Phase Transition Behavior in Side-chain Liquid Crystal Polymers of Different Chain-backbones

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1. Introduction

Side-chain liquid crystal polymers (SCLCPs) have attracted considerable attention because of the combination of polymeric properties and the electrooptic characteristics of low molar mass side chains. This unique feature makes these polymers a promising candidate for use in advanced electrooptic technologies \cite{1}. So far, many reported SCLCPs have been prepared by radical polymerization of vinyl monomers possessing mesogenic substituents. Difference of the phase behaviors in these polymers is mainly derived from the difference in the mesogenic groups used.

We have been continuing the project on the synthesis and the application of poly(fumarate)s, which can be prepared either by radical or methathesis polymerization of fumarates \cite{2, 3} or by polymer reaction of poly(fumaric acid) \cite{4}. The resulting polymers possess a rigid backbone originating from the bulky side-chains. Recently, we became interested in expanding the poly(fumarate)s to SCLCPs, since the effect of the polymer backbone in SCLCPs has not extensively been studied for well-defined polymers \cite{5}. Besides the rigidity of the polymer backbone, one of the most important features of poly(fumarate)s is the capability of the high side-chain density especially when liquid crystallinity is expected. Introduction of a mesogenic group into every methylene unit of the polymer backbone doubles the mesogenic density as compared to the vinyl polymers, leading to a facile appearance of liquid crystal phase \cite{6, 7}.

Here we report the phase transition behaviors of novel poly(fumarate)s bearing cyanobiphenyl mesogenic groups. Increase in the mesogen density results in the formation of enantiotropic liquid crystal phase in a relatively wide temperature range.

2. Experimental

Fumarate monomers 1 and 2 were newly synthesized by the modified Williamson method followed by esterification. They were polymerized with benzoyl peroxide (BPO) as an initiator in bulk at 80 °C for 10 days. The

![Scheme 1 Synthesis of P1 and P2.](image-url)
molecular weights of the polymers were measured by GPC (chloroform eluent, calibrated by polystyrene standard). Phase transition temperatures of monomers and polymers were determined by differential scanning calorimetry (DSC) using a Rigaku Thermo plus DSC8230. The heating and cooling rates were 10 °C min⁻¹. The clearing points and the glass transition temperatures (T_g) were determined by the heating and cooling scans, respectively. Polarized optical micrographs (POMs) of the samples were taken by an Olympus BX-50 microscope with a heating stage attached to a temperature controller.

3. Results and discussion

Fumarates 1 and 2 were polymerized with BPO to furnish the corresponding polymers P1 and P2, respectively. The molecular weights (M_w) of P1 and P2 were 11000 and 16000, respectively, and the polydispersions (M_w/M_n) were 1.1 and 1.9, respectively.

Phase transition behaviors of P1 and P2 were characterized by DSC and POM measurements. The DSC trace of P1 clearly displayed the presence of a liquid crystal phase, whereas P2 did not show any mesophases (Fig. 1). This liquid crystal phase of P1 was observed upon both heating and cooling cycles, indicating the enantiotropic liquid crystal phase. The clearing points of P1 dramatically increased as compared to that of the monomer 1 (from 26.3 °C for 1 to 141.7 °C for P1). On the other hand, an increase in the transition temperature from the glass state to liquid crystal phases is less significant (from -0.5 °C for 1 to 34.0 °C for P1). These results suggest the expansion of the liquid crystal temperature range upon polymerization. Similar phase behavior was also observed for P2. The T_g of 45.7 °C for P2 is much higher than that of 2 (-19.2 °C).

The POM measurements supported the DSC results. The POM image of P1, measured at 100 °C upon cooling, exhibited fan-shaped textures, revealing the smectic phase of the mesophase (Fig. 2). On the other hand, P2 did not show any specific textures over the temperature range measured. Considering the fact that many vinyl polymers bearing cyanobiphenyl groups exhibit liquid crystal phases [8], the rigid poly(fumarate) backbone requires more mesogenic groups for use as SCLCPs. In other words, higher mesogen density is more advantageous for realization of SCLCPs. Since poly(fumarate)s bearing a mesogenic group at every methylene unit of the polymer backbone were revealed to possess a wide liquid crystal temperature range, they are promising functional materials for the practical utility in advanced electrooptic technologies.

References