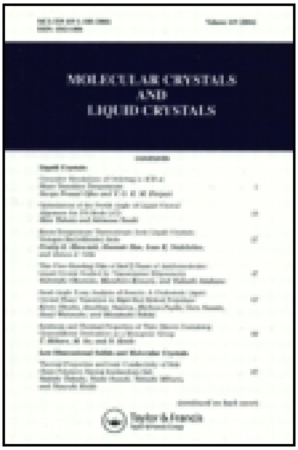

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Phase Transitions of Side Chain Liquid Crystal Polyamines

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Phase Transitions of Side Chain Liquid Crystal Polyamines

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Novel side-chain liquid crystalline polyamines (SCLCPs) were synthesized by ring-opening polymerization of aziridine monomers. Their thermal and liquid crystalline properties were examined with a polarizing microscope and a differential scanning calorimeter. Aziridine monomers showed no liquid crystalline phases. SCLCPs with nitro or 2-hydroxyethyl terminal groups in the side chains exhibited a smectic A phase with a fan-shaped texture. However, SCLCP with ethylazobenzene side-groups and SCLCP with nitroazobenzene side-groups with a methyl lateral substituent did not formed a liquid crystalline phase

Keywords: Aziridine Monomer; Liquid Crystal Polyamine; Ring-Opening Polymerization; Phase Transitions; X-Ray diffraction Measurement; Smectic A

INTRODUCTION

Research in synthese and physicochemical properties of thermotropic side chain liquid crystal polymers was reported by many groups. Many side chain liquid crystal polymers are synthesized by radical polymerization of vinyl monomers such as mesogenic acrylates and methacrylates.[1] Liquid crystalline polysiloxanes and polyesters are also prepared by hydrosilation reactions and polyesterification, respectively.[2] Liquid crystalline polyethers are performed by ring-opening polymerization of oxiranes with mesogenic groups.[3] Consequently, as polymer backbones, polyacrylate, polymethacrylate, polysiloxane, and polyester appeared in many papers. It is concerned that a polyamine chain is also useful as the polymer backbone. The polyamine with ethyleneimine units can be obtained by ring-opening polymerization of oxazoline or aziridine derivatives.

Recently, we synthesized novel liquid crystalline polyamines with azobenzene mesogenic side-groups by ring-opening polymerization of aziridine monomers. In this paper, we describes thermal and liquid crystalline properties of side chain liquid crystal polyamines.

EXPERIMENTAL

MATERIALS

2-Methylethylenimine (0.2 mmol) and 6-bromo 1-(4-(substituted phenylazo)phenoxy)hexane (0.2 mmol), triethylamine (0.4 mmol) were dissolved in tetrahydrofuran (50ml) and stirred for a week at room temperature. Tetrahydrofuran was evaporated under reduced pressure at room temperature. The residue was dissolved in chloroform and washed with water. The chloroform solution was dried with $MgSO_4$. Chloroform was evaporated and the crude monomer was obtained. The crude monomer was purified by recrystallization from a hexane solution.

An aziridine monomer was dissolved in tetrahydrofuran and diethylsulfate was added in the tetrahydrofuran solution as a polymerization initiator. The tetrahydrofuran solution was stirred for a week at 50°C and, after the reaction, was concentrated by evaporation of the solvent. The polymer (FIGURE 2: *n*=average of polymerization degree obtained from Mn) was reprecipitated from a tetrahydrofuran solution into hexane.

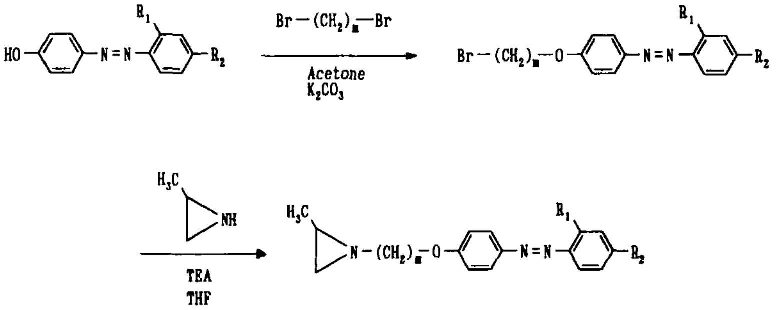
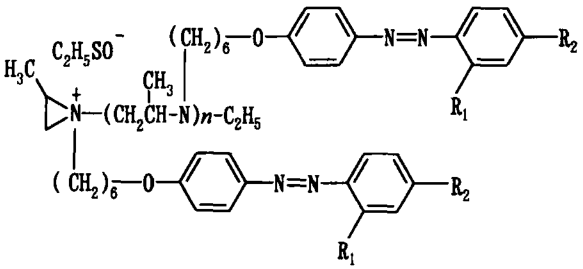


FIGURE 1. SYNTHETIC SCHEME OF AZIRIDINE MONOMERS: R_1=H, CH_3; R_2=NO_2, CH_2CH_2OH, C_2H_5.



R_1=H, CH_3; R_2=NO_2, CH_2CH_2OH, C_2H_5

FIGURE 2. STRUCTURES OF SIDE CHAIN LIQUID CRYSTAL POLYAMINES.

MEASUREMENTS

The phase transitions were examined with a Shimadzu differential scanning calorimeter (DSC-50Q), a Mettler Thermosystem 3000 and a Nikon polarizing microscope equipped with a Mettler FP900 system (FP90-FP82). The temperature variable X-ray diffraction measurements were performed with a Rigaku X-ray diffractometer RINT2100 system using Ni-filtered Cu-Kα radiation. The liquid crystalline samples in the X-ray diffraction measurement were placed on a Linkam hot stage system (TC600PH).

RESULTS AND DISSCUSION

An aziridine monomer (AZ6N), having a nitroazobenzene unit, exhibited a solid-isotropic phase transition (64.5°C) and no mesophase (FIGURE 3, TABLE 1). The aziridine monomers except AZ6N also did not show a liquid crystalline phase (TABLE 1).

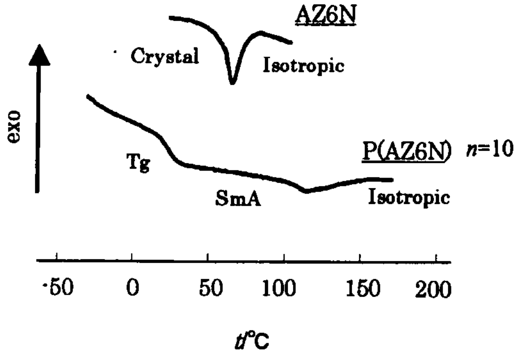


FIGURE 3. DSC CURVES OF AZ6N AND P(AZ6N).

A side chain liquid crystalline polyamine [P(AZ6N)] obtained from AZ6N exhibited glassy-smectic A and smectic A-isotropic phase transitions. As shown in FIGURE 3, the glassy-smectic A phase transition (glass transition), which was not observed for low-molecular-weight AZ6N, was clearly detected by DSC. P(AZ12N), having a longer methylene spacer (dodecamethylene) than P(AZ6N), and P(AZ6EtOH) with a hydroxyethyl terminal group in the side chain also showed a smectic A phase. These liquid crystalline polyamines formed batonnets, a fan-shaped texture, and a perpendicular structure with the optical uniaxial property, which is characterized by conoscopic observation.

TABLE 1. PHASE TRANSITIONS OF AZIRIDINE MONOMERS AND POLYAMINES

	n	m	R_1	R_2	Phase transition temp./°C 1)				
polymer									
P(AZ6N)	10	6	H	NO_2	G	24.9	SmA	115.0	I
P(AZ6N)	20	6	H	NO_2	G	40.0	SmA	176.0	I
P(AZ12N)	10	12	H	NO_2	G	17.9	SmA	80.8	I
P(AZ6EtOH)	10	6	H	C_2H_4OH	G	15.2	SmA	106.7	I
P(AZ6Et)	10	6	H	C_2H_5	G		15.9		I
P(AZ6MN)	10	6	CH_3	NO_2	G		16.6		I
monomer									
AZ6N		6	H	NO_2	K		64.5		I
AZ12N		12	H	NO_2	K		53.3		I
AZ6EtOH		6	H	C_2H_4OH	K		45.9		I
AZ6Et		6	H	C_2H_5	K		52.0		I
AZ6MN		6	CH_3	NO_2			—		

1) G: Glassy K: Solid SmA: Smectic A I: Isotropic

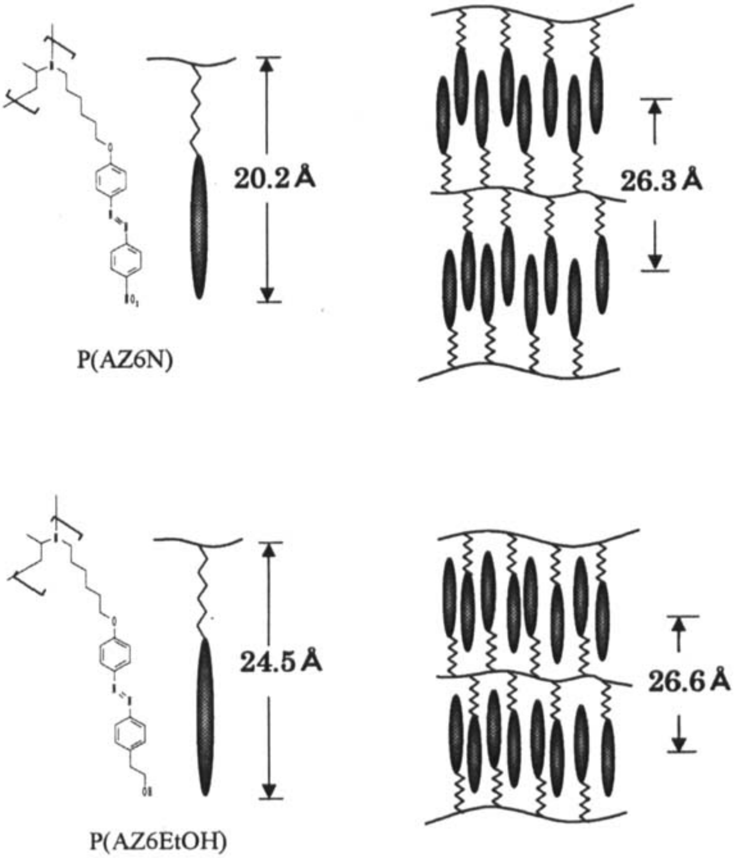


FIGURE 4. POSSIBLE PACKING MODELS OF P(AZ6N) AND P(AZ6EtOH).

P(AZ6Et) with ethylazobenzene side-groups and P(AZ6MN) with nitroazobenzene side-groups with a methyl lateral substituent did not formed a liquid crystalline phase and showed a grassy-isotropic phase transition. The X-ray diffraction patterns in the smectic A phases of

P(AZ6N) and P(AZ6EtOH) consist of sharp reflections at small angles, corresponding to the layer spacing, and a wide-angle diffuse halo, showing low order inside the layer. The smectic A layer spacing determined from the first-order small-angle reflection is 26.3 Å, while the extended length of the side chain is 20.2 Å (FIGURE 4). In the case of P(AZ6EtOH), the smectic A layer spacing is 26.6 Å, and the side chain length is 24.5 Å (FIGURE 4).

In general, the nitroazobenzene units overlap each other and form a dimmer structure.[4] In this case, a possible packing model in the smectic A phase of P(AZ6N) is a partial bilayer structure. It is expected that P(AZ6EtOH) forms a monolayered packing that the mesogenic side-chains interdigitate, as shown in FIGURE 4.

CONCLUSIONS

The side chain liquid crystalline polyamines can be synthesized by ring-opening polymerization of the mesogenic aziridine monomers. The introduction of polar head groups such as the nitro or hydroxyl groups enhanced the ability in the liquid crystal formation. The aziridine monomers are polymerizable at room temperature under the presence in the polymerization initiator. Above 130 ℃, the aziridine monomers polymerize under the absence of the initiator. This nature of the aziridine monomers is useful to prepare oriented anisotropic films by bulk polymerization.[5]

References

[1] C. B. McArdle (editor), *Side Chain Liquid Crystal Polymers*, Blackie, Glasgow (1989). N. A. Plate and V. P. Shibaev(editors), *Comb-Shaped Polymers and Liquid Crystals*, Plenum Press, New York (1987). P. J. Collings and J. S. Patel (editors), *Handbook of Liquid Crystal Research*, Oxford University Press, Oxford (1997).

[2] B. Reck and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, 6, 291 (1985). S. Berg, V. Krone, H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **7**, 381(1986). G. W. Gray, D. Lancey, G. Nestor, and M. S. White, *Makromol. Chem., Rapid Commun.*, 7, 71(19986).

[3] F. Cser, K. Nyitrai, J. Horvath, and G. Hardy, *Eur. Polym. J.*, **21**, 259 (1985).

[4] S. Ujiie and K. Iimura, *Macromolecules*, 25, 3174 (1992).

[5] D. Braun, G. Frick, M. Klimes, and J.H. Wendorff, *Liq. Cryst.*, **11**, 929(1992). R.A. Hikmet, *Macromolecules*, **25**, 5759(1992). S. Ujiie and K. Iimura, *Rep. Prog. Polym.*

Phys. Jpn., **38**, 207(1995). D. J. Broer, H. Finkelmann, and K. Kondo, *Makromol. Chem.*, **189**, 185(1988).