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Synthesis and properties of polyimides having alkyloxycarbonyl side chain

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Summary

A series of polyimides having alkyloxycarbonyl side chains were synthesized from dialkyl 2,5-bis(4-aminophenoxy)terephthalate and PMDA. The inherent viscosities of poly(amic acid)s were in the 1.42~0.63dL/g range. The polyimides exhibit typical 2-step thermal degradation, and lowered transition temperature for longer side chain. Wide-angle X-ray diffractograms revealed that all polymers are partially crystalline, and layered structures were observed for polymers with longer side chain. The pretilt angle is in the 8°~10° range, and increases as the length of the side chains increase.

Introduction

The introduction of flexible side chain into the rigid polymer backbone has attracted a lot of interest because of lowered transition temperature and the observation of mesophase or layered structure etc[1-7]. The long alkyl side chains lower transition temperature of polymers by reducing the interaction between main chains and by increasing the entropy of polymers[8]. The incompatibility resulting from the unfavorable interaction between the polar main chains and the nonpolar alkyl side chains can lead to layered structure.

In recent, many publications have reported polyimides with long alkyl side chain to achieve high pretilt angle[9-13]. The pretilt angle plays an important role in the design of LC devices, and a pretilt angle greater than 5° is required for a supertwisted nematic(STN) LCD to prevent the generation of disclination loops[14].

In this article, novel polyimides having alkyloxycarbonyl side chains were prepared from dialkyl 2,5-bis(4-aminophenoxy)terephthalate, and the influence of side chains on the structure and properties of polymers was studied. The LC alignment and pretilt angle of polymers induced by mechanical rubbing were also investigated.

Experimental

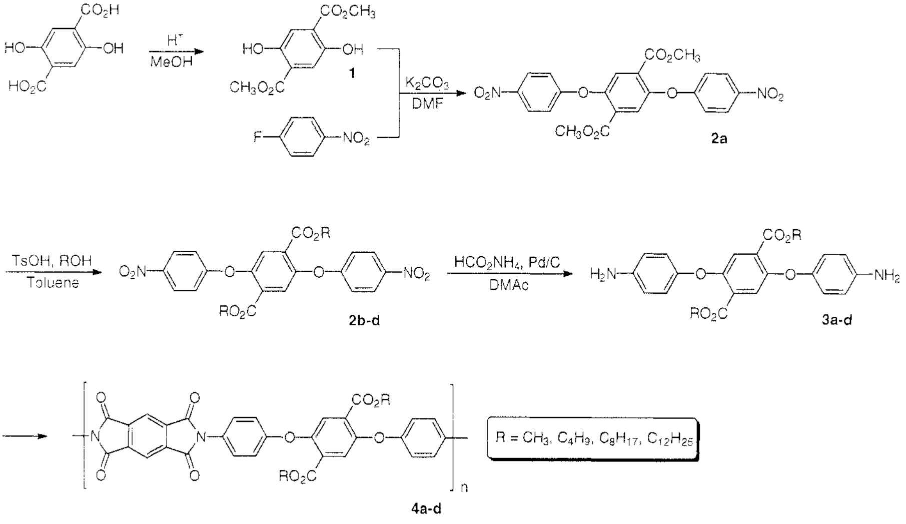
Materials and Instruments

PMDA(pyromellitic dianhydride), 2,5-dihydroxyterephthalic acid, 1-fluoro-4-

nitrobenzene, sulfuric acid, potassium carbonate, *p*-toluenesulfonic acid monohydrate, 1-butanol, 1-octanol, 1-dodecanol, ammonium formate and 10 wt% palladium on carbon were purchased from Aldrich Chemical Co. The reaction solvents such as methanol(Mallinckrodt), DMF(Aldrich), toluene(Aldrich) were used as received. DMAc(Fischer) was distilled at a reduced pressure after stirring with calcium sulfate for 3 days.

Melting temperatures were determined using Haake-Buchler melting point apparatus. FT-IR spectra were recorded on a Mattson Infinity gold spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained from a 300-MHz Bruker AM 300 spectroscope at room temperature.

Inherent viscosities were determined using an Ubbelohde type viscometer at 25℃ for poly(amic acid)s in DMAc. Thermal analyses of polyimides were carried out with a Perkin-Elmer PE PC series TGA 7 thermogravimetric analyzer and a PE PC series DSC 7 thermal analyzer at a scanning rate of 20℃/min under a nitrogen atmosphere. Wide-angle X-ray diffractograms were obtained in transmission mode using Ni-filtered Cu Kα radiation on a Rigaku Geiger Flex D-max X-ray diffractometer.



Scheme 1. Synthesis of monomers and corresponding polyimides.

Monomer Synthesis

*Dimethyl 2,5-dihydroxyterephthalate(**1**)*

To a 250mL 2-neck round-bottomed flask equipped with a condenser were added 2.08g(10.5mmol) of 2,5-dihydroxyterephthalic acid, 100mL of methanol, and 2mL of conc. sulfuric acid. The reaction mixture was refluxed for 24hr, and cooled down to RT. Recrystallized product was collected by filtration and dried *in vacuo.*

yield : 98%, mp : 176.6~177.7℃; IR (KBr, cm^{-1}) ν = 3300~3100, 2926, 1685, 1444, 1197, 1177 and 792; ^{1}H-NMR (in DMSO-d_6, ppm) δ = 9.82(s, 2H), 7.27(s, 2H) and 3.88(s, 6H)

*Dimethyl 2,5-bis(4-nitrophenoxy)terephthalate (**2a**)*

To a 100mL 3-neck round-bottomed flask equipped with a nitrogen inlet tube and a condenser were added 2.26g(10mmol) of **1**, 2.96g(21mmol) of 1-fluoro-4-nitrobenzene, 2.76g(20mmol) of potassium carbonate, and 30mL of DMF. The reaction flask was heated at 65℃ for 24hrs. The reaction mixture was poured into 500mL of methanol-water mixture(1:1 by volume). The yellow crude product was filtered and recrystallized from DMAc-methanol mixture.

yield : 57%, mp : 205.5~206.3℃; IR (KBr, cm^{-1}) ν = 3110~3020, 2966, 1725, 1610, 1590, 1508, 1484, 1342, 1259, 1238, 891, 850 and 579; ^{1}H-NMR (in DMSO-d_6, ppm) δ = 8.27(d, 4H), 7.82(s, 2H), 7.22(d, 4H) and 3.70(s, 6H)

Transesterification

General procedure

To a 250mL 2-neck round-bottomed flask equipped with a condenser were added 2.34g(5mmol) of **2a**, 25mmol of *n*-alkyl alcohol(in the case of butyl alcohol, 10mL used), 1.00g of toluenesulfonic acid monohydrate, and 90mL of toluene. The reaction mixture was refluxed for 3 days, then was washed with an aqueous sodium bicarbonate solution, and then washed with distilled water. After the evaporation of toluene, the crude product was recrystallized from alcoholic solvent.

*Dibutyl 2,5-bis(4-nitrophenoxy)terephthalate (**2b**)*

recrystallized from isopropyl alcohol.

yield : 88%, mp : 167.2~168.2℃; IR (KBr, cm^{-1}) ν = 3120~3070, 2960, 2934, 2873, 1729, 1611, 1589, 1512, 1485, 1466, 1339, 1227, 1178, 1107, 895 and 855; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 8.26(d, 4H), 7.76(s, 2H), 7.01(d, 2H), 4.18(t, 4H), 1.50(quint, 4H), 1.24(sextet, 4H) and 0.83(t, 6H)

*Dioctyl 2,5-bis(4-nitrophenoxy)terephthalate (**2c**)*

recrystallized from ethanol.

yield : 89%, mp : 110.7~111.5℃; IR (KBr, cm^{-1}) ν = 3120~3070, 2953, 2922, 2853, 1716, 1610, 1590, 1512, 1487, 1466, 1341, 1239, 1168, 1108, 892, 848 and 579; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 8.27(d, 4H), 7.77(s, 2H), 7.01(d, 4H), 4.17(t, 4H), 1.51(quint, 4H), 1.35~1.15(m, 20H) and 0.88(t, 6H)

*Didodecyl 2,5-bis(4-nitrophenoxy)terephthalate (**2d**)*

recrystallized from ethanol

yield : 95%, mp : 91.5~92.4℃; IR (KBr, cm^{-1}) ν = 3120~3070, 2948, 2917, 2850, 1715, 1611, 1590, 1512, 1488, 1466, 1342, 1241, 1169, 1114, 895, 846 and 579; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 8.26(d, 4H), 7.77(s, 2H), 7.01(d, 4H), 4.17(t, 4H), 1.51(quint, 4H), 1.35~1.15(m, 36H) and 0.88(t, 6H)

Reduction of nitro group

General procedure

To a 100mL 3-neck round-bottomed flask equipped with a nitrogen inlet tube and a condenser were added 1.5mmol of **2a-d**, 0.95g(15.1mmol) of ammonium formate, 0.10g of 10wt% palladium on carbon, and 20mL of DMAc. The reaction mixture was stirred in a stream of nitrogen for 36hrs. After filtration, the filtrate was poured into 150mL of distilled water. The precipitate was filtered and then recrystallized.

*Dimethyl 2,5-bis(4-aminophenoxy)terephthalate (**3a**)*
recrystallized from isopropyl alcohol.
yield : 84%, mp : 220.2~220.8℃; IR (KBr, cm^{-1}) ν = 3462, 3371, 2960~2940, 1699, 1630, 1509, 1494, 1310, 1235, 1205 and 827; ^{1}H-NMR (in DMSO-d_6, ppm) δ = 7.11(s, 2H), 6.75(d, 4H), 6.58(d, 4H), 5.03(s, 4H) and 3.73(s, 6H)

*Dibutyl 2,5-bis(4-aminophenoxy)terephthalate (**3b**)*
recrystallized from isopropyl alcohol.
yield : 85%, mp : 131.5~132.1℃; IR (KBr, cm^{-1}) ν = 3460, 3368, 2960~2850, 1698, 1628, 1510, 1486, 1417, 1289, 1241, 1211 and 832; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 7.34(s, 2H), 6.81(d, 4H), 6.66(d, 4H), 4.20(t, 4H), 3.57(s, 4H), 1.59(quint, 4H), 1.32(sextet, 4H) and 0.86(t, 6H)

*Dioctyl 2,5-bis(4-aminophenoxy)terephthalate (**3c**)*
The filtered reaction mixture was poured into distilled water, and then extracted with diethyl ether. After evaporation of diethyl ether, the crude product was recrystallized from *n*-heptane.
yield : 85%, mp : 104.6~106.6℃; IR (KBr, cm^{-1}) ν = 3460, 3368, 3230~3030, 2960~2850, 1698, 1628, 1511, 1487, 1415, 1287, 1241, 1210 and 833; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 7.33(s, 2H), 6.81(d, 4H), 6.65(d, 4H), 4.19(t, 4H), 3.56(s, 2H), 1.60(quint, 4H), 1.50~1.10(m, 20H) and 0.87(t, 6H)

*Didodecyl 2,5-bis(4-aminophenoxy)terephthalate (**3d**)*
The filtered reaction mixture was poured into distilled water, and then extracted with diethyl ether. After evaporation of diethyl ether, the crude product was recrystallized from ethanol.
yield : 87%, mp : 101.6~102.5℃; IR (KBr, cm^{-1}) ν = 3462, 3379, 2960~2830, 1685, 1618, 1510, 1480, 1412, 1311, 1242, 1201 and 834; ^{1}H-NMR (in $CDCl_3$, ppm) δ = 7.33(s, 2H), 6.81(d, 4H), 6.65(d, 4H), 4.19(t, 4H), 3.56(s, 2H), 1.59(quint, 4H), 1.50~1.10(m, 36H) and 0.88(t, 6H)

Polymerization

Poly(amic acid)
The polymerization is given below as a general procedure. To a 100mL 2-neck round-bottomed flask were added 1mmol of dimethyl 2,5-bis(4-aminophenoxy) terephthalate and 5mL of DMAc. Diamine/DMAc solution was stirred in a stream of argon for 1 hour, and 1mmol of PMDA was added into the flask. After an additional 12 hrs, viscous poly(amic acid)/DMAc solution was obtained.

Polyimide
Poly(amic acid) solution was cast onto a glass plate and heated at 80℃ for 1 hour. The poly(amic acid) films were imidized by sequential heating at 160℃ for 1 hour, 200℃ for 1 hour, and 250℃ for 30 min in the stream of nitrogen. The polyimide films were stripped off by dipping distilled water.
The flexible polyimide films were obtained for all cases. From the FT-IR spectrum of polyimide, the characteristic absorption bands of imide group were observed near

1780 & 1720(asym. and sym. stretch of C=O, imide I), and 1390cm^{-1}(C-N-C stretch, imide II). The intensity of alkyl C-H stretching band increases with longer side chain.

4a) Analysis calcd for $C_{32}H_{18}N_2O_{10}$: C, 65.09; H, 3.07; N, 4.74. Found: C, 65.33; H, 3.12; N, 4.59
4b) Analysis calcd for $C_{38}H_{30}N_2O_{10}$: C, 67.65; H, 4.48; N, 4.15. Found: C, 67.22; H, 4.69; N, 4.22
4c) Analysis calcd for $C_{46}H_{46}N_2O_{10}$: C, 70.21; H, 5.89; N, 3.56. Found: C, 70.39; H, 6.01; N, 3.44
4d) Analysis calcd for $C_{54}H_{62}N_2O_{10}$: C, 72.14; H, 6.95; N, 3.12. Found: C, 71.98; H, 7.03; N, 3.05

LC cell preparation and pretilt angle measurement

The poly(amic acid) solutions(3wt% in DMAc) were spin-coated on glass substrate at 3500rpm for 40s. The poly(amic acid) films were heated at 80℃ for 1hr, and then baked at 160℃ for 1hr, 200℃ for 1hr and 250℃ for 30min. The polyimide films were mechanically rubbed with a laboratory rubbing machine(Wanda Co.) using a rayon velvet cloth(Yoshikawa Co., YA-20-R), and assembled in the antiparallel rubbing direction. Rubbing density[15] was controlled in the 60 to 240 range. A nematic LC, 5CB(4-*n*-pentyl-4'-cyanobiphenyl) containing 1.0wt% Disperse Blue 1 as a dichroic dye was injected into the cell. The pretilt angle was measured by the crystal rotation method with a laboratory apparatus[16].

Results and Discussion

Properties of polyimides

The thermal properties of polymers were investigated by TGA and DSC at a heating scan of 20℃/min under a nitrogen atmosphere, and summarized in Table 1. The thermal stability of polymers was evaluated by T_0 and T_{10}. Polymers exhibited typical 2-step thermal degradation as shown in Figure 1. The first degradation which begins around 400℃ results from side chain cleavage, and weight loss percentage during the first degradation was almost coincident with the weight fraction of the side chain in polyimide repeat unit. The second degradation corresponds to the thermal degradation of the polyimide backbone.

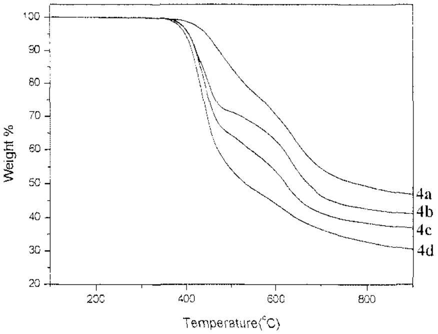


Figure 1. TGA pyrogram of polyimides **4a-d**

Table 1. Inherent viscosities of poly(amic acid)s and thermal properties of polyimides.

polymer	η_{inh} a)(dL/g)	T_g b)(℃)	Thermal stability				
			T_o c)(℃)	T_{10} d)(℃)	T_{d1} e)(℃)	T_{d2} f)(℃)	RW_{900} g)(%)
4a	1.42	-	415	473	482	631	46.9
4b	1.33	195	397	423	436	635	41.0
4c	1.12	149	404	421	438	620	36.9
4d	0.63	132	400	412	434	610	30.5

a) measured at 25℃ in DMAc with the concentration of 0.2g/dL
b) obtained from the second heating scan of DSC at the scan rate of 20℃/min under N_2 atm.
c) onset temperature of degradation
d) 10% weight loss temperatures
e) the first maximum degradation temperature
f) the second maximum degradation temperature
g) residual weight % at 900℃

The glass transition temperatures of polymers are observed in the range of 195~132℃, and decrease monotonically with the increasing the length of side chains. In the case of **4a** with the shortest side chain, no discernible phase transition behavior was observed up to 320℃. Polyimide with dodecyloxycarbonyl side chain, **4d** exhibited a broad endotherm around 220℃ in the DSC thermogram as shown in Figure 2, and this endotherm was sharpened more after annealing. This endotherm can be regarded as the formation of mesophase[2], and will be discussed later with wide-angle X-ray diffraction.

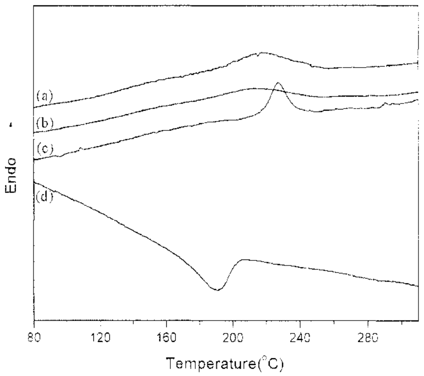


Figure 2. DSC thermogram of **4d** (a) the first heating scan (b) the second heating scan (c) the third heating scan after annealing at 200℃ for 2hrs (d) the first cooling scan.

Wide angle X-ray diffractograms(Figure 3) were obtained in the transmission mode with 2θ ranging from 2° to 30°. All polymers exhibit partially crystalline X-ray patterns, and the reflectance of layered structure is observed for polymers **4c-d** with longer side chains. The d-spacing of layered structure calculated from Bragg's law is 17.1Å and 27.3Å for polymers **4c-d**, respectively. The polyimides **4a-b** with shorter side chain have a weak reflectance around 4.2°, and d-spacing of this reflectance is close to 21.9Å, the length of the repeating unit for the analogue polyimide without alkyloxycarbonyl side chain[17].

In the case of **4d**, rather broad-reflectances at somewhat lower angles are observed at room temperature as shown in Figure 3(b). These reflectances disappear at elevated temperatures approximately 280℃ above the endothermic transition from DSC thermogram indicating the formation of mesophase. On cooling, weak reflectances reappear at temperatures below 200℃.

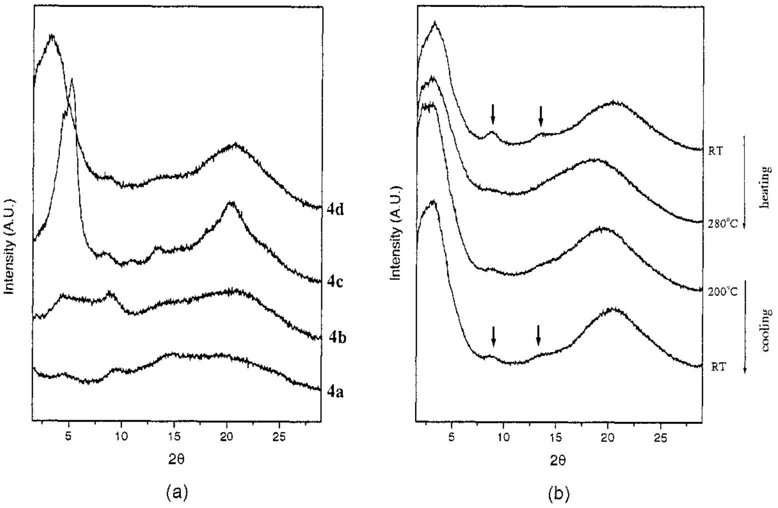


Figure 3. Wide-angle X-ray diffractograms for (a) **4a-d** at r.t. (b) **4d** at various temperatures.

LC alignment properties

The pretilt angles of the LC molecules on rubbed polyimide thin films were measured by the crystal rotation method, and are listed in Table 2. On the whole, the pretilt angle increases slightly with the increasing of side chain length. On the other hand, no remarkable dependence of pretilt angle on rubbing density was observed. All polymers show a pretilt angle greater than 7.9°.

Table 2. Pretilt angle of polyimides under various rubbing densities(RD)

Polymer	Pretilt angle(°)			
	RD = 60	RD = 120	RD = 180	RD = 240
4a	8.3	8.1	7.9	8.0
4b	8.0	8.9	8.2	8.5
4c	8.9	9.3	9.9	9.6
4d	10.2	9.3	9.8	10.5

A variety of factors have been proposed to understand mechanisms of the pretilt angle of the LC molecules on rubbed polyimides. In general, high pretilt angle by the introduction of long alkyl side chains are thought to be caused by van der Waals interation between the LC molecules and the alkyl side chains of the polyimides[11,16,18]. Some reports have also suggested that the pretilt angle is governed by the polyimide backbone structure in order to explain the pretilt angle on rubbed polyimides without side chain[19-21].

For the polymer **4a-d**, the polyimide backbone structure plays a major role in determining pretilt angle, and additional increment of the pretilt angle with longer side chains may be attributed to the van der Waals interaction.

Conclusion

A new series of polyimides having alkyloxycarbonyl side chains were prepared from dialkyl 2,5-bis(4-aminophenoxy)terephthalate. The chemical structures of polyimides were confirmed by FT-IR spectroscopy and elemental analysis. The polyimides were thermally stable up to 400℃, and exhibited 2-step pyrolysis and lowered transition temperatures due to long side chains. All polymers are partially crystalline, and layered structures were observed for longer side chains. High pretilt angles greater than 7.9° were achieved by mechanical rubbing, and it was found that pretilt angle values increase slightly as the length of side chains increase.

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