

Synthesis and Mesomorphism of Polymers with Banana-Shaped Mesogens in the Main Chain

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Abstract

In this work, we report the synthesis and characterization of azomethine-ester polymers that consist of banana-shaped mesogen in their backbone. Two parts of the key structure of five-ring bent-core mesogen were modified by connecting different angle of central unit (Ar), and introducing lateral substituent into the outer ring (X). The synthetic details includes (1) placing the dioxydodecamethylene unit as a flexible spacer, (2) possessing 2,3- or 2,7-naphthylene, or 1,2-phenylene connection on the central unit, and (3) introducing fluorine or chlorine substituent (X = F or Cl) into the outer phenylene unit.

1. Introduction

Non-conventional liquid crystalline molecules with banana-shaped or bent-core mesogens have revealed unique insights into mesomorphism and its associated electro/optic properties. For instance, achiral banana-shaped molecules could form the chiral mesophase with a spontaneous polarization in the layer plane [1-4]. In spite of vigorous theoretical work and many experimental efforts, the existence of

biaxial nematic phases has not been proved distinctively in low molar mass thermotropic liquid crystals. While there are a considerable number of studies concerned with low molar mass banana-shaped or bent-core molecules, little attention has been given to polymeric materials containing banana-shaped or bent-core mesogenic unit in the backbone.

In 2002, we first reported the synthesis and properties of the new main-chain liquid crystalline poly(azomethines) with banana-shaped mesogen [5]. In 2003 [6] and 2004 [7], Galli and coworkers have reported the so-called banana polymers consisting of a regular alternation of a banana unit and flexible spacer in the main chain synthesized by the acyclic diene metathesis polymerization. In 2004, we first reported the main chain polymers containing banana-shaped mesogens could form B phases [8].

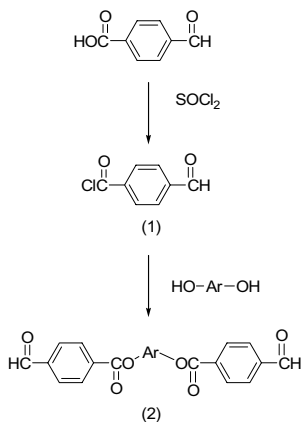
In this study, new poly(azomethine-esters) varying the bend-angle of a central core in the mesogen were synthesized and the effects on the liquid crystalline properties were investigated. In addition, the liquid crystalline behavior of the banana-shaped mesogen with all ester-linking group will be included and discussed in comparison with that of the poly(azomethine-esters).

2. Experimental

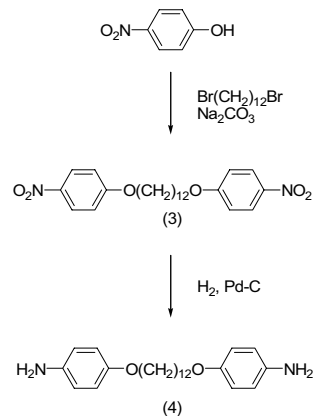
Synthesis. The polymers were synthesized through the synthetic route as shown in Schemes 1-4 [7]. Since the synthetic procedures used to prepare the polymers were essentially the same, one representative polymer is given in the following:

First, 1,2-phenylene bis(4-formyl benzoate) was prepared by reaction of catechol and 4-formyl benzoyl chloride in tetrahydrofuran with triethylamine at 0°C. Next, dodecane-1,12-bis(p-oxynitrophenyl), which was prepared by the nucleophilic substitution reaction of dibromododecan with 4-nitrophenol, was reduced with Pd/C in EtOH to dodecane-1,12-bis(p-oxyaminophenyl). Finally, the polymer was prepared by poly condensation reaction between aniline and dialdehyde monomers.

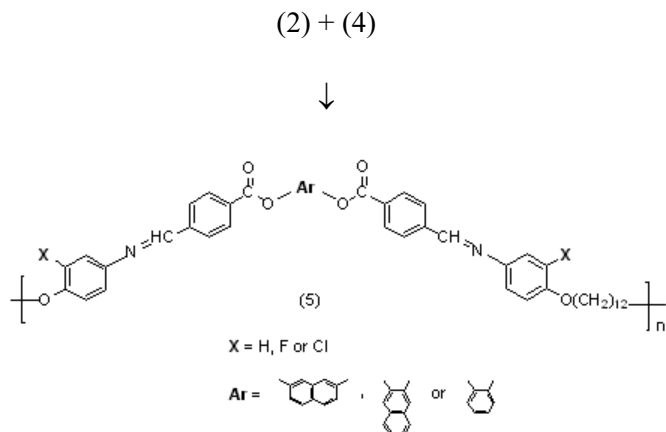
IR (KBr pellet, cm^{-1}): 3079 (aromatic = CH, st), 2928, 2852 (aliphatic CH, st), 1738 (C=O, st), 1684 (C=N, st), 1621, 1506 (aromatic C=C, st). ^1H NMR ($\text{CF}_3\text{CO}_2\text{D}$, δ in ppm): 9.53 (2H, s, N=CH), 8.83-8.74 (4H, d, ArH), 8.64-8.58 (4H, d, ArH), 8.10-8.02 (4H, d, ArH), 7.93 (1H, br s, ArH), 7.77-7.41 (7H, m, ArH), 4.40 (4H, t, OCH_2), 2.2 (4H, br s, OCH_2CH_2), 1.71(16H, br s, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_4$).



Scheme 1. Synthetic route to compounds 2.



Scheme 2. Synthetic route to compounds 4.






Scheme 3. Synthetic route to polymers 5.

Characterization. IR and NMR spectra were obtained by a Jasco 300E FT/IR and Bruker DPX 200 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by differential scanning calorimeter (duPont TA 910 DSC) and polarizing optical microscopy (Zeiss, Jenapol). DSC measurements were performed in a N_2 atmosphere. The DSC heating and cooling rates were of 20 °C/min. Optical textures were observed by a

polarizing microscope equipped with a camera and a thermo-controller (Mettler FP82HT). X-ray analysis was performed in transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder which was sealed with a window of 7 μm thick Kapton films on both sides. The sample was heated with cartridge heaters and its temperature monitored by a thermocouple placed close to the sample. Subtracting the scattering from the Kapton gave a background scattering correction.

Table 1. Designation of polymers containing bent-core mesogens with Ar/X

X \ Ar	 (2,7)	 (2,3)	 (1,2)
H	5a	5b	5c
F	5d	5e	5f
Cl	5g	5h	5i

3. Results and Discussion

All polymers were only soluble in a strong acid such as H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H}$ etc.. The solution viscosities were measured on 0.16 g/dL solution in H_2SO_4 at 30°C , and the values are in the range of 0.59-0.79 dL/g. All of the polymers were semi-crystalline. The melting temperatures (T_m) of polymers are ranged from 188°C to 229°C depending on the structure (see Table 2). Polymer derived from 2,7-naphthalenediol could not show the melting transition before thermal degradation, while polymers derived from 2,3-naphthalenediol seem to form B-phase according to polarizing microscopic observation (see Figure 3). Polymer derived from 1,2-

phenylenediol showed an optical texture corresponding to smectic phase, and as a shear is applied a more distinctive broken fan texture was observed (see Figure 4).

4. Conclusion

By DSC measurement and cross-polarizing microscopic observation, it was concluded that polymers with $\text{Ar/X} = 1,2/\text{H}$ and $2,3/\text{H}$ form smectic phases, and polymers with $\text{Ar/X} = 2,3/\text{F}$ and $2,3/\text{Cl}$ form B phases: polymer with $\text{Ar/H} = 2,7/\text{H}$ showed thermal decomposition before melting.

5. Acknowledgements

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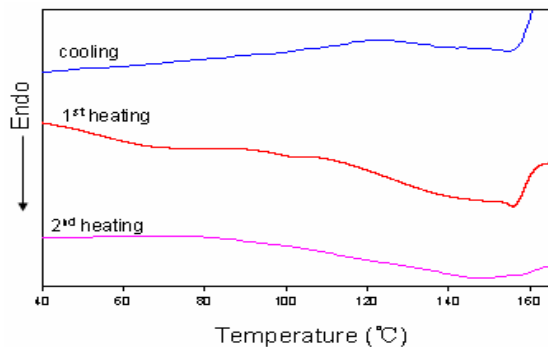
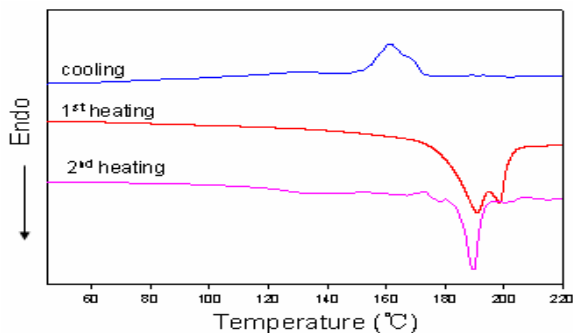
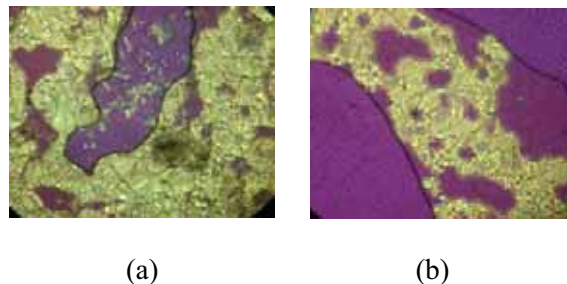
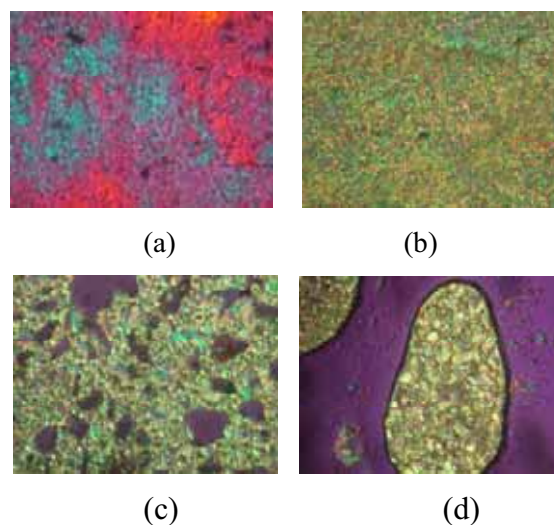
6. References

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Table 2. Yield, thermal transition temperature, and enthalpy change^a

Polymer	Yield (wt%)	^b η_{inh} (dl/g)	T_{k-k} (°C)	ΔH_{k-k} (J/g)	T_m (°C)	ΔH_m (J/g)
5a	79.9	-	-	-	-	-
5b	88.1	0.59	195	4.6	229	13.92
5c	85.6	0.62	195	4.11	225	2.48
5e	89.5	0.79	-	-	156	15.1
5h	85.6	0.62	-	190	198	22.5

^a T_{k-k} and ΔH_{k-k} stand for the temperature and the enthalpy change for the solid-to-solid transition, respectively. ^bInherent viscosity was measured on 0.16 g/dL solution in H₂SO₄ at 30°C.

**Figure 1.** DSC thermograms of polymer **5e** with Ar/X = 2,3/F on heating and cooling scans.**Figure 2.** DSC thermograms of polymer **5h** with Ar/X = 2,3/Cl heating and cooling scans.**Figure 3.** Cross-polarized optical micrographs for (a) polymer **5e** with Ar/X = 2,3/F taken at 260°C and (b) polymer **5h** with Ar/X = 2,3/Cl taken at 178°C on heating (x300).**Figure 4.** Cross-polarized optical micrographs of polymer **5c** with Ar/X = 1,2/H on heating : taken at (a) 150°C, (b) 200°C and (c) 250°C, and (d) after shearing at 250°C.