Preparation of polymethacrylate-based side-chain liquid crystalline polymers with various lengths of aliphatic spacer and their electrorheology

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Abstract−Three kinds of side-chain liquid crystal polymers (SCLCPs) were prepared in which the lengths of the flexible aliphatic spacer were 6, 8, and 12 methylene units. The SCLCPs consisted of a polymethacrylate backbone carrying cyanobiphenyl mesogenic groups as side chains. All the polymers exhibited liquid crystalline behavior of smectic A phase. The glass transition temperature decreased with increasing aliphatic spacer length. Electrorheological (ER) suspensions were prepared by dispersing the SCLCP particles in silicone oil and their ER effects were investigated. The ER response increased with increasing aliphatic spacer length, indicating that the spacer length between the polymethacrylate backbone and polar mesogenic groups influenced the ER behavior.

Key words: Electrorheology, Electrorheological Fluid, Suspension, Side-chain Liquid Crystal Polymer

INTRODUCTION

Electrorheological (ER) fluids are suspensions of polarizable non-conducting or semiconducting particles in a nonconducting continuous phase of low relative polarizability [1-4]. In the absence of an electric field, they have the properties of suspensions of neutral solid particles. Upon the application of an electric field, particles form an organized structure and the ER fluids exhibit a remarkable change in rheological properties, including a drastic increase in apparent viscosity and yield stress. Due to their fast response time and controllable shear viscosity, the ER fluids have been widely used for various engineering applications such as dampers, clutches and adaptive structures [2].

To solve the limitations of water-based ER systems, such as thermal stability, poor durability and corrosion, anhydrous ER fluids using semiconducting polymer particles [5] and semiconducting polymer-nanocomposites [6-8] were used for ER fluids and showed promising ER responses.

Side-chain liquid crystal polymers (SCLCPs) have also been proposed for ER fluids to avoid the above limitations. SCLCPs, which show combined properties of liquid crystals and polymers, have attracted great research interest because of their potential applications. SCLCPs comprise three structural units: a polymer backbone, flexible spacer, and mesogenic group. The flexible spacer is introduced to decouple the motions of the mesogenic groups to self-assemble from that of the polymer backbone. SCLCPs therefore show polymer characteristics coupled with the electro-optic properties of low molar mass mesogens. This combination of properties has led to the proposed use of SCLCPs in areas such as optical information storage and nonlinear optics [9].

SCLCPs especially showed a relatively large change in shear stress under electric field, because the motion of the terminal mesogens was free from that of the polymer backbone [10], but their ER response was too weak for practical use [11-12]. In addition, the response time for an applied electric field was low, which was one of the problems in homogeneous ER fluids composed of SCLCPs. To overcome this problem, dilution by low viscosity silicone [12], blend system or immiscible fluids [10], and dilution by liquid crystal solvents [13] were tried.

We prepared three kinds of SCLCPs by varying the aliphatic spacer length between a polymer backbone and mesogenic groups. The SCLCPs were composed of a polymethacrylate backbone and cyanobiphenyl mesogenic groups as side chains with various lengths of aliphatic spacer. ER suspensions were prepared by dispersing the SCLCPs in silicone oil. The ER response of the SCLCP suspensions and the effect of spacer length on their ER response were investigated.

EXPERIMENTAL

1. Preparation of Monomer

Monomers for SCLCPs of a polymethacrylate backbone carrying cyanobiphenyl mesogenic groups as side chains were prepared by using a procedure similar to that described by Shibaev et al. [14] and others [9,15]. Identical procedures were used to prepare all the monomers, including aliphatic spacers sourced from 6-bromo-1-hexanol (6-BH, TCI), 8-bromo-1-hexanol (8-BH, TCI), and 12-bromo-1-hexanol (12-BH, TCI), and hence a representative description is given for the monomer synthesis using 6-BH as a spacer source.

4-Hydroxyhexyloxy-4′-cyanobiphenyl was prepared by refluxing a phenolate solution for 24 h. The phenolate solution was obtained by adding 6-BH (5.00 g) dissolved in dimethylformamide (16.75 mL, Aldrich) to a stirred solution of 4-cyano-4′-hydroxybiphenyl (5.00 g, TCI), K_2CO_3 (5.00 g, TCI), and ethanol (90 mL). After the reaction was over, the reaction mixture was filtered hot to remove the KBr by-product. Distilled water was added to the filtrate which was shaken. The organic layer was separated, washed with water,

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and dried. The residue was twice recrystallized from benzene to obtain 4-hydroxyhexyloxy-4′-cyanobiphenyl.

4-Hydroxyhexyloxy-4′-cyanobiphenyl (5.00 g) and triethylamine (3.38 g, Aldrich) were dissolved in tetrahydrofuran (THF, 70 mL) at 5 °C. 4-[ω-(2-Methylpropenoyloxy)hexyloxy]-4′-cyanobiphenyl was obtained by acylation of the dissolved solution by slowly adding methacryloyl chloride (3.71 g, Aldrich) solution dissolved in THF (70 mL) at 5 °C for 24 h. The reaction mixture was filtered to remove triethylamine salt and the THF in the filtrate was evaporated by a rotary evaporator. The filtrate was separated, washed with water, and dried. The residue was twice recrystallized from methanol. The reaction scheme for the synthesis of the monomer using 6-BH as a spacer source is presented in Fig. 1.

The monomers synthesized using 6-BH, 8-BH, and 12-BH are here designated as BP-6, BP-8, and BP-12, respectively, with the number representing the methylene number of n-aliphatic substituent in the flexible spacer.

2. Preparation of SCLCP

SCLCPs of different lengths of the flexible aliphatic spacer were obtained by radical polymerization of the respective monomer (BP-6, BP-8, or BP-12) in THF (10 mL) in the presence of N_2. THF was used as a solvent while the initiator was 2,2-azoisobutyronitrile (AIBN, Aldrich). The monomer (BP-6, BP-8, or BP-12) was taken in an amount of 15% by weight and the initiator 0.1% by weight. The polymerization was conducted at 60 °C for 24 h. The polymers were filtered and washed three times by methanol to remove by-products and were dried in vacuum for 24 h. The reaction scheme for the synthesis of the SCLCP from BP-6 is presented in Fig. 2.
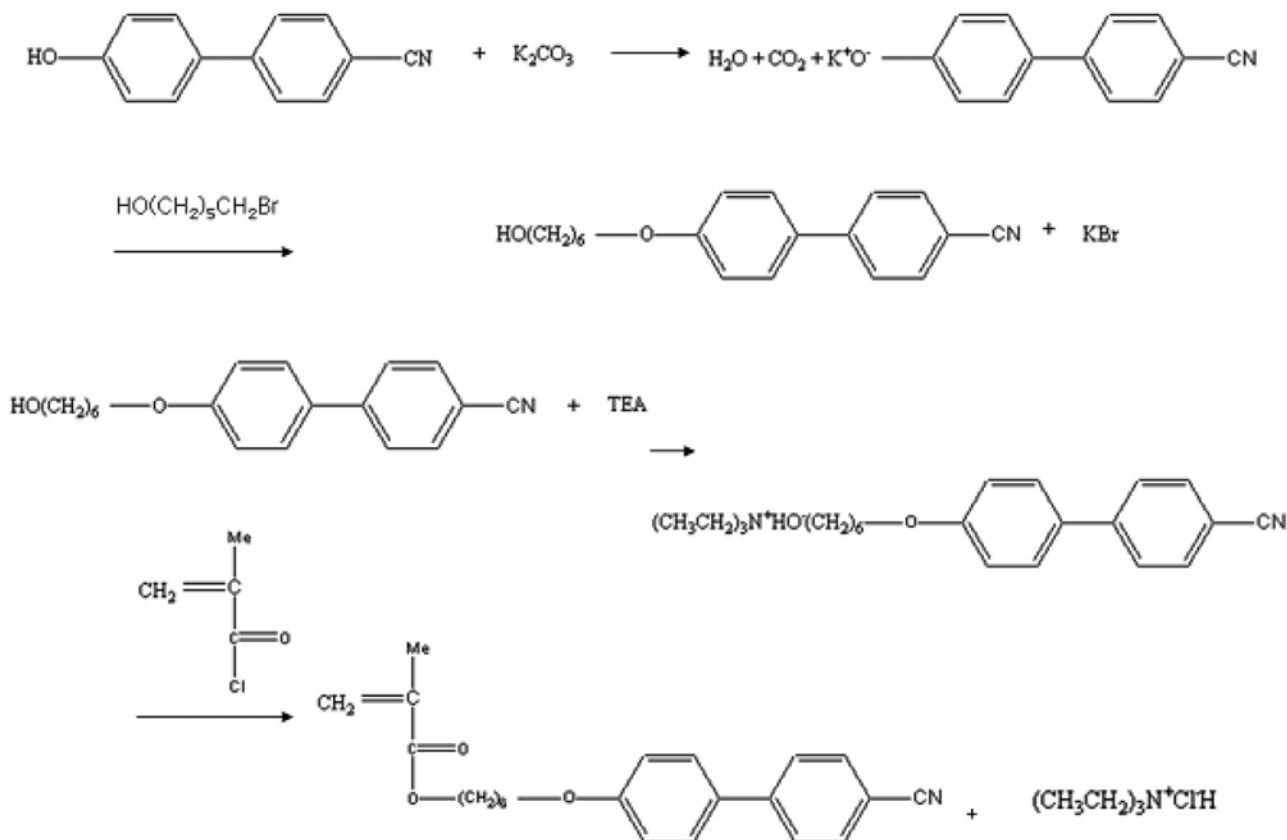

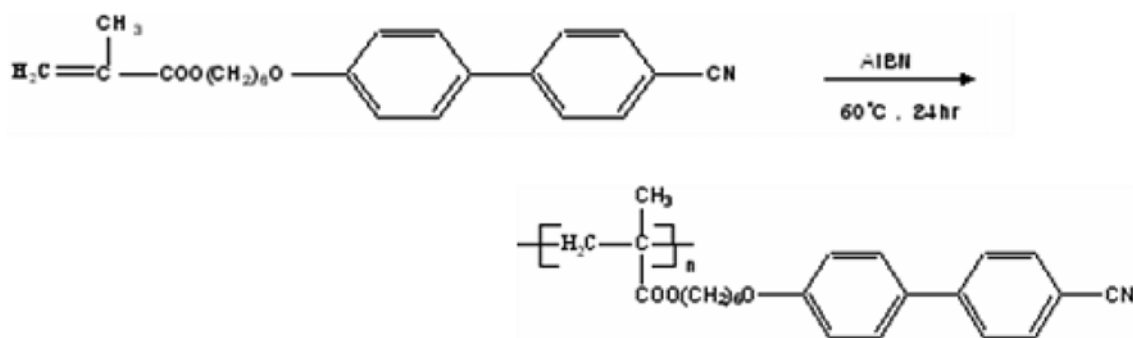Fig. 1. Reaction scheme for the synthesis of the monomer using 6-BH as a spacer source.

Fig. 2. Reaction scheme for the synthesis of the SCLCP from BP-6.

3. Measurements

ER suspensions were prepared by dispersing SCLCP particles in silicone oil (Donyang Silicone, η_c=100 cP, ρ_c=0.96 g/cm³). Rheological experiments were performed at 25 °C on a Rheometric ARES rheometer fitted with parallel plates, and modified for the application of large electric fields. Potential differences were supplied by a high-voltage dc power supply. Samples were placed between the parallel plates and sheared for 1 min at a large shear rate (>40 s⁻¹) and zero field strength to ensure a uniform particle distribution. No sedimentation and distortion of samples were observed after the shearing. The desired electric field was then applied for 1 min with no shear prior to measurements. Attainment of the steady state under the applied electric field was confirmed by changing the application time of the electric field. The time for attaining the steady state was observed as less than 10 sec. Rheological measurements were performed by shearing the suspension at a constant shear rate under the applied electric field, and recording the shear stress transmitted by the suspension.

The dielectric constants of SCLCP particles were measured by using compressed disks with a Fluke impedance analyzer (Fluke 6306A RLC meter). The conductivities of SCLCP particles were measured by the two-probe method using compressed disks with a picoammeter (Keithley 485).

The conductivities of the SCLCP particles were measured as 1.92×10^{-12}, 1.71×10^{-12}, and 1.52×10^{-12} S/cm for SCLCPS of BP-6, BP-8, and BP-12, respectively; almost the same regardless of the aliphatic spacer length. The dielectric constants of the SCLCP particles were measured as 9.7, 12.7, and 15.2 at 100 Hz for SCLCPs of BP-6, BP-8, and BP-12, respectively, increasing with increasing aliphatic spacer length.

RESULTS AND DISCUSSION

Fig. 3 shows the FT-IR spectra of BP-6 and the SCLCP of BP-6 for comparison. The monomer, BP-6, formation was confirmed by the following characteristic absorptions of the FT-IR spectrum (Fig.
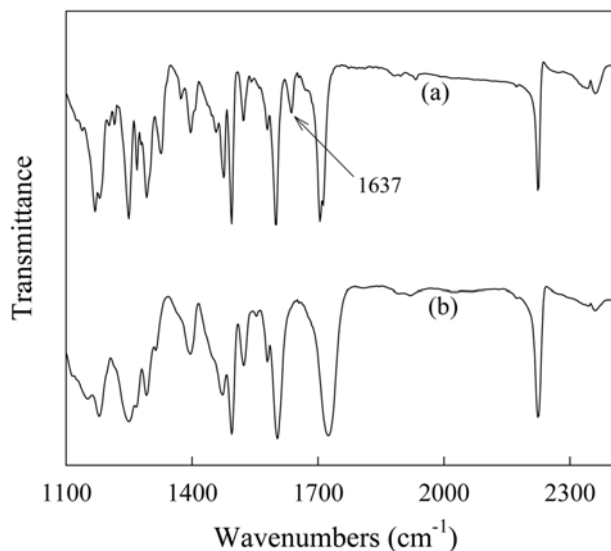
3(a)) of this compound (cm⁻¹): 2,223 (C≡N); 1,704 (C=O); 1,637 (C=C); 1,598, 1,494 (C-C aromatics); 1,249, 1,168 (C-O-C). The FT-IR spectrum (Fig. 3(b)) of the SCLCP of BP-6 shows the following characteristic absorptions (cm⁻¹): 2,223 (C≡N); 1,724 (C=O); 1,602, 1,494 (C-C aromatics); 1,251, 1,278 1,168 (C-O-C). The alkene stretch at 1,637 cm⁻¹ in the spectrum of BP-6 was not present in that of the corresponding SCLCP, indicating the formation of the SCLCP of BP-6. For SCLCPs of BP-8 and BP-12, the removal of the alkene stretch peak in the FT-IR spectra was also observed.

The molecular weights of the SCLCPs were measured by gel permeation chromatography (GPC), using THF as the eluent. A calibration curve was obtained using polystyrene standard. The molecular weight, polydispersities, and average degree of polymerization are listed in Table 1. The number average molecular weights of the SCLCPs range from 5,780 to 9,113 g/mol with corresponding degrees of polymerization in range 16-23.

The thermal properties of the SCLCPs were determined by differential scanning calorimetry (DSC). Two samples were used for

Table 1. Molecular weight, polydispersities (PD), and number average degree of polymerization (DP) for the SCLCPs

	$\overline{M_n}$	$\overline{M_w}$	PD	DP
SCLCP of BP-6	5780	16903	2.92	16
SCLCP of BP-8	9113	28079	3.08	23
SCLCP of BP-12	8662	25033	2.74	19

Table 2. Thermal properties of the SCLCPs extracted from the second heating DSC trace

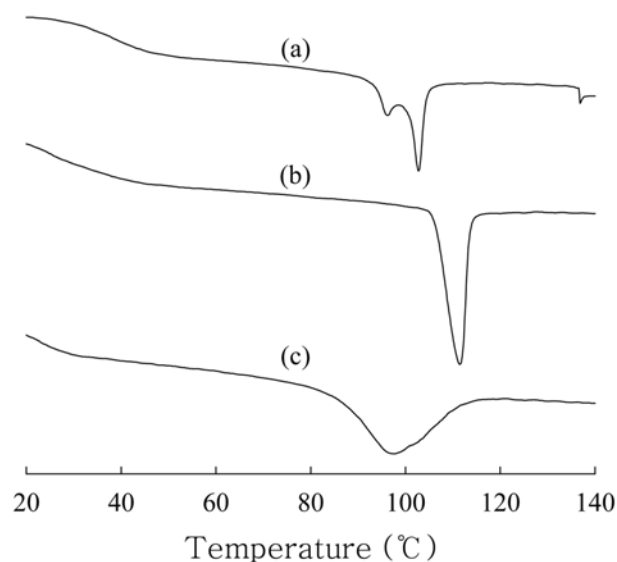|	T_g (°C)	T_{si} (°C)	ΔH_{si} (J/g)
Polymer of BP-6	44	102.7	4.19
Polymer of BP-8	40	111.5	6.02
Polymer of BP-12	27	97.5	9.97

Fig. 3. FT-IR spectra of (a) BP-6 and (b) SCLCP of BP-6.

Fig. 4. DSC thermograms of the SCLCPs during second heating; (a) SCLCP of BP-6, (b) SCLCP of BP-8, and (c) SCLCP of BP-12.

each SCLCP and the results averaged. The heating and cooling rate in all cases was 10 ℃/min. All SCLCPs exhibited a glass transition temperature. The thermal property data of the SCLCPs are listed in Table 2. The glass transition temperature (T_g), clearing temperature (T_{si}), and associated enthalpy change were extracted from the second heating cycle of the DSC time-temperature profile. The glass transition temperature decreased with increasing spacer length. The traces are shown in Fig. 4. When viewed through polarizing optical microscopy, on cooling from the isotropic phase, poorly defined liquid crystal phases appeared for all SCLCPs and these phases were assigned as smectic A.

The SCLCP suspensions showed typical ER behavior, which is characterized as a Bingham fluid, exhibiting a yield stress under an applied electric field. The steady-shear rheological response of ER suspensions is usually modeled as that of a Bingham fluid [16].

$$\tau = \tau_o + \eta \dot{\gamma} \tag{1}$$

where τ is the shear stress, τ_o is the yield stress, η is the viscosity, and $\dot{\gamma}$ is the shear rate.

The ER behavior under various electric field strengths is presented in Fig. 5 for a 5 wt% SCLCP suspension of BP-12 in silicone oil. Without an electric field, the suspension behaved like a Newtonian fluid with the slope of 1.0. By applying an electric field to the suspension, the shear stress for the ER suspension increased and the suspension showed a yield stress, thereby demonstrating shear thinning behavior. The shear stress and yield stress increased with increasing electric field strength. The steady-shear rheological response under the applied electric field is equivalent to the flow behavior of the Bingham fluid - an apparent yielding phenomenon at low shear rates and shear thinning behavior approaching a constant viscosity at high shear rates.

The shear stress as a function of shear rate is presented in Fig. 6 for 5 wt% SCLCP suspensions of different lengths of aliphatic spacer (BP-6, BP-8, and BP-12) at the electric field strength of 1.5 kV/mm. The shear stress increased with increasing aliphatic spacer length
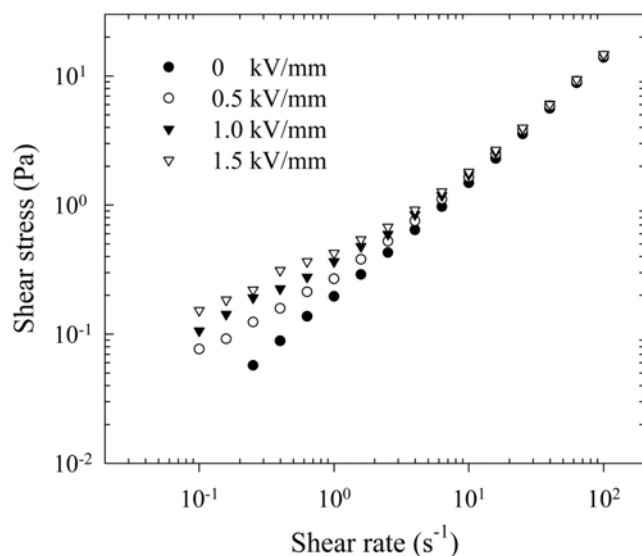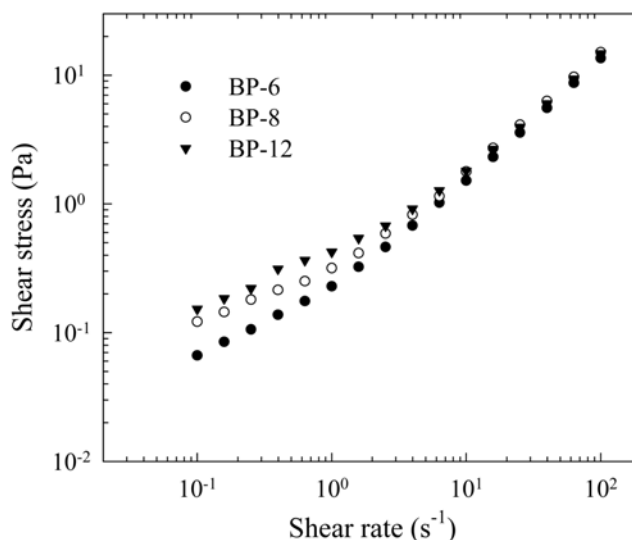

Fig. 6. Shear stress as a function of shear rate for 5 wt% SCLCP suspensions of BP-6, BP-8, and BP-12 at the electric field strength of 1.5 kV/mm.

at low shear rates, while the shear stresses were almost the same at high shear rates.

At low shear rates, polarization forces are dominant over hydrodynamic forces and the shear stress is mainly determined by polarization forces induced by the applied electric field.

At high shear rates, hydrodynamic forces are dominant. The shear stress arises from purely hydrodynamic forces and the suspension viscosities are independent of the polarization forces - the shear stress is proportional to shear rates and suspensions viscosities of various SCLCP suspensions approaching a constant value.

The results showed that at low shear rates the spacer length between the polymethacrylate backbone and polar mesogenic groups influenced the ER response. In SCLCPs, the flexible spacer is introduced to decouple the motions of the mesogenic groups to self-assemble from that of the polymer backbone. The glass transition temperature (Table 2) exhibited a decrease with increasing aliphatic spacer length, supporting that the decoupling between the polymethacrylate backbone and the mesogenic groups increased with increasing aliphatic spacer length.

The conductivities of the SCLCP particles were measured as 1.92×10^{-12}, 1.71×10^{-12}, and 1.52×10^{-12} S/cm for SCLCPs of BP-6, BP-8, and BP-12, respectively, slightly decreasing with increasing aliphatic spacer length; almost the same regardless of the aliphatic spacer length. The conductivities do not agree with the ER behavior, indicating the conductive effect is minor on the ER effect of SCLCPs.

The ER response depends on the interfacial polarization, and the polarization force per pair interaction is given by [16]

$$F = 12\pi\varepsilon_o\varepsilon_c a^2 \beta^2 E^2 \tag{2}$$

where a is the particle radius, ε_o the permittivity of free space, ε_c the dielectric constant of the continuous phase, and E the applied electric field strength. The term $\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c)$ is the relative polarizability of the particle where ε_p is the particle dielectric constant. Therefore, the ER response will increase by enhancing the relative polarizability β and hence the particle polarization, which

Fig. 5. Shear stress as a function of shear rate for a 5 wt% SCLCP suspension of BP-12 in silicone oil.

is related to ε_p. The dielectric constants of the SCLCP particles were measured as 9.7, 12.7, and 15.2 at 100 Hz for SCLCPs of BP-6, BP-8, and BP-12, respectively. Therefore, the polarizability β of the SCLCP particles in silicone oil (ε_c=2.7) was 0.46, 0.53, and 0.61 for SCLCPs of BP-6, BP-8, and BP-12, respectively, increasing with increasing aliphatic spacer length, consistent with the ER behavior.

Therefore, the ER enhancement with increasing aliphatic spacer length seems to arise from decoupled motions of the mesogenic groups from the polymer backbone, which would lead to the increased polarization and hence enhanced ER response.

CONCLUSION

Three kinds of monomers for SCLCPs, with different aliphatic spacer lengths between the polymethacrylate backbone and cyanobiphenyl mesogenic groups, were synthesized and used to prepare the corresponding SCLCPs by radical polymerization. The ER effects of the SCLCP suspensions were investigated. The ER response increased with increasing aliphatic spacer length. The interactions between the polymethacrylate backbone and polar mesogenic groups decreased due to the increasing flexibility of the spacer, resulting in a decoupling between the polymethacrylate backbone and polar mesogenic groups, which seems to enhance the ER response. The measured glass transition temperatures also supported the decoupling between the polymethacrylate backbone and mesogenic groups.

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