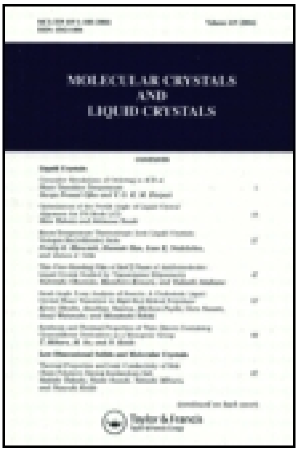

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Phase Transitions of Liquid Crystalline Polymethacrylates having 4-(4-Substituted Phenylazo)phenyl Benzoate in a Mesogenic Side Chain

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Phase Transitions of Liquid Crystalline Polymethacrylates having 4-(4-Substituted Phenylazo)phenyl Benzoate in a Mesogenic Side Chain

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Two types of liquid crystalline polymethacrylates, having 4-(4-substituted phenylazo)phenyl benzoate in a mesogenic side chain, were prepared. The relationship between the shape of the mesogenic side chain and the liquid crystallinity was studied.

Keywords: liquid crystalline polymethacrylate, nematic, smectic, thermal property, shape of mesogenic side chain

INTRODUCTION

Side chain liquid crystalline polymers with various types of mesogenic side chains have been prepared up to the present.[1,2] In side chain liquid crystalline polymers, the formation of liquid crystalline phases is directly affected by the molecular shape of a mesogenic side chain and interactions between mesogenic side chains.

We have synthesized two types of liquid crystalline polymethacrylates [P(m)-n-R, P(p)-n-R] having 4-(4-substituted phenylazo)phenyl benzoate, as shown in Figure 1. In a metha-linkage type of P(m)-n-R with a bent mesogenic side chain, a spacer is attached to a metha position of a mesogenic core. In a para-linkage type of P(p)-n-R with a linear mesogenic side chain, however, the spacer is attached to a para position of the mesogenic core.

In this paper, phase transitions of P(m)-n-R and P(p)-n-R are compared.

RESULTS AND DISCUSSION

The methacrylic monomers were synthesized through the reaction scheme shown in Figure 2. The liquid-crystalline polymethacrylates [P(m)-n-R, P(p)-n-R] were obtained by radical polymerization of the methacrylic monomers.

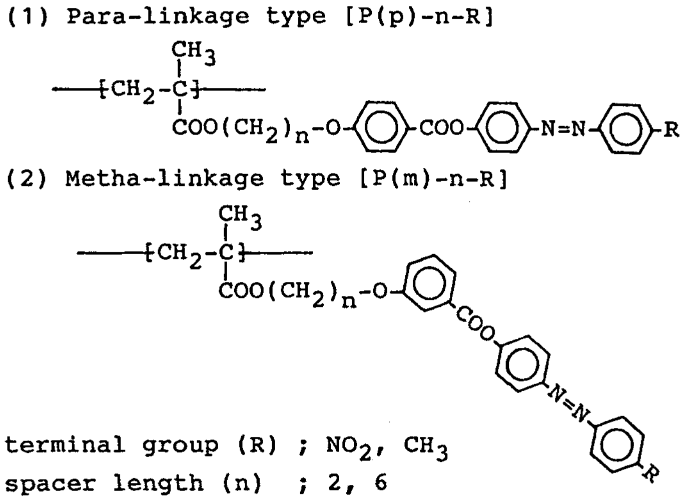

FIGURE 1 Structures of P(p)-n-R with the linear mesogenic side chain and P(m)-n-R with the bent mesogenic side chain.

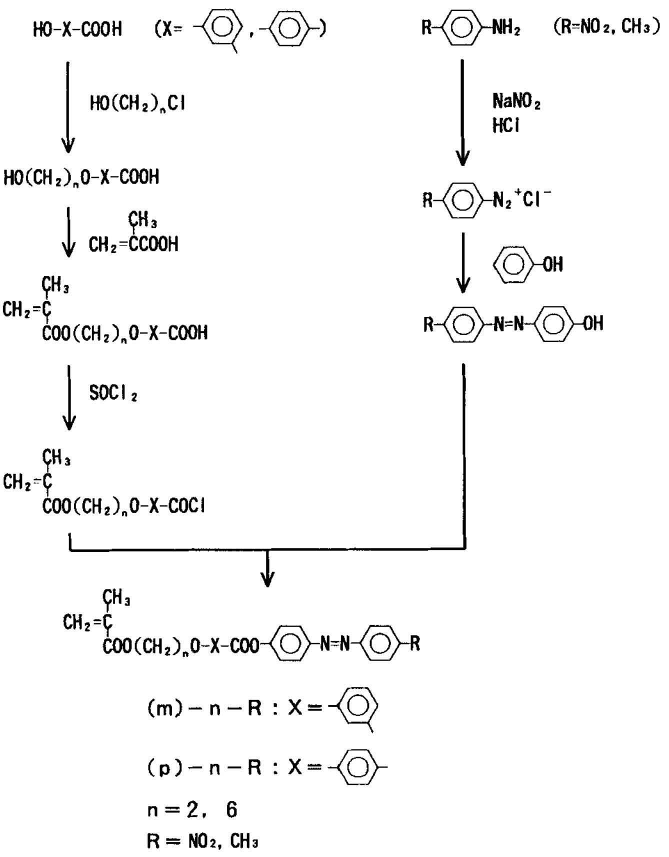

FIGURE 2 Synthetic scheme of methacrylic monomers.

TABLE I

Phase transition temperatures of methacrylic monomers

Sample	Phase transition temp.[a] / °C							
(m)-2-NO_2	K	124	I					
(m)-6-NO_2	K	84	I					
(m)-2-CH_3	K	95	I					
(m)-6-CH_3	K	75	I					
(p)-2-NO_2	K	155	N	200	I			
(p)-6-NO_2	K	123	Sm	185	N	208	I	
(p)-2-CH_3	K	110	N	166	I			
(p)-6-CH_3	K	97	N	163	I			

a)K ; solid phase: N ; nematic phase: Sm ; smectic phase: I ; isotropic phase. The phase transition temperatures are quoted from the first heating run since the monomers are polymerized by heating.

TABLE II

Phase transitions of polymethacrylates

Sample	$\overline{Mn}$	Phase transition temp.[a] / °C						
P(m)-2-CH_3	16000	G	61	I				
P(m)-6-CH_3	53000	G	46	I				
P(m)-2-NO_2	20000	G	84	Sm	194	I		
P(m)-6-NO_2	16000	G	36	Sm	190	I		
P(p)-2-CH_3	39000	G	85	X	208	N	291	I
P(p)-6-CH_3	19000	G	61	X	126	N	248	I
P(p)-2-NO_2	14000	G	55	Sm	295	I		
P(p)-6-NO_2	14000	G	45	Sm	295	I		

a) G; glassy state: X; unidentified phase: Sm; smectic phase: N; nematic phase: I; isotropic phase.

The phase transitions were measured with a Mettler DSC 20 and an Olympus polarizing microscope BH-2 equipped with a Mettler FP52 hot stage apparatus. Molecular weights of the polymers were determined by a Toso GPC HLC-802UR, calibrated with standard polystyrenes.

The thermal properties of methacrylic monomers are summarized in Table I. The rod shape of all methacrylic monomers [(p)-n-R] formed liquid crystalline phases. However, the bent shape of all methacrylic monomers [(m)-n-R] exhibited no mesophases because the bent molecules in (m)-n-R have larger excluded volumes than the rod shape of molecules in (p)-n-R and are difficult to form a liquid crystalline orientation.

The para-linkage type of P(p)-2-CH_3 and P(p)-6-CH_3 formed enantiotropically nematic phases with schlieren textures. However, the metha-linkage type of P(m)-

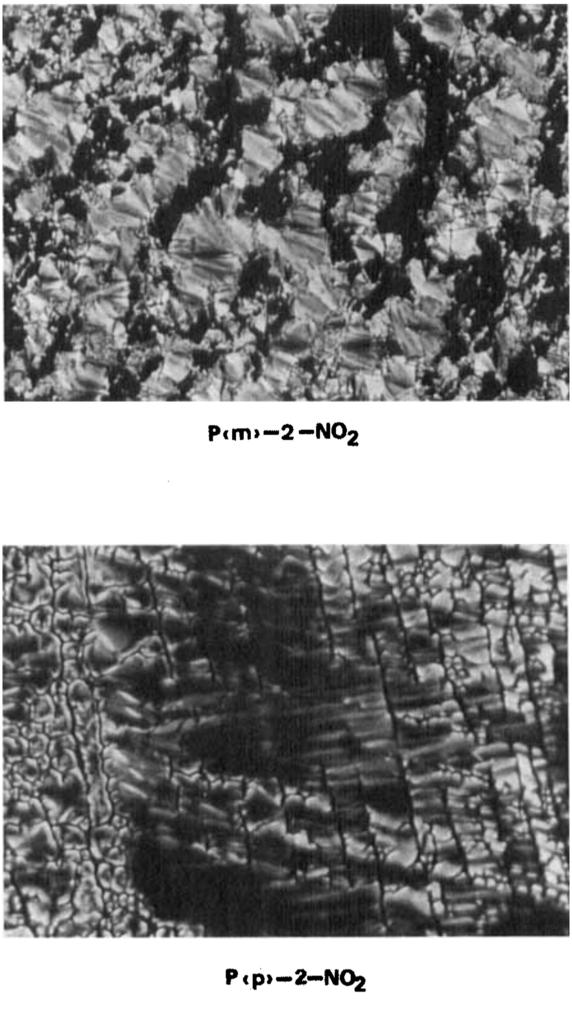

FIGURE 3 Smectic textures of P(m)-2-NO_2 and P(p)-2-NO_2. See Color Plate XX.

n-CH_3 exhibited no mesophase. This demonstrates that P(p)-n-CH_3 with the linear mesogenic side chain has higher liquid crystallinity when compared to P(m)-n-CH_3 with the bent mesogenic side chain. In addition, this corresponds to the fact that, in general, a rigid-rod molecular shape is competent to form a liquid crystalline orientational order.

On the other hand, both P(m)-n-NO_2 and P(p)-n-NO_2 exhibited enantiotropically smectic phases with fan textures. The smectic fan textures are shown in Figure 3.

Phase transition temperatures of P(m)-n-R and P(p)-n-R are summarized in Table II. P(p)-n-NO_2 exhibited a higher smectic-isotropic phase transition temperature when compared to P(m)-n-NO_2. This demonstrates that P(p)-n-NO_2, having the linear mesogenic side chain, forms the smectic phase with enhanced thermal stability when compared to P(m)-n-NO_2 having the bent mesogenic side chain. This also corresponds to the fact that the linear mesogenic side chain is competent to form a mesophase in the same manner as the relationship between P(m)-n-CH_3 and P(p)-n-CH_3.

In general, as the spacer length (n) increases from 2 to 6, a temperature at which an isotropic phase forms decreases in the same manner as P(p)-n-CH_3. However, in the case of P(p)-n-NO_2 and P(m)-n-NO_2, having the nitro terminal group, the smectic-isotropic phase transition temperature is independent of the spacer length. P(m)-2-NO_2 and P(m)-6-NO_2, having the nitro terminal group, showed similar smectic-isotropic phase transition temperatures. Also, in P(p)-2-NO_2 and P(p)-6-NO_2, the smectic-isotropic phase transition temperatures were the same. In this case, the thermal stabilities of the smectic phases are not affected by the spacer length. In addition, smectic-isotropic transition enthalpies of P(m)-2-NO_2 and P(m)-6-NO_2 were 3.0 kJ/(unit mol) and 3.3 kJ/(unit mol), respectively. This also indicates that the thermal stability of the smectic phase in P(m)-2-NO_2 is similar to that in P(m)-6-NO_2.

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