Polyimides Having Dendron Side Chains

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The synthesis and characterization of soluble polyimides having dendron side chains were reported. The terphenylene diamine monomers having the first and second generation monodendrons, 3,4,5-tris(n-dodecyloxy)benzoic acid derivatives were successfully synthesized and the corresponding polyimides were obtained by the polycondensation with tetracarboxylic dianhydrides such as 3.3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) or 4,4'-Hexafluoroisopropylidendi(phtalic anhydride) (6FDA). The attempts to attach the dendron via polymer reactions were performed, however, the reactions were not completed. These novel polyimides having dendron side chains (dendronized PI) were soluble in common organic solvents, such as NMP and *m*-cresol. Theses dendronized PI can be applied for the alignment films of LCDs, and it was found that these films showed the vertical alignments of LC molecules probably due to the bulky structures of dendron moieties. Key words: Polyimide, Dendron, Alignment film, Vertical alignment

1. INTRODUCTION

Although polyimide have been widely used for microelectronics such as the alignment films for Liquid Crystal Displays (LCDs), the one of disadvantages of these polymers is that these are insoluble in common solvents. Therefore, solvent soluble polyimides that are processed without difficulty are desired. The authors have investigated the synthesis and characterization of soluble polyimides based on alkyl groups.^{1,2,3,4} and these polyimides were found to contribute the generation of pretilt angles of liquid crystals in case that these were utilized as the alignment films for LCDs.⁵ In this paper, the novel polyimides having dendron side chains (dendronized PI) are reported. The dendron structures are based on 3,4,5-tris(n-dodecyloxy)benzoic acid derivatives (Fig. 1). The introduction of dendron moieties by polymer reaction and the synthesis and polymerization of novel aromatic diamines having first or second generation of dendron were investigated.



Fig. 1 Dendron building block and monomers

2. EXPERIMENTAL

2.1 Dendron building blocks and monomers

These compounds are based on Percec type dendron. ⁶ 3,4,5-tris(n-dodecyloxy)benzoic acid (12G1-AG) and 3,4,5-tris[3',4',5'-tris(n-dodecyloxy)]benzoic acid (12G2-AG), and their corresponding acid chlorides were synthesized by the method in the previous paper. ⁶ 4-[3,5 -Bis(3-aminophenyl)phenyl]carbonylamino]phenyl 3,4,5-tris (n-dodecyloxy)benzyloxy benzoate (12G1-AG-Terphenyldiamine) and 4-[3,5-Bis(3- aminophenyl) phenyl]carbonylamino]phenyl 3,4,5-tris[3',4',5'-tris (n-dodecyloxy)benzyloxy]benzoate(12G2-AG-Terphenyl diamine) were synthesized by the following method *via* condensation reactions with 3,5-dibromo benzoic acid and 4-aminophenol, followed by Suzuki coupling reaction with 3-aminophenyl boronic acid (Fig. 2)

12G1-AG-Terphenyldiamine: mp 164.7°C (sharp single peak, DSC); TLC (1:1 hexane:ethylacetate), $R_{\rm f}$ =0.30. ¹H NMR (CDCl3, δ, ppm, TMS): 0.88 (t, 9H, CH₃, J=6.8 Hz), 1.26 (m, 48H, CH₃(CH₂)₈), 1.47 (m, 6H, CH₂CH₂CH₂OAr), 1.80 (m, 6H,

 CH_2CH_2OAr), 3.76 (s, 4H, N H_2), 4.05 (t, 6H, CH_2OAr , J=8.8 Hz), 6.69 (d, 2H, H_J, J=7.6 Hz), 6.87 (s, 2H, H_F), 6.99 (d, 2H, H_C, J=8.2 Hz),

7.20 (m, 4H, H_G and H₁), 7.39 (s, 2H, H_A,), 7.75 (d, 2H, H_B, J=8.2 Hz), 7.82 (s, 1H, H_E), 7.91 (s, 2H, H_D), 8.30 (s, 2H, NH); IR (KBr): 3370, 3280 (NH₂), 1730, 1650 (C=O), 1190, 1120 (-O-) cm⁻¹.

12G2-AG-Terphenyldiamin e: mp 68.3°C (DSC); TLC (20:1 dichloro methane :



ethylacetate), R_f=0.40. ¹H NMR (CDCl3, δ, ppm, TMS): 0.88 (t, 27H, CH3, J=6.4 Hz), 1.26 (m, 144H, CH₃(CH₂)₈), 1.42 (m, 18H, CH₂CH₂CH₂OAr), 1.71 (m, 18H, CH2CH2OAr), 3.77 (t, 4H, CH_2OAr , 4-(3',5') position, J=6.4 Hz), 3.90 (t, 8H, 3,5-(3',5') positions, J=6.4 Hz), 3.93 (t, 6H, CH_2OAr , 3,4,5-(4') positions, J=6.4 Hz), 5.07 (s, 6H, ArCH2OAr, 3,5-position), 5.09 (s, 6H, ArCH₂OAR, 3,5-position), 6.63 (s, 2H, ortho to CH₂, 4' position), 6.65 (s, 4H, ortho to CH₂, 3',5' position), 6.73 (d, 2H, H₁, J=7.6 Hz), 6.97 (s, 2H, H_{F} ,), 7.06 (d, 2H, H_{C} , J=8.2 Hz), 7.21 (m, 4H, H_{G} and H_1), 7.54 (s, 2H, H_A ,), 7.75 (d, 2H, H_B , J=8.2 Hz), 7.91 (s, 1H, H_E,), 7.99 (s, 2H, H_D,), 8.10 (s, 2H, NH), IR (KBr): 3370, 3280 (NH₂), 1710, 1640 (C=O), 1190, 1120 (-O-) cm⁻¹









12G2-AG-Terphenyldiamine

Fig. 2 Synthesis of diamine monomers having dendron moieties

2.2 Polymer synthesis and characterization

Poly(amic acid) preparations: As a typical example, to a 30-mL flask were added equimolar amounts of tetracarboxylic dianhydrides and diamines. The system was purged by nitrogen and NMP was added. Monomer concentration was kept at 20 wt%. The mixture was stirred at room temperature under nitrogen for 12 hours to allow viscosity to increase. The poly(amic acid) solution was diluted with NMP, and polymer concentration was kept at 10 wt%.

Polyimide preparations: As a typical example, to 10 g of above 10 wt% poly(amic acid) solution were added 5 molar ratio of pyridine and 4 molar ratio of acetic anhydride. The system was purged by nitrogen and

was stirred at 120°C under nitrogen for 5 hours. Powdered polyimides were obtained by precipitation into a large amount of methanol, filtered, and washed with large amounts of methanol, and dried at 100°C for 1 day.

Measurement: The inherent viscosities of polymers were measured as the index of molecular weights using Cannon Fenske viscometers at a concentration of 0.5 g/dL in NMP at 30°C. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetric analyzer Model TGA-50 in air or nitrogen at a heating rate of 10 °C /min. ¹H-NMR spectra were measured on a JEOL JNM-AL400 FT NMR in a dimethyl sulfoxide-d₆.

3. RESULTS AND DISCUSSION

3.1 Introduction of dendron side chain via polymer reaction

Soluble polyimides obtained from 4,4'-hexafluoro isopropylidenedi(phthalic anhydride) (6FDA) and 4,4'-diamino-3,3'-dihydroxybiphenyl (HAB) were reacted with 3,4,5-tris(n-dodecyloxy)benzoic acid (12G1-AG) using dicyclohexylcarbodiimide (DCC) as a dehydrating reagent (Fig. 3). The progress of reaction was monitored by SEC measurements, and polyimides having dendron structure were obtained. However, the peak of unreacted dendron was also observed. Although 6FDA/HAB polyimides are originally soluble, above dendronized polyimides have enhanced solubility in various common solvents such as dichlomethane. However, it is appears that the introduction of dendron groups via polymer reaction is less versatile methods because of the limitation of monomer combination, conversion control, molecular weight controls etc. Therefore, we terminated the further investigation and started to synthesize the diamine monomers having dendron moiety.



Fig. 3 Introduction of dendron moiety via polymer reaction

2.2 Synthesis of aromatic diamines having dendron moieties

It is anticipated that the diamine monomers having dendron moieties have a low reactivity toward dicarboxylic dianhydrides due to large steric hindrance of bulky dendrons. Therefore, a aromatic spacer was introduced between a dendron moiety and a terphenylene diamine unit (Fig. 1). Aliphatic spacers, that are common for many functional polymers such as liquid crystalline polymers, are not used because these probably reduce the thermal stability of polyimides. Terpnenyl diamine unit was used as a aromatic diamine backbone, and these diamines were synthesized via Suzuki coupling reaction. Generally, a diamine monomer is obtained from the corresponding nitro compound followed by reduction with Pd/C. In our study, this two-step procedure can be also applicable and Suzuki coupling reaction with 3-nitrophenyl boronic acid gave a better yields (92%) as compared with 3-aminoboronic acid (60%) in case of 12G1-AG Terphenyldiamine synthesis. However, it was observed that the reduction of the dinitro precursor of 12G2-AG-Terphenyldiamine easily cleaved their benzyloxy units. Therefore, the use of 3-aminophenyl boronic acid is a necessary method to obtain 12G2-AG-Terphenyldiamine.

3.3 Polymerization of aromatic diamines having dendron moieties

The polymerization of 12G1-Terphenyldiamine in NMP were investigated using BTDA, which is a representative aromatic tetracarboxylic dianhydride, and co-diamine monomer, DDE that is a conventional aromatic diamine (Table I). It consists of a poly(amic acid) synthesis followed by chemical imidization. The poly(amic acid)s were obtained by reacting diamines with an equimolar amount of BTDA at 60°C for room temperature under a nitrogen atmosphere. The polyimides were obtained by a chemical imidization at 120°C in the presence of pyridine as base catalyst and acetic anhydride as a dehydrating agent. These are the optimized synthetic conditions previously developed for the synthesis of soluble polyimides in our laboratory.¹⁻⁴ Although viscous poly(amic acid)s solution from above monomer were obtained, the precipitations were during imidization process. It was speculated that the hydrocarbon moiety of dendron reduce the solubility of polyimides in NMP, therefore, a polar aromatic solvent, *m*-cresol was used to improve the solubility of dendron moiety (Table I). Thus, soluble copolyimides based on BTDA // 12G1-Terphenyldiamine / DDE (50 / 50) was obtained. This copolyimide has a enough molecular weight ($\eta_{inh} = 0.56$) and the good film forming ability. On the other hand, homopolyimide based on BTDA / 12G1-Terpnenyl diamine was insoluble in NMP. The solubility of above copolyimides may be improved by the randomizing effect based on copolymerization as well as the entropy effect of long chain linear alkyl groups.3,4

It is well known that 6FDA give a soluble polyimide in combinations of most of aromatic diamines by the effect of two trifluoro methyl groups. The polyimide based on 6FDA / 12G1-Terphenyldiamine was readily soluble in NMP, however 12G2-Terphenyldiamine monomer, was itself insoluble in NMP. The polyimide based on 6FDA / 12G2-Terphenyldiamine was obtained in NMP / THF (1 / 1, a volume ratio) (Table I). It is interesting that the solubility of this dendronized PI has been dramatically changed and it is insoluble in polar aprotic solvents such as NMP, DMF and DMSO, but easily soluble in less polar solvents such as dichloromethane, chloroform, toluene and THF. This phenomena is probably affected by the huge hydrocarbon moieties of dendron side chains of polyimides.

Table I.Polyimides and copolyimides based on12G1-AG-Terphenyldiamine or12G2-AG-Terphenyldiamine

Dianhydride ^a	Diamine ^{b)}			PA	Pl	
	(mol %)	(mol %)	Solvent	η_{inh}^{d}	Solubility	$\eta_{mh}^{\ d}$
BTDA	12G1		NMP	0.31	Insoluble	
BTDA	12G1(50)	DDE (50)	NMP	1.00	Insoluble	
BTDA	12G1		m -creso	1	Insoluble	
BTDA	12G1(50)	DDE (50)	m -creso		Soluble	0.56
6FDA	12G1		NMP	0.21	Soluble	0.19
6FDA	12G2		NMP/THF		Soluble	0.12

a) BTDA; 3.3',4,4'-Benzophenonetetracarboxylic dianhydride. 6FDA; 4,4'-Hexafluoroisopropylidendi(phtalic anhydride). b) 12G1; 12G1-AG-Terphenyldiamine, 12G2; 12G2-AG- Terphenyldiamine c) Reaction conditions in NMP and NMP/THF (1/1); r.t., 24 h (polyamic acid), 120 °C, 2-4 h, pyridine, Ac₂O (polyimides). Reaction condition in *m*-cresol; 80°C, 2 h \rightarrow 200°C, 6 h. d) Measured at 0.5 g dL⁻¹ in the polymerization solvent at 30 °C.

3.4 Thermogravimetric analysis of polyimides having dendron side chain

The thermal stability of a dendronized PI was evaluated by 10% weight loss temperatures in TGA measurement. Ten percent weight loss temperatures of BTDA // 12G1-Terphenyldiamine / DDE (50 / 50) polyimide were 455°C in air and 451°C in nitrogen. Fig. 4 shows a TGA curve of BTDA // 12G1-Terphenyldiamine / DDE (50 / 50) in air. It shows a steep decrease of weight at 457°C, and this weight loss corresponds the calculated weights loss based on three dodecyloxy chains. Although it was concerned that long chain alkyl groups in dendron moieties somewhat decrease the thermal stability, it was found that above polyimide was stable at least at 457°C.



12G1-Terphenyldiamine / DDE (50 / 50) in air.

3.5 Application for the alignment films for LCDs

The LCDs performance test of polyimides using diamines having dendron side chain was examined at Cheil Ind. Inc, Korea. The alignment films containing 8 molar % of 12G1-Terphenyldiamine were utilized for the vertical alignment mode (VA-mode). Fig. 5 shows a V-T curve (voltage-transparency) of these test cells, and shows a dramatic change of T. The pretilt angles of LC molecules were over 89° in these test cells. It is recognized that extremely bulky and hydrophilic

dendron moiety affects the generation of pretilt angles.



Fig. 5 V-T curve of virtical alignment mode using alignment firms containing 12G1-AG-Terphenyldiamine

4. CONCLUSION

Novel polyimides having Percec type dendron side chains (dendronized PI) were successfully synthesized. The introduction of dendron *via* polymer reaction was possible but was not completed. Novel synthetic methods of aromatic diamine monomers having dendoron side chain were developed using Suzuki coupling reaction. Thus dendronized PIs were obtained using BTDA and co-diamine monomer, DDE. Solubility of dendronized PI is improved. It was found that these dendronized PIs were applicable for the alignment film in VA-mode LCDs. The further investigation and detail characterization have been continued.

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