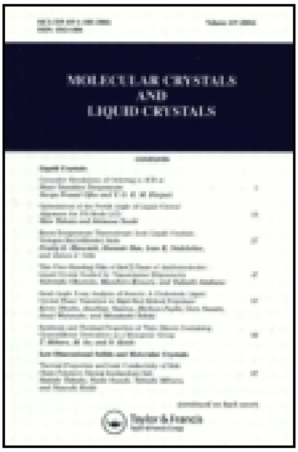

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Phase Transitions of Liquid Crystalline Polyacrylamide

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The liquid crystalline polyacrylamides (PAAD-R) having secondary or tertiary amide groups were synthesized and the thermal properties of PAAD-R were studied. PAAD-H with the secondary amide group exhibited enantiotropically smectic phases with enhanced thermal stability through the formation of hydrogen bonding between amide groups when compared to PAAD-M with the tertiary amide group. Also, a liquid crystalline polyacrylate, which has the same mesogenic side chain as PAAD-H, was prepared and the thermal properties of PAAD-H and PA were compared.

Keywords: liquid crystalline polyacrylamide, secondary amide group, hydrogen bonding, thermal property, smectic

INTRODUCTION

In general, organic compounds containing primary or secondary amide groups have much higher melting points when compared to organic ester compounds because of the formation of the hydrogen bonding between amide groups (e.g. phenylbenzoate; mp 69–72°C: benzanilide; mp 164–166°C). In addition, the hydrogen bonding sometimes enables organic molecules to form the liquid crystalline phase.[1,2]

We consider that the introduction of the hydrogen bonding group, just as the secondary amide group, into liquid crystalline polymers is effective for the improvement of thermal properties and liquid crystal formation.

We have synthesized liquid crystalline polyacrylamides (PAAD-R) and polyacrylate (PA) with the same mesogenic side chain as PAAD-R. This paper describes phase transitions of PAAD-R and PA.

RESULTS AND DISCUSSION

Figure 1 shows the synthetic scheme of monomeric acrylate and acrylamides. The monomers were identified by ^{1}H NMR measurement. PAAD-R and PA

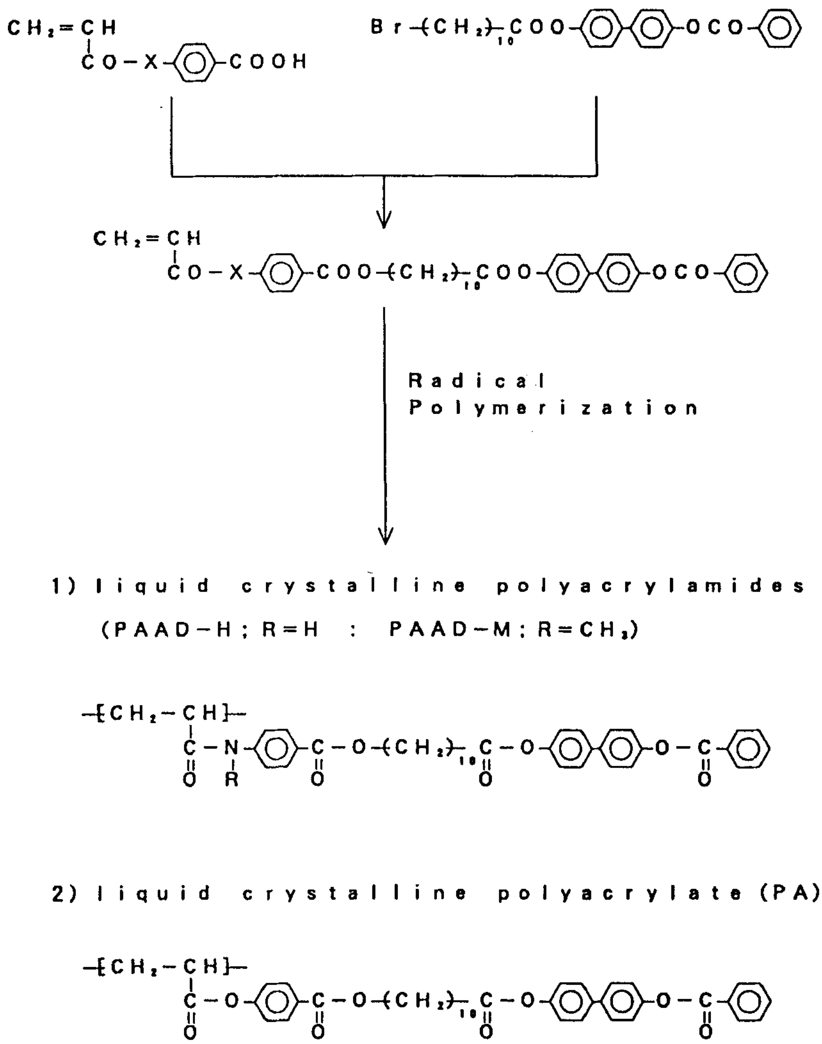

FIGURE 1 Structures of liquid crystalline polyacrylamides and polyacrylate.

were synthesized by radical polymerization of corresponding mesogenic monomers.

In PAAD-R, the mesogenic side chain is attached to the skeletal main chain through the amide linkage group. PA has the structure in which an ester linkage group displaces the amide linkage group in PAAD-R.

The phase transition temperatures were measured with a Mettler DSC 20 and an Olympus polarizing microscope BH-2 equipped with a Mettler hot stage apparatus, and summarized in Table I.

PA and PAAD-R all exhibited two types of enantiotropically ordered smectic phases with mosaic textures in the temperature range of T_g to T_i (Table I). The presence of mosaic textures indicates the formation of the ordered smectic phases.[3]

TABLE I

Phase transition temperatures

Sample	$\overline{Mn}$ a)	T_g b) / °C	T_s c) / °C	T_i d) / °C
Polyacrylamide				
PAAD-H	6000	92.5	157.9	209.8
	12000	94.6	164.3	241.1
PAAD-M	12800	39.0	126.0	156.0
Polyacrylate				
PA	6000	56.0	121.0	143.0
	18000	62.0	132.0	151.3

a) Number-average molecular weight determined with GPC, calibrated by standard polystyrenes.

b) Glass transition temperature.

c) Highly-ordered smectic-ordered smectic phase transition temperature.

d) Ordered smectic-isotropic phase transition temparature.

In the ordered smectic phases, forming in the temperature range of T_g to T_s (Table I), a single scattering peak in the wide-angle X-ray region was measured. This demonstrates that the ordered phases with mosaic textures are not solid phases.[4]

PAAD-H containing the secondary amide group showed a higher smectic-isotropic phase transition temperature when compared to PAAD-M containing the tertiary amide group. Also, the smectic-isotropic phase transition temperature (T_i) of PAAD-H was higher than T_i of PA. The increase in the thermal stability of PAAD-H is due to the formation of the hydrogen bonding between secondary amide groups.

The effect of temperature on the hydrogen bonding between secondary amide groups was examined by FT-IR measurements.[5] In the smectic phase (100°C and 130°C), the band of the stretching vibration of the amide N-H was measured at 3300 cm^{-1}, which indicates the stretching vibration due to the formation of the hydrogen bonding between amide groups. In the isotropic phase (220°C and 240°C), however, the band for the stretching vibration of the amide N-H shifted to a lower frequency at 3420 cm^{-1}. In this case, the smectic orientation of PAAD-H becomes disordered because the hydrogen bonding becomes less stable.

This paper demonstrates that the formation of the hydrogen bonding between secondary amide groups in liquid crystalline polymers acts effectively, forming the smectic phase with enhanced thermal stability.

Acknowledgment

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4. X-ray scattering curves were measured with a Rigaku Rad 2B system with CuK_α.
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