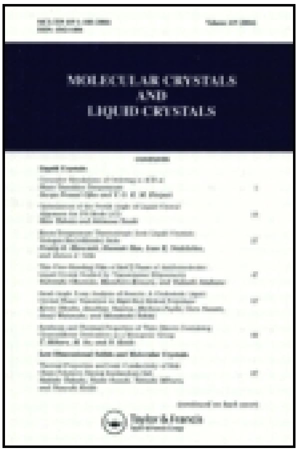

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Novel Thermotropic Liquid Crystalline Polymers: Rigid and Semi-Rigid Polymers with Flexible Side Chains

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NOVEL THERMOTROPIC LIQUID CRYSTALLINE POLYMERS: RIGID AND SEMI-RIGID POLYMERS WITH FLEXIBLE SIDE CHAINS

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Abstract Two series of rigid and semi-rigid polyesters and polyamids with flexible side chains were prepared by solution and melt as well as interfacial polycondensation of 2,5-dialkoxyterephthaloyl chloride with various diols and diamines. Thermal behaviors of the polymers were studied by DSC, TGA and polarizing microscopy. The results indicated that only rigid polymer systems form nematic mesophase. However, none of the semi-rigid polymers formed nematic melts. The structures of both polyesters and polyamides were also examined by the wide angle X-ray scattering. Analysis of sharp reflection, appeared at the lower angle of X-ray diffractograms of rigid polymers, suggested that rigid polymers crystallized to form a layered structure in the solid state.

INTRODUCTION

It is well known that flexible polymers show semi-crystallinity having the two-phase of crystalline and amorphous regions. If an external force is applied to this these systems, the polymer chains can easily be broken due to the extension of amorphous regions. Even in highly oriented flexible polymers, a large number of molecular defects still exist in polymer lattice. Therefore, they do not show high mechanical properties. However, rigid polymers show an entirely different molecular structure and phase behavior; they are no formations of chain foldings or entanglements. At high concentration, this type of polymer can have the increased parallel alignment of rods resulting from steric effect of rigid chains. The outstanding mechnical properties of rigid polymers are mainly derived from the high alignment of the rod-like molecules.

Some rigid polymers have been already commercialized or are in the developing stage. However, one of the glaring drawbacks with rigid polymers is the lack of processibility because of their intractability resulting from the polymer backbone stiffness. Several methods have been employed in solving this problem such as (i) the use of flexible linkages or spacers in rigid polymer main chains,[1-3] (ii) the use of non-linear aromatic molecular moieties[1,4] and (iii) coupling of flexible side chains onto rigid polymer backbone.[5] Since the middle of 1980's, the third type of polymers have been intensively studied by several research groups.[6-12] These polymers show sufficient solubility in common organic solvents because the side chains act as a solvent bound to the main chain. Moreover, many of them are liquid crystalline materials which have the transition temperatures of ordered structure before thermal decomposition.

The first rigid polymers with flexible side chains, so called, comb-like polymers were reported by Lenz et al. in 1983.[6,7] They prepared the fully aromatic polyesters by the polycondensation of terephthaloyl chloride and 2-n-alkylhydroquinone. The resulting polymers exhibited liquid crystalline properties and the temperature range of mesophase could be easily controlled by attaching the side chains with various lengths. Since then, numerous comb-like polymers have been reported by us and others.[6-12] Our continual research interests in this area has led us in synthesizing of modified polyesters and polyamides. In this paper we report synthetic method, characterization, and structure-property relationship between rigid and semi-rigid polymer systems with flexible side groups.

EXPERIMENTAL

Reagents

Hydroquinone(KoKusan) was purified by sublimation in vacuum. Thionyl chloride (Tokyo Kasei) and 1,1,2,2-tetrachloroethane(Fluka) was distilled prior to use. 1-Fluro-4-nitrobenzene, 4,4-biphenol(Tokyo Kasei), 1,5-naphthalene diol(Sigma), 4,4'-dihydroxybenzophenone(Tokyo Kasei), 4,4'-dihydroxydiphenylsulfone(Tokyo Kasei) were used without further purification. Several kinds of commercialized glycols(Aldrich) were also used without purification for the synthesis of the diamine monomers.

Monomer Synthesis

2, 5-Dialkoxyterephthaloyl chloride was obtained by saponification and chlorination after Claisen condensation of diethyl 2,5-dihydroxyterephthalate with alkyl bromide, as reported in the literature.[8] 1,2-Bis(4-aminophenoxy)alkanes can be prepared by reaction of 1-fluoro-4-nitrobenzene with various glycols and subsequent reduction using Pd/C and hydrazine hydrate as reducing agents. The yields of both steps were between 60 and 80%. The raw diamino compounds were recrystallized in ethanol. All compounds were characterized by IR, NMR and elemental analysis.

Synthesis of Polyesters

Solution Polycondensation(Method A); 10ml of pyridine was slowly added to 1.3g(0.11mol) of cold thionyl chloride with stirring. 2.1g(0.005mol) of 2,5-dialkoxyterephthalic acid in 10ml pyridine was then added dropwise subsequently. After 20min, diols(0.005mol) in 10ml pyridine was added and stirred at 80℃ for 4hrs. The viscous reaction mixture was poured into excess methanol. The product was filtered, washed with warm ethanol, and dried in a vacuum oven.

Solution Polycondensation(Method B); 2g(3.5×10^{-3}mol) of 2,5-dialkoxyterephthaloyl chloride and the equivalent amount of diols were added to 11ml of 1,1,2,2-tetrachoroethane. After the solution was stirred for 5min, 1.1g of pyridine was added slowly. The reaction was carried out at 100℃ for 4hrs with heavy stirring. The solution was then diluted by about twice the volume of the solvent and poured into excess methanol. The precipitated product was filtered off, washed with warm ethanol and dried in a reduced atmosphere.

Melt Polymerization(Method C); Equivalent amounts of 2,5-dialkoxyterephthaloyl chloride and diols were gradually heated to 270℃ with stirring under N_2 atmosphere. HCl produced in the reaction was removed by the continuous stream of dried N_2 gas. The polymer melt was cooled to room temperature, ground in a mill, washed with methanol and dried in a vacuum oven.

Synthesis of Polyamides

A typical method for the polymerization of diamino compounds with 2,5-dialkoxyterephthaloyl chloride is as follows; 0.01mol of the diamino compounds was mixed with 0.01mol of sodium carbonate(dissolved in 75ml distilled water) and cooled down to 0℃. To this solution was added 0.01mol(5.7g) of 2,5-dialkoxy terephthaloyl chloride in 120ml methylene chloride and the solution was stirred vigorously for 30min. Unreacted starting materials were removed by precipitating the solution into methanol. The filtered precipitates were successively washed with water and acetone several times and dried in a vacuum oven.

Measurements

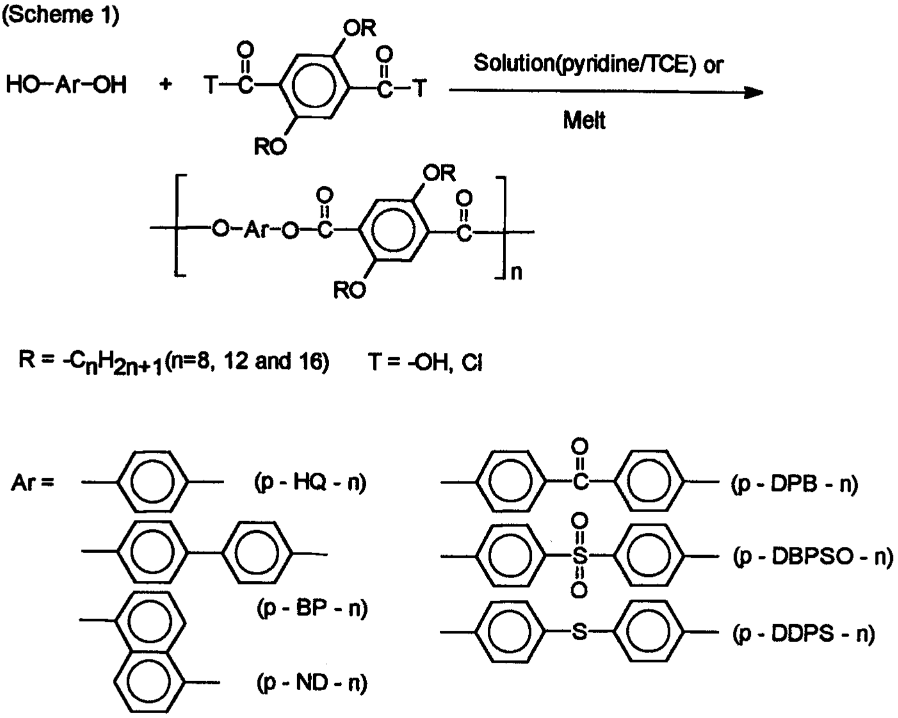
A differential scanning calorimeter and thermogravimetric analyzer(Model 9900, Du Pont) were performed for the study of thermal behavior and thermal stability of polymers. Wide-angle X-ray diffractograms were measured using a nickel-filtered Cu-K_α(λ=1.54Å) radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. Inherent viscosities of polyamides were determined in sulfuric acid or 1,1,2,2-tetrachloroethane at 30℃ using a Ubbelohde viscometer and of polyesters in p-chlorophenol at 45℃ for polyesters by means of a Cannon-Fenske viscometer, respectively. The characteristic textures of liquid crystalline phase were observed with Nikon AFX-II polarized microscope equipped with polarizers and a heating stage.

RESULTS AND DISCUSSION

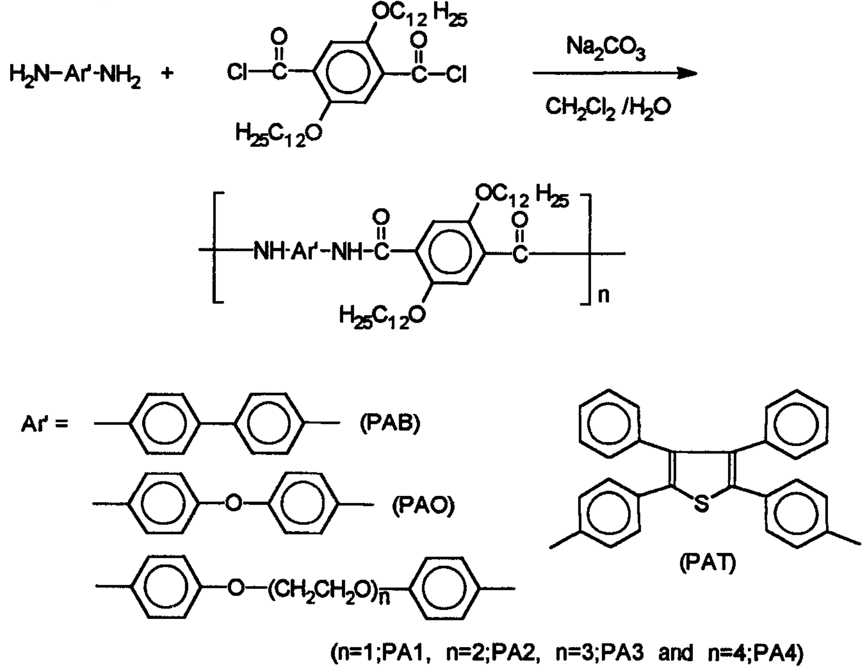
Synthesis

The preparation of aromaic polyesters with alkoxy side chains was developed based on the works of Ballauff.[8] In this method, the polymers can be obtained from the solution and melt polycondensation of 2,5-dialkoxyterephthaoyl chloride with diols in presence of pyridine as catalyst (Scheme 1). Also, a series of polyamides having flexible side chains was synthesized by the low temperature interfacial polymerization of 2,5-dialkoxyterephthaloyl chloride and diamines (Scheme 2). Here the diamines containing ethylene oxide units were prepared according to Ghatge and Jadhav[13] and 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene as described by Dilthey and Graef,[14] respectively. The structures of the resulting polymers were confirmed by their IR and ^{1}H-NMR spectra. The C/H/N ratios checked by the elemental analysis well matched the calculated values within the limits of experimental error. The yields of polymers were 71-96% and viscosities ranged from 0.15-2.51 dl/g(see Table 1 and 2). All of the polyesters were soluble in p-chlorophenol and soluble in chloroform, tetrahydrofuran, N, N-dimethylformamide, etc. This indicates that the solubility of rigid polymers can be improved by attaching flexible side branches onto the polymer backbone. Viscosities of the polyesters obtained by the melt polymerization showed higher values than the corresponding solution-polymerized products. In the case of polyamides, their viscosities were dependent on the main chain stiffness, i. e.,

(Scheme 1)



(Scheme 2)



viscosities reduced with the increasing number of ethylene oxide units. PAT showed a highest viscosity value due to the bulky rigid units.

Thermal Poperties and Structure of Polymers

Thermal properties of the polymers were studied by differential scanning calorimetry(DSC) and thermal gravimetric analyzer(TGA). Figure 1 shows DSC thermograms for the various polyesters having dodecyloxy side chains. It is known that wholly aromatic polyesters do not melt but decompose at around 600 ℃.[15] However, substituted polymers derived from hydroquinone(P-HQ-12) biphenol (P-BP-12) and naphthalene diol(P-ND-12) exhibit their melting points of 221, 220, 175℃, respectively. The first three polymers among this series show an unusual

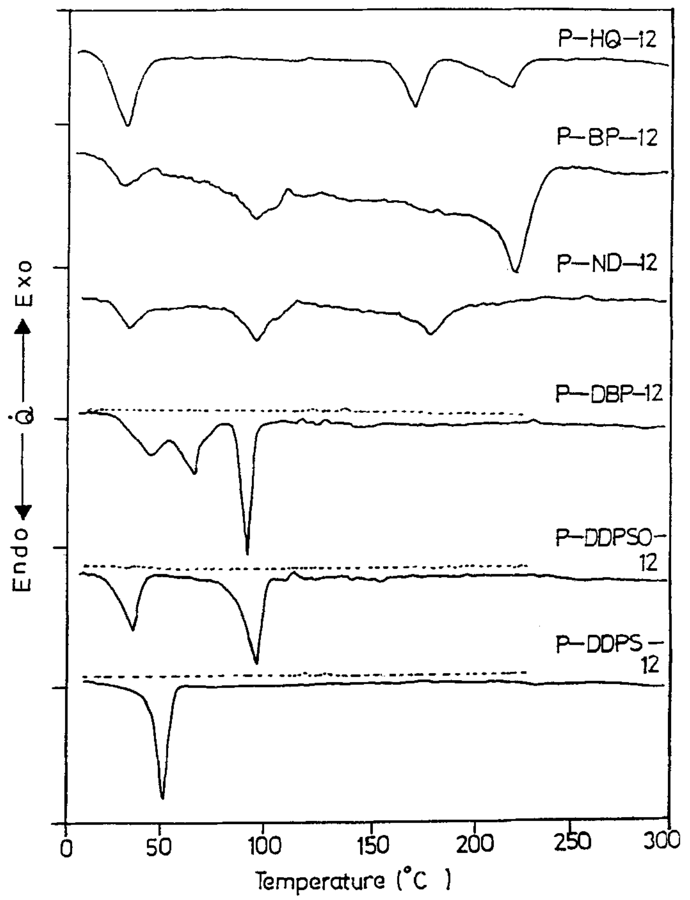


Figure 1. DSC curves of aromatic polyesters with dodecyloxy side chains (Heating rate 10℃/min in N_2 gas).

thermal behavior. Besides the isotropic melting point at high temperature, there are two additional endothermic peaks in low temperature region. Therefore, these comb-like polymers have four different phases. Such phases could be interpreted as enthalpy changes due to the side-chain crystallization and relaxation of the polymer backbone as reported elsewhere.[16] First transition peak at the lowest temperature may be described as the melting of the side chains. Second transition peak may also be explained from the fact that the layered structure of polymers become relaxed, but the rigid polymer backbone ordering may be preserved. Mesophase is observed above this transition temperature before isotropic melting. For example, Figure 2 shows polarized microphotograps of the P-BP-12 taken at 200℃. A threaded texture known as the nematic phase were observed in these polymers. Further developed texture can clearly seen by annealing at 200℃ for 45min. Similar texture was also observed both P-HQ-12 and P-ND-12 samples.

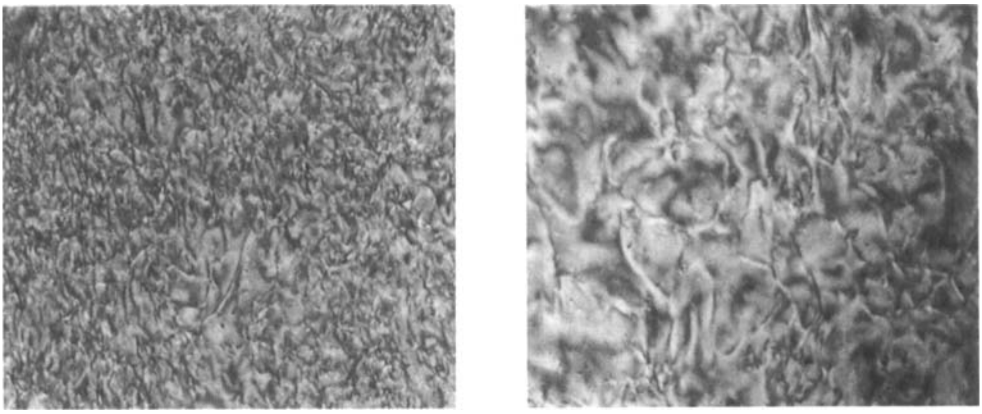


Figure 2. Microphotographs of the P-BP-12 taken at 200℃(left) and annealed at 200℃ for 45min(right) (Magnification 100X). See Color Plate I.

In the case of semi-rigid polymers containing ketone, sulfone and thio groups, enthalpy changes due to the side chain crystallization and solid-solid phase transition were only observed. Isotropic melting transition could not be detected in these polymers. Especially, DSC traces taken from the second heating process without annealing did not exhibit any peaks. Also, the transparency of the melt-crystallized samples indicates that the structure of these polymers becomes amorphous during melting process. Even after annealing for 1hr, crystallinity resulting from the side chain rearrangement was not recovered. As shown in the

Table 1. Yields, viscosities and thermal data of aromatic polyesters with flexible side chaine

Polymers	Polym. Method(a)	Yield (%)	η_{inh}(b) (dl/g)	T_s(c) (°C)	T_m(d) (°C)	T_i(e) (°C)	T_{id}(f) (°C)	5%weight loss (°C)
P-HQ-8	A	79	0.26	80	150(N)	?	300	375
P-BP-8	A	77	0.28	117	180(N)	250	302	380
P-ND-8	A	71	0.15	115	185(N)	232	290	380
P-HQ-12	C	85	0.49	39	172(N)	221	309	390
P-BP-12	B	96	1.09	43	103(N)	220	300	392
P-BP-12	C	87	2.51	47	106(N)	226	305	385
P-ND-12	B	87	0.53	45	110(N)	175	293	390
P-DBP-12	B	81	0.33	49/64/92 (-)(g)	-	-	300	390
P-DDPSO-12	B	80	0.32	46/96 (-)	-	-	326	390
P-DDPS-12	B	82	0.40	51 (-)	-	-	302	392
P-BP-16	B	89	0.30	69/97	132(N)	155	285	380
P-ND-16	B	88	0.39	50/70	91(N)	149	295	378

(a) A : Terephthalic acid-diol polycondensation in solution (Used thionyl chloride in pyridine as catalyst)

B : Terephthaloyl chloride-diol polycondensation in solution

C : Terephthaloyl chloride-diol polycondensation in the melt

(b) Measured at a concentration of 0.5g/dl in p-chlorophenol at 45°C

(c) T_s : Side chain caystallization temperature

(d) T_m : Mesophase transition temperature (N : Nematic phase)

(e) T_i : Isotropic melting temperature

(f) T_{id} : Initial decomposition temperature

(g) No enthalpy changes were observed by second heating process in DSC

Table 1, isotropic melting point(T_i) decreases with increasing length of the side chains. Molecular weights which can be estimated by the viscosities also show strong effects on T_i; the increase of T_i with increasing molecular weight. TGA results showed that the initial decomposition of this polymer series occurred at around 285~326℃ under the N_2 atmosphere. The lower decomposition temperature found in comparison to unsubstituted polymers is apparently due to the presence of side chains. Five percent weight loss was observed at 375~392℃.

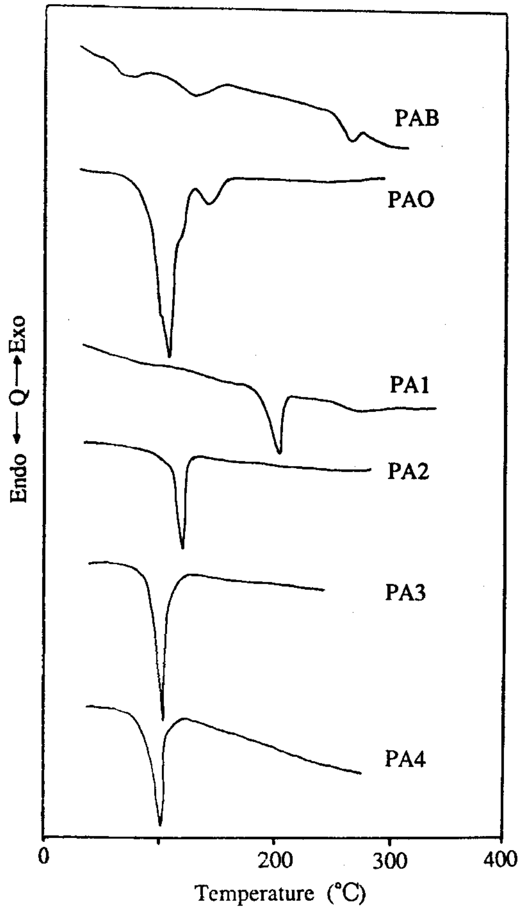


Figure 3. DSC thermograms for dodecyloxy side chains (Heating rate 10℃/min in N_2 gas).

Wholly aromatic polyamides with flexible side chains and polyamides with alkoxy side chains containing ether or ethylene oxide unit in main chain were also prepared in an attempt to study the possibility of formation of liquid crystalline phase. In Figure 3, DSC curves of all polyamides prepared in this work are compared. PAB having no hinge in the main chain revealed similar thermal behavior as the polyester system discussed previously. PAB also has four different phases like polyesters. Liquid crystalline phase was observed above 129 ℃. However, ethylene oxide linked polymers do not show any liquid crystalline characteristics. This may be caused by the interruption of side chains onto the rigid segments. Polyamide containing ether linkage, PAO, shows only the endothermic peaks due to the side chain crystallization at around 100~140℃.

Table 2. Yields, viscosities and thermal data of various polyamides with flexible side chains

Polymers	Yield (%)	η_{inh} (dl/g)	T_s[(d)] (°C)	T_t[(e)] (°C)	T_i[(f)] (°C)	T_{id}[(g)] (°C)	10%weight loss (°C)
PAB	89	0.36[(a)]	71/81	129(N)	265	330	380
PAO	85	0.35[(a)]	103/119	-	-	327	390
PA1	85	0.29[(a)]	-	-	205	293	390
PA2	84	0.20[(b)]	-	-	122	279	370
PA3	80	0.18[(b)]	-	-	105	279	360
PA4	80	0.16[(b)]	-	-	101	275	370
PAT	94	0.62[(c)]	150	-	370	371	390

(a) Measured at a concentration of 0.5g/dl in sulfuric acid
(b) Measured at a concentration of 0.25g/dl in 1,1,2,2-tetrachloroethane
(c) Measured at a concentration of 0.5g/dl in chloroform/trifluroacetic acid (20 : 1 vol.%) at 25°C
(d) Melting temperature of side chains
(e) Mesophase transition temperature (N: Nematic phase)
(f) Isotropic melting temperature
(g) Initial decomposition temperature

Thermal stability data of the family of polyamides are listed in Table 2. The structural modification of wholly aromatic polyamide via the introduction of side branches onto the para-phenylene ring in the backbone results in a lowering of thermal stability compared to the original Kevlar-type polymer. The onset of weight loss in PAB, which is dodecyloxy-substituted polyamides, is exhibited at 330°C. This T_{id} value is much lower than that of the poly(1,4-phenyleneterephthalamide). In addition, a significant decrease in thermal stability of PA1, PA2, PA3 and PA4 is seen with an increase of the ethylene oxide units within the polymer backbone, as expected.

Figure 4 represent X-ray powder patterns of the melt-polymerized polyesters and polyamides at room temperature. They show well-defined Bragg reflections due to high crystallinity. The sharp reflections appearing at low angles demonstrate that these polymers crystallize to a layered structure. This is similar to what was observed in other comb-like polymers by Ballauff,[17,18] Watanabe[9] and us.[10,11] An almost linear relation between the side chain lengths and layer spacing is observed. The peaks in P-HQ-12 found at 20.3, 10.3 and 6.9 Å indicate the

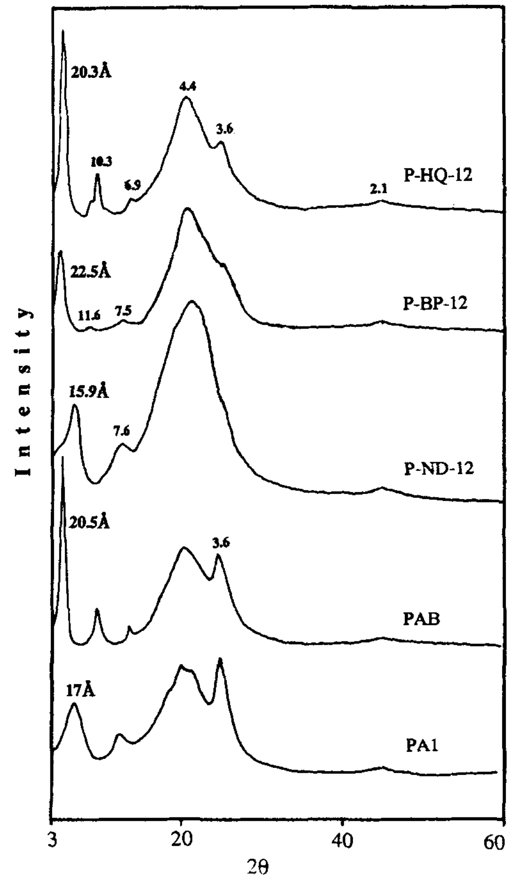


Figure 4. X-ray diffractograms of polyesters and polyamides with dodecyoxy side chains

layer reflections of first, second and third order, respectively. By annealing for several hours, these reflections resulted in a sharpening which is indicative of an increase in crystallinity. Similar results are observed in P-BP-12 and P-ND-12. The peaks at 3.6 Å in broad reflections can be assigned to the distance between the main chains.[19] Stronger reflections at about the same d-spacings observed in polyamides (PAB and PA1) suggest that the main chains are well ordered due to the hydrogen bonding.

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