the focus of polyimide research has been shifting toward obtaining soluble and processable materials by structural modifications on the requisite monomers. Several approaches to soluble polyimides including introduction of side groups [3~5] or enlarged monomers containing angular bonds [7~9] and use of noncoplanar or alicyclic monomers have been developed. Especially, a literature survey revealed that the polyimides containing alicyclic moiety showed enhanced solubility [10~12]. Most of the above approaches for soluble polyimides are aimed at reduction of several types of chain-chain interactions, such as chain packing and charge transfer and electronic polarization interactions.

In this study, we report a series of new polyimides having alicyclic unit and alkyl side chains. These dianhydride monomers had been prepared from O-alkylation of durohydroquinone, side-chain bromination, and followed by Diels-Alder reaction with maleic anhydride, as shown in Scheme 1. As their polymerization counterpart 4,4'-

oxydianiline was chosen and the polymerization was carried out in NMP at room temperature. The precursors thereby formed were chemically imidized using triethyl amine and acetic anhydride.

Experimental

Materials and Measurements

Dimethyl sulfoxide(DMSO) was used after drying over 4Å molecular sieves. DMF and NMP were distilled over MgSO$_4$ and CaH$_2$, respectively. Acetic anhydride and Et$_3$N were purified by vacuum distillation. Duroquinone, bromine, and other reagents were used as received. 4,4'-Oxydianiline was purified by sublimation.

Melting points were measured using IA 9100 Digital melting point apparatus without correction. Elemental analyses were performed on a Vario EL (Elementar) microanalyzer. FT-IR-spectra of synthesized compounds were recorded on Mattson Infinity Gold series FT-IR spectrophotometer. ^{1}H-, ^{13}C-NMR spectra were obtained from a 300 MHz Bruker AM 300 spectroscope. Thermal analyses of polymers were carried out with a Perkin-Elmer PE PC Series TGA 7 thermogravimetric analyzer and a Perkin-Elmer PE PC Series DSC 7 thermal analyzer at a scan rate of 20°C/min. under N$_2$. Inherent viscosities were determined using an Ubbelhode type viscometer at 25°C for 0.2g/dL solutions in NMP. Wide angle X-ray diffractograms were taken in transmission mode using Ni-filtered CuK$_\alpha$ radiation on an X-ray diffractometer consisting of an 18kW rotating anode X-ray generator operated at 50kV x 20mA (Rigaku Co.).

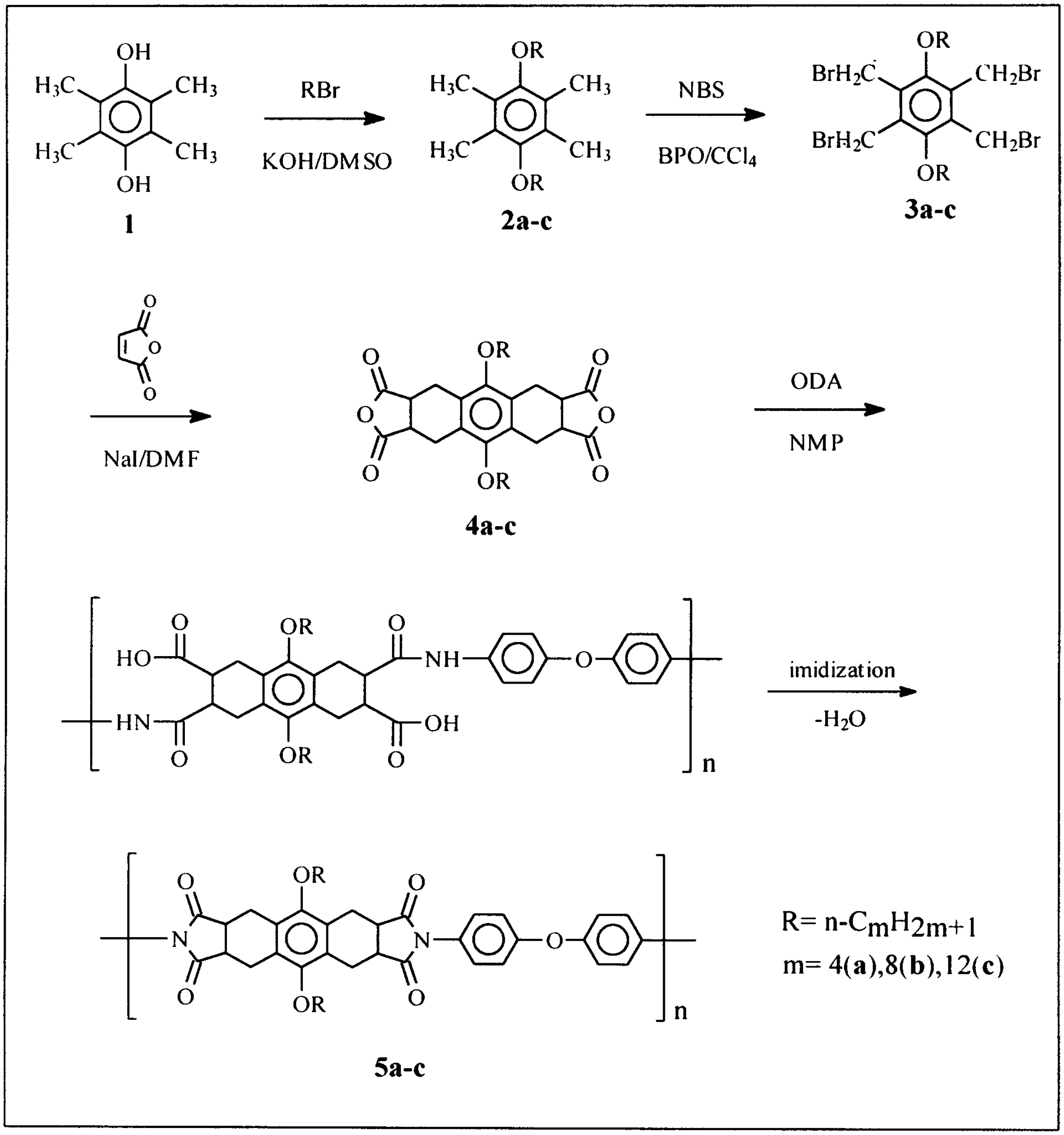
*Synthesis of 1,4-dialkyloxy-2,3,5,6-tetramethylbenzene(**2a~c**)*

In a 250ml of 2-necked round bottom flask equipped with N$_2$ gas inlet were added 4.2g (25.3mmol) of durohydroquinone, 3.54g (63.1mmol) of potassium hydroxide and 50ml of dry DMSO. After dissolving the compounds was placed 75.8mmol of *n*-alkylbromide in the flask. The resulting mixture was stirred at room temperature for 48 hours and poured into 200ml of distilled water. The crude product was obtained by suction filtration and air-dried. The product was recrystallized from MeOH.

2a) Yield : 89.9% ; m.p. : 74.7~75.4 °C ; FT-IR(KBr, cm^{-1}) : 2957~2867(alkyl chain stretch), 1466(CH$_2$ scissors vib. in alkyl group), 1082(C-O-C stretch in ether) ; ^{1}H-NMR (CDCl$_3$, δ ppm) : 0.98 (t, 6H), 2.15 (s, 12H), 1.48 (m, 4H), 1.78 (quint., 4H) and 3.64 (t, 4H) ; ^{13}C-NMR (CDCl$_3$, δ ppm) : 13.0, 14.2, 19.6, 32.6, 72.8, 127.8 and 151.9.

2b) Yield : 66.2% ; m.p. : 71.9~72.4 °C; FT-IR(KBr, cm^{-1}) : 2931~2851 (alkyl chain stretch), 1470(CH$_2$ scissors vib. in alkyl group), 1086(C-O-C stretch in ether) ; ^{1}H-NMR (CDCl$_3$, d ppm) : 0.98(t, 6H), 1.29~1.48(m, 20H), 1.78(quint., 4H), 2.15(s, 12H) and 3.63(t, 4H) ; ^{13}C-NMR (CDCl$_3$ δ ppm) : 13.5, 14.8, 23.4, 26.9, 30.0, 30.3, 31.0, 32.6, 73.6, 128.3 and 152.4.

2c) Yield : 65.4% ; m.p. : 83.3~84.2 °C ; FT-IR(KBr, cm^{-1}) : 2920~2849(alkyl chain stretch), 1472(CH$_2$ scissors vib. in alkyl group), 1087(C-O-C stretch in ether) ; ^{1}H-NMR (CDCl$_3$, δ ppm) ; 0.98(t, 6H), 1.29~1.48(m, 36H), 1.78(quint., 4H), 2.15(s, 12H) and 3.63(t, 4H) ; ^{13}C-NMR (CDCl$_3$, δ ppm) : 13.5, 14.8, 23.4, 26.9, 30.1, 30.3(overlapped), 30.4, 31.1, 32.6, 73.6, 128.3 and 152.4



Scheme 1. Synthetic route to monomers and polymers

*Synthesis of 1,4-dialkyloxy-2,3,5,6-tetrakisbromomethylbenzene(**3a~c**)*

In a 500ml three necked round bottom flask equipped with N_2 inlet and magnetic stirrer were placed 130ml of carbon tetrachloride, 26.13g (146.8mmol) of N-bromosuccinimide, 22.6mmol of 1,4-dialkyloxy-2, 3, 5, 6-tetramethylbenzene(**2a~c**) and added spatula tip of benzoylperoxide(BPO). After refluxing under nitrogen atmosphere for 8 hours, succinimide byproduced was removed by hot filtration and carbon tetrachloride was evaporated. The product was recrystallized from EA/MeOH mixture to give fine crystals.

3a) Yield : 48.9% ; m.p. : 128 °C ; FT-IR(KBr,cm^{-1}) : 2958~2871(alkyl chain stretch), 1466(CH_2 scissors vib. in alkyl group), 1197(C-O-C stretch in ether), and 636, 515(C-Br stretch) : ^{1}H-NMR ($CDCl_3$, δ ppm) ; 1.04 (t, 6H), 1.48 (m, 4H), 1.78 (quint., 4H), 4.15 (t, 4H) and 4.76 (s, 8H) : ^{13}C-NMR ($CDCl_3$, δ ppm) ; 14.2, 19.4,23.5, 32.5, 73.8, 131.1 and 153.8

3b) Yield : 56.9% ; m.p. : 72.0 °C ; FT-IR(KBr,cm^{-1}) : 2920~2851(alkyl chain stretch), 1465(CH_2 scissors vib. in alkyl group), 1198(C-O-C stretch in ether), and 647, 517(C-Br stretch) ; ^{1}H-NMR ($CDCl_3$, δ ppm) : 0.92(t, 6H), 1.36~1.57 (m, 20H), 1.89(quint., 4H), 4.15 (t, 4H) and 4.72 (s, 8H) ; ^{13}C-NMR ($CDCl_3$, δ ppm) : 14.8, 23.4, 23.9, 26.6, 29.9, 30.1, 32.5, 75.9, 138.9 and 154.3

3c) Yield : 74.8% ; m.p. : 69.8 °C ; FT-IR(KBr,cm^{-1}) : 2918~2850(alkyl chain stretch), 1466(CH_2 scissors vib. in alkyl group), 1196(C-O-C stretch in ether), and 646, 518(C-Br stretch) ; ^{1}H-NMR ($CDCl_3$, δ ppm) : 0.88(t, 6H), 1.36~1.57 (m, 36H), 1.89(quint., 4H), 4.15 (t, 4H) and 4.72 (s, 8H) ; ^{13}C-NMR ($CDCl_3$, δ ppm) : 14.8, 23.4, 23.9, 26.5, 30.0, 30.1, 30.2, 30.9, 32.6, 75.9, 133.9 and 154.3

*Synthesis of 9, 10-dialkyloxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic-2,3:6, 7-dianhydride(**4a~c**)*

0.01mol of 1,4-dialkyloxy-2,3,5,6-tetrakisbromomethylbenzene(**3a~c**), 0.035mol of maleic anhydride and 0.1mol of dry sodium iodide were placed in 250ml of round bottom flask filled with 70ml of dry DMF. The mixture was heated up to 85 °C in nitrogen atmosphere for 36 hours. After cooling to room temperature, reaction mixture was poured into 10% of aq. sodium bisulfite solution, and filtered off the precipitate. Crude product obtained was washed well with two portion of 100ml of distilled water and dried in vacuum. And then, in a 100ml of round bottom flask equipped with nitrogen inlet, placed 30ml of acetic anhydride and add crude product. After refluxing of reaction mixture for 12 hours, the flask was placed in refrigerator for 12 hours. Resulting product was obtained by suction filtration followed by washing with diethyl ether and recrystallized from dichloromethane/pet-ether to give crystals.

4a) Yield : 34% ; m.p. : not measured by DSC ; FT-IR(KBr,cm^{-1}) : 2926~2876(alkyl chain stretch), 1844, 1772(C=O stretch in cyclic anhydride), 1455(CH_2 scissors vib. in alkyl group), 1111(C-O-C stretch in ether) ; ^{1}H-NMR(DMSO-d_6, 110 °C, δ ppm) : 0.98(t, 6H), 1.52(m, 4H), 1.71(q, 4H), 2.63(d, $J_{geminal}$=12Hz), 3,28(d, $J_{geminal}$=12Hz) 3.66~3.55(m, 4H), 3.75(broad s, 4H) ; ^{13}C-NMR(DMSO-d_6, 110 °C, δ ppm) : 14.6, 19.8, 23.5, 32.9, 40.9, 75.3, 128.6, 150.8 and 175.5

4b) Yield : 35% ; m.p. : 309 °C (by DSC) ; FT-IR(KBr,cm^{-1}) : 2928~2872(alkyl chain stretch), 1844, 1783(C=O stretch in cyclic anhydride), 1456(CH_2 scissors vib. in alkyl group), 1110(C-O-C stretch in ether) ; ^{1}H-NMR ($C_2D_2Cl_4$, δ ppm) : 0.89(t, 6H), 1.30~1.51 (m, 20H), 1.83(quint., 4H), 2.56(d, $J_{geminal}$=12Hz), 3.55(d, $J_{geminal}$=12Hz), 3.61 (overlapped, broad s, 8H) ; ^{13}C-NMR ($C_2D_2Cl_4$, δ ppm) : 14.0, 22.8, 22.9, 32.1, 40.8, 75.0, 128.3, 150.3 and 175.0

4c) Yield : 38% ; m.p. : 274 °C (by DSC) ; FT-IR(KBr,cm^{-1}) : 2924~2871(alkyl chain stretch), 1844, 1783(C=O stretch in cyclic anhydride), 1456(CH_2 scissors vib. in alkyl group), 1109(C-O-C stretch in ether) ; ^{1}H-NMR($C_2D_2Cl_4$, δ ppm) : 0.87(t, 6H), 1.26~1.51 (m, 36H), 1.83(quint., 4H), 2.57(d, $J_{geminal}$=9Hz), 3.51(d, $J_{geminal}$=9Hz), 3.61(s, 4H) 3.62(t, 4H) ; ^{13}C-NMR ($C_2D_2Cl_4$, δ ppm) : 14.0, 22.5, 22.6, 25.9, 29.1-29.5, 30.0, 31.7, 40.0, 75.3, 127.2, 149.9 and 173.4

Polymerization

0.2mmol of the dianhydrides thus obtained were added to stirred solutions of 0.2mmol

of ODA in anhydrous NMP (solid content 7~10% w/v) under N_2 at room temperature. After the solutions were stirred for 48hours, 0.44 mmol of Et_3N and 0.44 mmol of acetic anhydride were added. After these solutions were stirred for 24 hours, they were diluted with 5ml of NMP and then poured into 50ml of MeOH. The precipitates were filtered, washed with hot MeOH and finally vacuum-dried at 100 °C for 24 hours.
5a) FT-IR(KBr, cm^{-1}) : 2958-2870(aliphatic CH), 1781 & 1711(C=O stretch in imide) 1386(C-N-C) 1239(C-O-C) ; Elemental analysis for $(C_{38}H_{38}N_2O_7)_n$ Calc. C 71.84 H 5.99 N 4.41 Found C 71.69 H 5.94 N 4.33
5b) FT-IR(KBr, cm^{-1}) : 2927-2855(aliphatic CH), 1780 & 1714(C=O stretch in imide), 1384(C-N-C) 1239(C-O-C) ; Elemental analysis for $(C_{46}H_{54}N_2O_7)_n$ Calc. C 73.90 H 7.23 N 3.75 Found C 73.21 H 5.94 N 3.72
5c) FT-IR(KBr, cm^{-1}) : 2958-2870(aliphatic CH), 1781 & 1711(C=O stretch in imide), 1386(C-N-C) 1239(C-O-C) ; Elemental analysis for $(C_{54}H_{70}N_2O_7)_n$ Calc. C 75.42 H 8.15 N 3.26 Found C 74.35 H 8.15 N 3.27

Results and discussion

Synthesis of Monomers

Monomers(**4a~c**)were prepared by bis-Diels-Alder reaction from maleic anhydride and 1,4-dialkyloxy-2,3,5,6-tetrakisbromomethylbenzene(**3a~c**), which had been synthesized from duroquinone as a starting material via consecutive reduction, alkylation with *n*-alkylbromide and side-chain bromination of methyl groups using NBS, as shown in Scheme 1. Williamson reaction was applied to synthesize compound **2a~c** in DMSO. 1,4-dialkyloxy-2,3,5,6-tetrakisbromomethylbenzene(**3a~c**) had been synthesized by reaction of excess NBS with **2a~c** under BPO as an initiator. Excess succinimide byproduced after bromination was completely removed by extraction with hot water before recrystallization. Bis-Diels-Alder reaction was conducted to obtain monomeric dianhydrides below 80 °C under nitrogen flows, and FT-IR spectra of crude products showed that those were a mixture of carboxylic acid and anhyride because it was worked up in water. These mixtures were dehydrated by treating with acetic anhydride, then recrystallized in acetic anhydride(**4a**) or CH_2Cl_2/pet-ether mixed solvent(**4b,4c**). After drying, there were crystalline materials with anhydride peaks at 1844, 1783cm^{-1} in the FT-IR. The ^{1}H-NMR was confirmatory with 0.9~1.8 ppm of alkyl side chains and doublets of ca. 2.5 and 3.5ppm splitted by geminal hydrogen atom of alicyclic unit in the monomers.

Polymerization

The polymerization reactions were carried out in two steps, as shown in Scheme 1. Poly(amic acid)s were first prepared from reaction with dianhydride monomers(**4a~c**) with ODA in NMP and subsequently cyclized with Et_3N 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 NMP, implying that incorporation of the side groups and alicyclic unit in the polymer backbone greatly enhances solubility of the resulting polymers. Polymers were thoroughly purified by precipitating from large excess of MeOH and repeated washing with hot MeOH. Structures of the polymers thus obtained were characterized by FT-IR spectroscopy and elemental analyses. The polyimides show typical imide bands at 1780, 1710 and 1386cm^{-1}. The bands at 1650cm^{-1} of the poly(amic acid) spectrum, which is due to the carbonyl groups in amide linkages, completely disappeared in the polyimide spectrum, indicating a complete imidization (Figure 1).

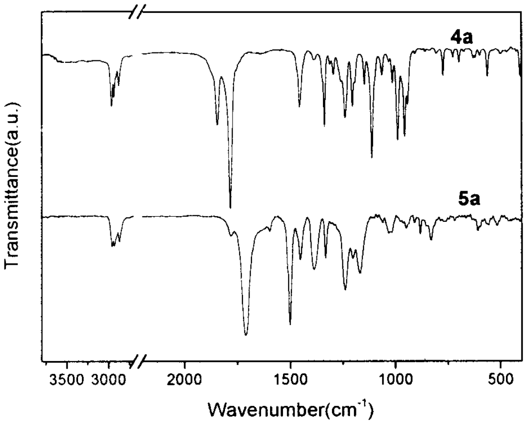


Figure 1. FT-IR Spectra of monomer(**4a**) and polymer(**5a**)

Properties of Polymers

The inherent viscosities of the polymers were 0.30~0.84 dL/g range, as measured in 0.2g/dL NMP solution at 25 °C, showing that they were medium to high molecular weight polymers. The solubility behavior of the polymers was determined for the as-polymerized powder samples in excess solvents. As listed in Table 1, polyimides prepared showed good solubility in polar solvent such as NMP, *m*-cresol, DMAc, HMPA, H_2SO_4. Especially they show better solubility than the polyimides from pyromellitic dianhydrides having side chains [13]. It means that the alicyclic unit in polymer main chain plays an important role in increasing solubility.

Table 1. Inherent viscosities and solubilities of polymers

Polymer code	η_{inh} a) (dL/g)	Solubility b)				
		NMP	*m*-Cresol	DMAc	HMPA	H_2SO_4
5a	0.84	+++	++	++	++	+++
5b	0.30	+++	++	++	++	+++
5c	0.45	+++	++	++	++	+++

a) Determined at 25℃ in NMP(0.2g/dL). b) - : insoluble, ++ : soluble on heating, +++ : soluble at r.t.

Phase transitions of the polymers were evaluated by differential scanning calorimeter (DSC), as shown in Table 2. T_gs were obtained from second heating scans of as-polymerized **5a~c** samples at 20 °C min. heating rate and they are represented in Table 2. The glass transition temperatures(T_gs) of **5a**, **5b** and **5c** were observed at 259, 163 and 124 °C, respectively. The observation that T_g decrease with increasing side chain length demonstrates that the flexible side chains exert an attractive interaction with the rigid main chain at high temperature, as already observed in many polyimides with flexible side chain system [4,5,13]. In addition, by the variation of side chain lengths, the adjustment of T_gs in the range of 124~259 °C will be possible.

Table 2. Thermal properties of polymers.

Polymer code	T_g(℃)	Thermal stability in N_2			
		$T_{d1}{}^a$(℃)	$T_{d2}{}^b$(℃)	$T_{10}{}^c$(℃)	$R_{900}{}^d$(%)
5a	259	452	643	443	50.1
5b	163	466	664	447	45.8
5c	124	463	656	434	42.3

a) 1^{st} max. degradation temperatures evaluated by its derivative curve
b) 2^{nd} max. degradation temperatures evaluated by its derivatives curve
c) Temperatures at 10% weight loss d) Residue at 900℃

Thermal resistance of the polymers were measured by TGA and evaluated by temperatures of 10% weight loss(T_{10}) and residual weights at 900 °C(R_{900}), as summarized in Table 2. Thermal analysis revealed that the polyimides were stable up to 440 °C under nitrogen at 20 °C/min. scan rate. It shows similar thermal stability as compared with other polyimides having alicyclic unit in the main chain[10]. All polyimides show two-step pyrolysis behavior with increasing temperature. The first degradation temperatures were in 452~463 °C range, and the second in 643~664 °C. These results apparently show that the first drastic degradation mainly originates from the degradation of the side chains, and the second degradation is thought to arise from that of polymer backbone.

From wide-angle X-ray diffractograms of the polyimide prepared, crystalline structure was studied. The diffractograms were obtained from as-polymerized samples and reproduced in Figure 2.

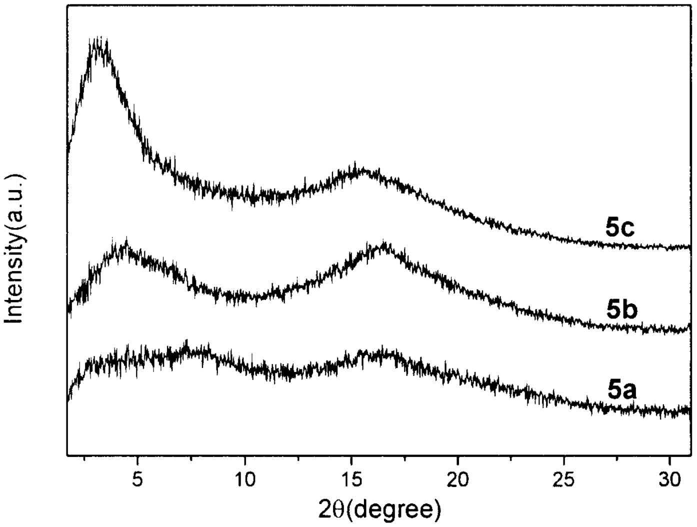


Figure 2. X-ray Diffractograms of polymers

At wider angle they showed only broad reflections originated from their very low crystallinities. The peaks in smaller angle regions are the characteristic of typical layered crystalline structure which usually develops more tightly with increasing side chain length. The layer spacing calculated from the peak points was 19.2Å(2θ=4.60) and 24.6A(2θ=3.58) for **5b** and **5c**, respectively. Under consideration that the carbon numbers of side chain are 8(**5b**) and 12(**5c**), the polyimides synthesized have a loose-layered structure with reasonable layer spacing. Detailed studies on structure are in progress and these results will be published later.

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