Synthesis and Characterization of New Azomethine Polymers Containing Bent-Core Mesogen with Sharp Bend Angle

***Eun Chol Kim*[1], *E-Joon Choi*[1]*, *Chang-Woo Ok*[2] *and Wang-Choel Zin*[2]**

[1]**Dept. of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, 730-701, Korea**

TEL:82-54-478-7704, e-mail: ejchoi@kumoh.ac.kr

[2]**Dept. of Material Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea**

Keywords : ***Lateral substituent, bent-core mesogens; azomethine-ester polymers; ferroelectricity, banana-phas***

Abstract

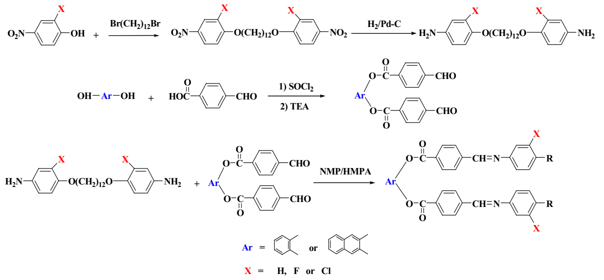
Six azomethine polymers containing bent-core mesogen were synthesized with variation of a bent structure of central core (1,2-dioxyphenylene or 2,3-dioxynaphthylene), and a lateral halogen substituent (X = H, F or Cl). The properties of the polymers were characterized by FT-IR, NMR spectroscopy, DSC, polarizing optical microscopy, and X-ray diffractometry.

1. Introduction

Classical thermotropic liquid crystals are commonly composed of linear molecules, because their structural linearities can give an advantage in the formation of mesophases. However, recently, many unconventional liquid crystals with non-linear structures have been reported by a number of research groups.[1-4] In 1996, Niori et al. observed the first obvious example of ferroelectricity in a smectic phase formed by achiral banana-shaped molecules. It was known that even when the bent-core mesogens do not contain achiral unit, their tilted smectic mesophases can show the chirality due to decrease of molecular symmetry and the ferroelectricity due to spontaneous polarization. Although the bent-core mesogens with higher than 140° bend angle can form calamitic phase[1], the bent-core mesogens with 110° to 140° bend angle can form B-phase[2]. In this study, we have synthesized azomethine polymers containing sharp bend angle in central core with variation of a lateral halogen substituent (X=H, Cl or F) and their mesomorphic properties were investigated.

2. Experimental

Synthetic route to polymers containing bent-core mesogen is shown in Scheme 1. First, dodecane-1,12-bis(p-oxynitrophenyl) was prepared by substitution reaction of dibromododecan with 4-nitrophenol. Then, dodecane-1,12-bis(p-oxyaminophenyl) was prepared by hydrogenation reaction of the nitro compound. Next, 1,2-phenylene bis(4-formyl benzoate) was prepared by reaction of catechol and 4-formyl benzoyl chloride. Finally, the polymer was obtained by polycondensation reaction between the diamine and the dialdehyde monomers.



Scheme 1. Synthetic route to polymers.

3. Results and discussion

The synthetic route followed to obtain the azomethine polymers containing bent-core mesogen used a modified literature procedure and is shown in the scheme 1. The structure of obtained polymers were identified by FT-IR and NMR spectrometry. The results were in accordance with expected formulae. All polymers were not dissolved in to common organic solvents. They were only soluble in strong acids, such as H_2SO_4, CF_3CO_2H, etc. Yields and viscosities are summarized in Table 1. The Yields are higher than 85%. The values of solution viscosities are in the range of 0.3-0.8 g/dL.

TABLE 1. General properties and transition temperature of polymers

Ar/X	Yield (wt%)	$^a\eta_{inh}$ (dl/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_i (°C)
1,2/H	86	0.89	--	225	2.48	^{b}
1,2/F	86	0.31	36	109	17.6	182
1,2/Cl	89	0.40	53	181	1.75	^{b}
2,3/H	88	0.88	--	229	13.9	^{b}
2,3/F	87	0.81	--	200	32.0	^{b}
2,3/Cl	86	0.62	--	190	22.5	^{b}

^{a}Inherent viscosity was measured on 0.16 g/ dℓ solution in H_2SO_4 at 30 ℃.

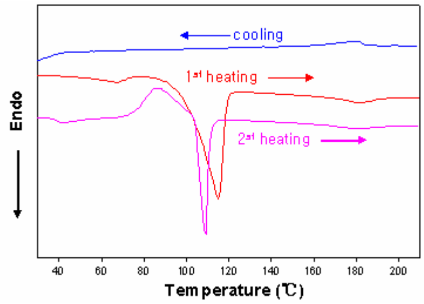


Fig. 1. DSC thermograms of polymer with Ar/X = 1,2/F on heating and cooling scans.

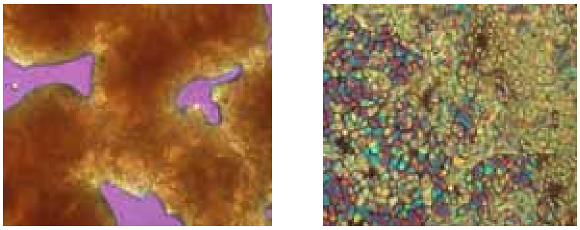
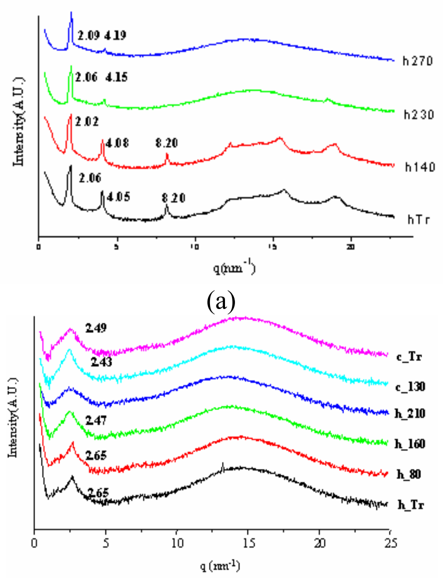

(a) (b)

Fig. 2. Opticl micrographs of polymer with Ar/X= 1,2/F on heating to isotropic liquid. (a) at 109℃; (b) at 175℃.

Figure 1 shows DSC thermogram of polymer with Ar/X = 1,2/F. In the DSC thermogram, a glass transition and two endothermic peaks were appeared: on heating T_g at 36℃, T_m at 109℃and T_i at 182℃. The transition temperatures of remaining polymers were included in Table 1. The T_gs and T_ms of the polymers was in the range of 36-53℃ and 109-229℃, respectively. The T_ms of the 2,3-polymers are higher than those of the 1,2-polymers. It is note that the polymers with X = F show the highest ΔH_m.



(a)

(b)

Fig. 3. The X-ray scattering patterns of polymers at a given temperature (h: heating; c: cooling). (a) Ar/X = 2,3/F and (b) Ar/X = 1,2/Cl.

Using an polarizing optical microscope, we could confim the thermal sequnce determined by DSC on heating and cooling cycles. Using an optical microscope with crossed polarizer, on heating to isotropic liquid we could identify phase transition. When the polymer with Ar/X=1,2/F is heated slowly, at the clearing point the optical texture of the smectic phase. Figure 2(a) shows T_m of polymer with Ar/X = 1,2/F at 109℃ and the optical texture of the smectic phase for polymer with Ar/X = 1,2/F appear in figure 2(b).

In Figure 3(a), as heated to 230℃ polymer with Ar/X = 2,3/F showed sharp peaks in the small-angle region and a broad diffuse reflection at the wide angle region. This is indicative of smectic mesophase. In Figure 3(b), the melt state of the polymer with Ar/X = 1,2/Cl showed a liqud-like reflection. According to X-ray measure-ments, all of the polymers except for the polymer with Ar/X = 1,2/Cl can form a smectic mesophase in the melt. The polymer with Ar/X = 1,2/Cl could only form a nematic mesophase.

4. Summary

All of the polymers were soluble only in strong acid such as H_2SO_4, CF_3CO_2H, etc. The inherent viscosities were in the range of 0.3-0.8 g/dL. Three polymers with Ar/X = 2,3/F, 2,3/Cl, 1,2/F have been designated to be a smectic mesophase in the melt, while polymer with Ar/X = 1,2/Cl has been formed a nematic mesophase.

5. References

1. H. Matsuzaki, Y. Matsunaga, Liq. Cryst; **14**, 105. (1993).
2. T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem; **6**, 1231, (1996).
3. S. Demel, C. Slugovc, F. Stelzer, K. Fodor-Csorba, and G. Galli, Macromol. Rapid Commun; **24**, 636 (2003).
4. E-J. Choi, J-C. Ahn, L-C. Chien, C-K. Lee, W-C. Zin, D-C. Kim, and S-T. Shin, Macromolecules; **37**, 71 (2004).