

Induced smectic A and C phases formed by liquid crystalline binary mixtures consisting of side-chain polymer and twin compound

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Liquid crystalline binary mixtures were synthesized by mixing a side-chain polymer with an ethyl end group and a twin compound with a nitro end group. Their thermal and liquid crystalline properties were examined. The liquid crystalline binary mixtures having the twin component with even-numbered central methylene units exhibited an induced smectic A phase. On the other hand, the liquid crystalline binary mixtures having the twin component with odd-numbered central methylene units showed induced smectic A and C phases. In the induced smectic C phase, the liquid crystalline binary mixtures formed a schlieren with two brushes in addition to a schlieren with four brushes.

1. INTRODUCTION

The noncovalent interactions, such as Coulombic forces, hydrogen bondings, and donor-acceptor effects, can act effectively in producing the new liquid crystalline systems,^[1-8] which are of considerable interest in both fundamental and technological viewpoints. The mixing of liquid crystals allows to enhance the liquid crystallinity and can lead to the induction of smectic phases.^[6-8]

In recent, the liquid crystalline binary mixtures (LCBMs) consisting of twin compounds were prepared and their thermal and liquid crystalline properties were examined.^[8] An induced smectic C phase, which was produced by LCBMs having an odd-membered twin component with odd-numbered central methylene units, formed an induced smectic C phase having an antiferroelectric-like zigzag orientational

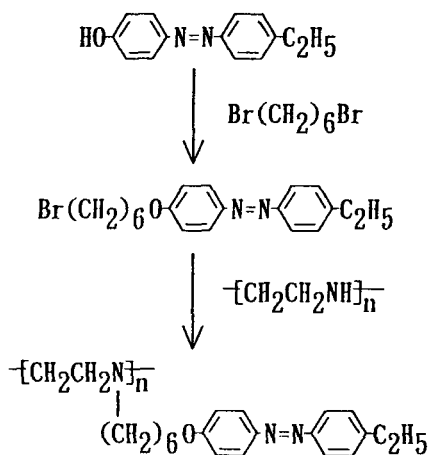
ordering. However, LCBMs having an even-membered twin component did not show the induced smectic C phase. This difference in the liquid crystal formation is related to the conformation of the twin molecules.

In this work, we prepared new liquid crystalline binary mixtures [P62/TNm(x)] consisting of a side-chain polymer and a twin compound and examined the formation of induced smectic phases. This paper describes the thermal and liquid crystalline properties of P62/TNm(x).

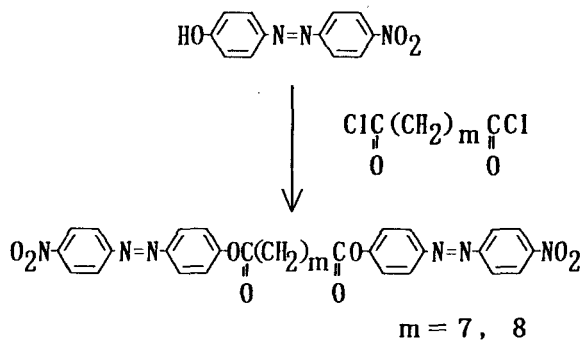
2. EXPERIMENTAL

2.1. Synthesis of side-chain liquid crystalline polymer (Scheme 1)

Synthesis of 4-(4-(ethyl)phenylazo)phenol. 4-Ethylaniline was dissolved in hydrochloric acid, and the solution was cooled below 5°C. For the diazotation, a



Scheme 1. Synthesis of liquid crystalline polymer (P62).



Scheme 2. Synthesis of twin liquid crystals (TN7, TN8).

small amount of sodium nitrite was added at a temperature below 5°C. To the cooled solution, a mixture of sodium hydroxide solution with phenol was added. The reaction mixture was stirred for 1h about 5°C and after the reaction was acidified with conc. hydrochloric acid. The precipitate was isolated by filtration and dried.

Synthesis of 6-bromo-1-(4-(4-(ethyl)phenylazo)phenoxy)hexane. 4-(4-(Ethyl)phenylazo)phenol was dissolved in acetone, and potassium carbonate and 1,6-dibromo-

hexane were added. The reaction mixture was refluxed for 60h. The precipitated potassium bromide was filtered off, and the filtrate was evaporated under reduced pressure. Chloroform was added to the crude product, and the chloroform solution was extracted ten times with water and evaporated. The product was recrystallized from the acetone solution.

Synthesis of *side-chain liquid crystalline polymer*. 6-Bromo-1-(4-(4-(ethyl)phenylazo)phenoxy)hexane and polyethyleneimine were dissolved in a mixture solution of tetrahydrofuran(THF) and acetonitrile. To the reaction mixture, potassium carbonate was added, and the reaction mixture was refluxed for 300h. After the reaction, the mixture was filtered off, and the filtrate was evaporated. The crude product was dissolved in THF, and the polymer was reprecipitated by adding hexane.

2.2. Synthesis of liquid crystalline twin compounds (Scheme 2)

4-(4-(Nitro)phenylazo)phenol was prepared by the same method as synthesis of 4-(4-(ethyl)phenylazo)phenol.

Synthesis of *di{4-(4-(nitro)phenylazo)phenyl}sebacate and di{4-(4-(nitro)phenylazo)phenyl}azelate*. 4-(4-(Nitro)phenylazo)phenol and triethylamine were dissolved in THF. To the THF solution, sebacoyl chloride(or azeloyl chloride) was added dropwise and the mixture was stirred for 10h. After the reaction, THF was evaporated under reduced pressure and the residue was dissolved in chloroform. The chloroform solution was washed with water and dried over MgSO₄. The product was recrystallized from the chloroform-hexane (1:1) solution.

2.3. Measurements

Molecular weights of the polymers were measured with a Toso GPC system (HLC-8020), calibrated with polystyrene standard samples. The thermal and liquid crystalline properties of the polymers were examined with a Shimadzu DSC 50Q system and an Olympus polarizing microscope (BH-2) with a Mettler FP80 hot stage equipped with a Mettler FP90 temperature controller.

3. RESULTS AND DISCUSSION

3.1. Phases transitions of side-chain polymer and twin compounds

The side-chain liquid crystalline polymer (P62, $M_n=9300$) showed a nematic phase with a schlieren texture. P62 exhibited glass-nematic and nematic-isotropic phase transitions (Fig. 1).

The twin compounds (TN7, TN8) also exhibited a nematic phase with marble and schlieren textures. TN8 with the even-numbered central methylene units showed higher clearing point than TN7 with the odd-numbered central methylene units (Fig. 2).

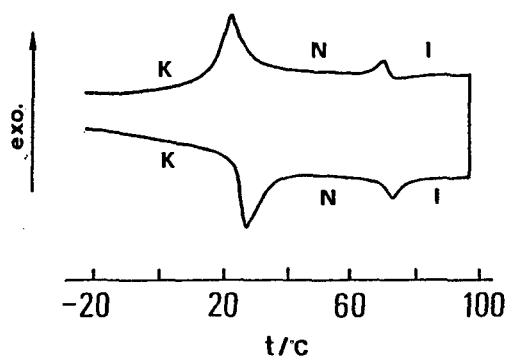


Fig. 1. DSC curves of liquid crystalline polymer (P62): K; solid phase: N; nematic phase: I; isotropic phase.

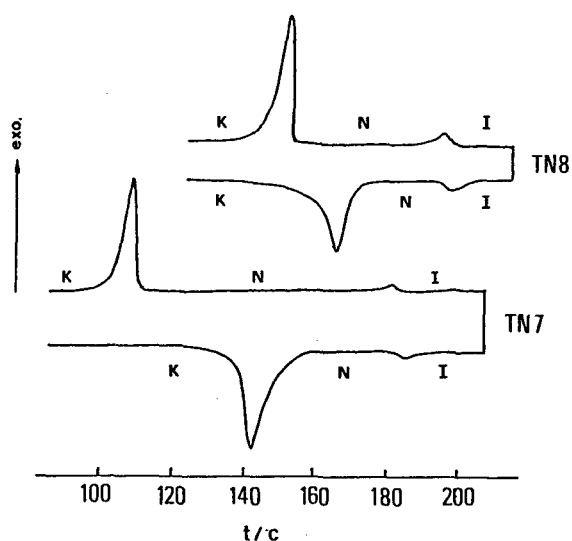


Fig. 2. DSC curves of twin liquid crystals (TN7 and TN8).

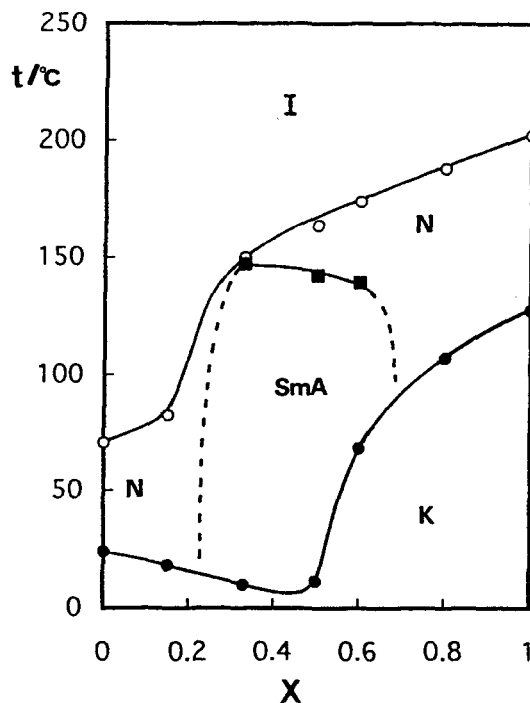


Fig. 3. Phase transition temperatures of liquid crystalline mixtures [P62/TN8(x)]: K; solid phase: SmA; induced smectic A phase: N; nematic phase: I; isotropic phase: x; mole fraction of TN8.

3.2. Phase transitions of liquid crystalline mixtures with even-membered twin component

Fig. 3 shows the liquid crystalline mixtures [P62/TN8(x)] consisting of P62 and TN8 with even-numbered central methylene units. P62/TN8(x) with $x=0.33, 0.5, 0.6$ clearly exhibited an induced smectic A phase with a fan texture, as well as a nematic phase. The formation of the induced smectic A phase is due to interactions between ethylazobenzene and nitroazobenzene units, such as the donor-acceptor effects.

3.3. Phase Transitions of liquid crystalline mixtures with odd-membered twin component

The liquid crystalline binary mixtures [P62/TN7(y)] having a twin component with odd-numbered central methylene units exhibited induced smectic A and C phases (Table 1). Fan and homeotropic textures formed in the induced smectic A phase. In the induced smectic C phase, broken fan and schlieren textures were observed on cooling from the induced smectic A phase. Unfortunately, a glass transition temperature could not be found by DSC measurement in the range from -100°C to 170°C .

P62/TN7(y) showed a schlieren with

Table 1. Phase transition temperatures of P62/TN7(y)

y ^a	Phase transition temp. ^b /°C
0.33	SmC 51 SmA 127.6 N 135.2 I
0.4	SmC 40 SmA 117.7 N 140.2 I
0.5	SmC 44 SmA 120.6 N 146.7 I

a) y: mole fraction of TN7.

b) SmC: induced smectic C phase; SmA; smectic A phase; N; nematic phase; I; isotropic Phase.

two brushes in addition to a schlieren with four brushes exhibiting by ordinary smectic C liquid crystals. The existence of these schlierens indicates the formation of an antiferroelectric-like zigzag orientational ordering. [8-11]

The formation of the induced smectic C phase in P62/TN7(y), which was not created by P62/TN8(x), is due to a conformation of TN7 with the odd-numbered central methylene units. The same feature also was found for the liquid crystalline binary systems consisting of odd-membered twin compounds. [8]

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