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Thermal diffusivity of side-chain-polymer smectic liquid crystals

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ABSTRACT

The thermal diffusivity in the smectic liquid crystals (LCs) of side-chain P*m*BE*n* polymers was measured using the temperature wave method. P*m*BE*n* polymers form two types of smectic LCs that differ in their degree of side-chain overlap, which affects the thermal diffusivity. Smectic A_1 (SmA_1) LCs with fully interdigitated side chains have 20% greater thermal diffusivity than smectic A_d LCs with side chains overlapping at the alkyl tail. The results for magnetically oriented SmA_1 LCs show that the thermal diffusivity component along the LC director direction ($\alpha_{//}$) is larger than that perpendicular to the director direction ($\alpha_\perp$). Upon increasing the number *m* of methylene units in the spacer from 5 to 12, $\alpha_{//}$ increases from 2.50×10^{-7} to 3.11×10^{-7} m^2 s^{-1} and is larger for odd-*m* homologues, although $\alpha_\perp$ is almost constant around 1.25×10^{-7} m^2 s^{-1}. These variations in thermal diffusivity in P*m*BE*n* polymers are correlated with the smectic LC structures characteristic of side-chain LC polymers.

1. Introduction

Reducing the size and increasing the performance of electronic devices results in the generation of more heat in a smaller space. The importance of heat dissipation in such devices drives the demand for electrically insulating materials with high thermal conductivity. Although organic polymers are lightweight and flexible electrical insulators, they typically have very low thermal conductivities [1]. Although the thermal conductivity of polymer materials can be improved by doping them with inorganic fillers with high thermal conductivity, improvements in thermal conductivity are small even for large filler concentrations because the polymer matrix plays a major role in the heat-transfer process [2]. Moreover, high filler content leads to an undesirable weight increase and poor processability; thus, improving the thermal conductivity in polymers faces important challenges.

One proven method to increase the thermal conductivity in polymers is to stretch the polymer chains. Polyethylene (PE) fiber bundles subjected to ultra-high drawing and PE nanofibers exhibit thermal conductivities as high as 40 and 104 W m^{-1} K^{-1}, respectively, although among common thermoplastics, high-density PE exhibits the highest thermal conductivity (ca. 0.5 W m^{-1} K^{-1}) [3,4]. Main-chain liquid crystal (LC) polymers are attractive materials because they can spontaneously extend the chain backbone along the LC-orientation direction due to orientational order of mesogens contained in the backbone [5–8]. The most extended polymer chains, as well as LCs, can be macroscopically aligned by external fields such as flows and magnetic fields. In a previous study, we reported an injection-molded main-chain smectic LC polymer film that exhibits a maximum thermal conductivity of 1.2 W m^{-1} K^{-1} in the direction normal to the film [9]. Within these films, the polymer chains lie along the film normal. Such anisotropic thermal conductivity and polymer orientation leads to features contrary to those found in conventional LC polymers wherein the polymer chains are arranged along the flow direction and the greatest thermal conductivity is in the flow direction. The anomalous chain orientation in the film is ascribed to 40-nm-thick chain-folded lamellae, which prefer mutual sliding parallel to the film face [5,10,11]. In other studies, main-chain LC network films with the LC director aligned along the film normal were prepared by photoreaction in the presence of electric and magnetic fields along the film normal, and thermal conductivities of 2.4 and 0.34 W m^{-1} K^{-1}, respectively, were reported for these films [12,13].

The present paper reports the thermal diffusivity of the smectic LCs of side-chain LC polymers. The thermal diffusivity α is related to the thermal conductivity λ by $\lambda = \alpha \rho C_P$, where ρ and C_P are the mass density and heat capacity, respectively. Side-chain LC polymers have mesogens that are each connected to a polymer-chain backbone via a flexible spacer and form their own peculiar smectic structures. In smectic LCs, the side-chains are aggregated into layers and the backbones are confined in sublayers between the

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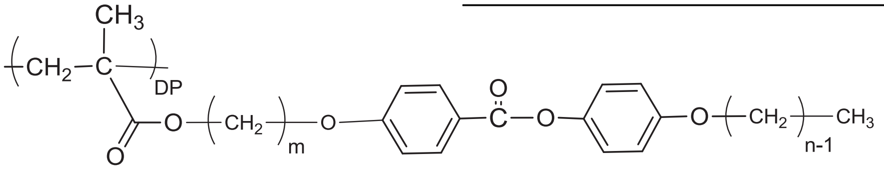
side-chain layers. The chain backbones are elongated preferentially perpendicular to the LC director, which corresponds to the average direction of the long axes of the mesogens [14–18]. The side chains extending from neighboring backbone sublayers overlap with each other in an antiparallel manner. The degree of overlap is affected by the side-chain chemical structure. This study examines smectic-liquid-crystalline P*m*BE*n* polymethacrylates. P*m*BE*n* has phenyl benzoate mesogens that attach an alkyloxy tail with *n* carbon atoms at one end and alkyl spacers with *m* methylene units at the other end. The chemical structure is shown below.



P*m*BE*n* polymers form the two types of smectic LCs. P*m*BE1 with $m = 5$–12 form smectic A_1 (SmA_1) LCs with fully interdigitated side chains. P4BE*n* and P6BE*n* with $n = 4$, 6 form smectic A_d (SmA_d) LCs with side chains overlapped only at the alkyl tail.

The results demonstrate that the smectic structure affects the thermal diffusivity α of P*m*BE*n*. The thermal diffusivity α of SmA_1 LCs is 20% greater than that of SmA_d LCs. The SmA_1 LC of P*m*BE1 increases α with *m*, which is larger for odd-*m* members. These variations in α between P*m*BE*n* smectic LCs are associated with the smectic structure characteristic of side-chain LC polymers. Larger α is expected for smectic LCs with side chains fully interdigitated and with backbones confined within a smaller space between layers of side chains.

2. Experiment

2.1. Materials

P*m*BE*n* polymers were prepared by atom-transfer radical polymerization [19]. The number- and weight-average molecular weights (M_n and M_w) of the polymers were determined using size-exclusion chromatography with polystyrene standards. None of the polymers crystallized and the LC phase vitrified. Table 1 gives the temperatures and the enthalpy changes of the phase transitions, which were determined by differential scanning calorimetry (DSC) thermograms (PerkinElmer Pyris1 DSC) measured at a heating rate of 10 °C min^{-1}.

Table 1
Characterization of polymers.

Sample	M_n[a] (kg mol^{-1})	PDI[a]	T_g[b] (°C)	T_1[c] (°C)	ΔH_1[c] (kJ mol^{-1})	T_i[d] (°C)	ΔH_i[d] (kJ mol^{-1})
P4BE1	18.4	1.26	56.6	–	–	102	0.544
P5BE1	36.1	1.21	64.2			132	5.61
P6BE1	19.0	1.48	40.2	69	0.200	109	0.872
P7BE1	24.5	1.35	39.0			130	5.68
P8BE1	27.8	1.27	34.0	99	–[e]	110	2.57
P9BE1	18.9	1.29	27.9			131	5.75
P10BE1	26.0	1.53	26.0			120	3.54
P12BE1	22.1	1.30	18.2			113	4.06
P4BE4	19.3	1.24	48.5			114	5.36
P4BE6	19.0	1.17	53.1			140	7.40
P6BE6	21.4	1.18	41.3			120	7.79

[a] Measured by SEC.
[b] Glass transition.
[c] LC–LC transition.
[d] Isotropization of LC.
[e] Overlap with the endothermic peak at T_i.

2.2. Methods

Monodomain LC films with the director oriented parallel or perpendicular to the film surface were prepared by applying a 3.8 T magnetic field to a polymer film in an aluminum pan. The film was cooled from the isotropic liquid phase to 30 °C at a rate of 0.1 °C min^{-1}. The film thickness was ca. 300 μm. The LC orientation was evaluated by X-ray diffraction (XRD) patterns measured using Cu Kα radiation with a Bruker D8 DISCOVER equipped with a Vantec 500 detector.

The thermal diffusivity α of the films in the thickness direction was measured at 23 °C based on a temperature wave (TW) analysis method [20] using an ai-Phase Mobile 1u (ai-Phase Co. Ltd., Tokyo, Japan). With a TW generated by ac Joule heating of the front surface, the thermal diffusivity α is related to the phase shift $\Delta\theta$ of the TW at the rear film surface by

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}t - \frac{\pi}{4}, \tag{1}$$

where ω is the angular frequency of the TW, *t* is the film thickness, and α is calculated from the slope of the plot of $\Delta\theta$ versus $\omega^{1/2}$ with known *t*. The results for α are averages of five measurements.

The thermal conductivity λ is evaluated from α using

$$\lambda = \alpha\rho C_P, \tag{2}$$

where ρ and C_P are the density and heat capacity, respectively. The

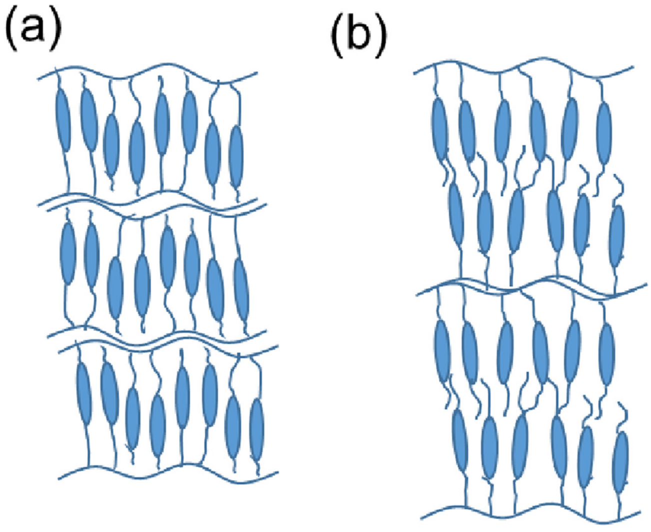


Fig. 1. Smectic layer structures formed by P*m*BE*n* polymers. (a) The SmA_1 structure in P*m*BE1 ($m = 5$–12) and (b) SmA_d structure in P4BE4, P4BE6, and P6BE6.