Macromolecules 1994, *27*, 1603-1610

Effects of Annealing Siloxane Side-Chain Liquid Crystalline Polymers in the Biphasic Region

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Received September 7, 1993®

ABSTRACT: Siloxane-based side-chain liquid crystalline polymers (SCLCP) can be induced to phase separate by annealing near the clearing point in the biphasic region. This has been observed by differential scanning calorimetry (DSC), in which the isotropization endotherm becomes split, and in optical microscopy experiments. The effect was observed in all samples, independent of the chemical structure of the SCLCP synthesized. Only annealing at or below the maximum of the DSC clearing point endotherm was effective in inducing biphasic separation. When the samples were reheated above the clearing point, the demixed phases persisted for varying lengths of time, dependent on the nature of the spacer group covalently linking the mesogen side group to the siloxane backbone. Optical microscopy supports the demixing, which is proposed to be due to the distribution in molecular weight of the siloxane backbone. The effect of annealing in the biphasic region on the crystalline melting point and the glass transition was also examined. The number of precipitations of the SCLCP, which leads to a change in molecular weight distribution, also has an effect on the rate of the separation process.

Introduction

Thermotropic side-chain liquid crystal polymers (SCLCP) consist of rigid mesogenic units attached via a sufficiently flexible spacer group to a polymer backbone. The spacer group must be of sufficient length to allow decoupling of the motions of the side chain and the randomly coiled main chain, enabling the mesogens to exist in an anisotropic liquid crystalline state.[1] As a general rule, the liquid crystalline phase is stabilized upon polymerization into states of higher order with higher transition temperatures than those of the constituent monomers.[2]

The biphasic region of liquid crystalline polymers (LCP) (the temperature region between the liquid crystalline and isotropic state where the two phases coexist) is of much theoretical and practical interest in SCLCP systems. Although ordering can occur due to surface interactions between substrate and SCLCP, an important property of these materials is the ability to switch the orientation of the mesogenic units by application of an ac voltage to films between electrodes.[3] The voltage required is of the order of a few hundred RMS volts, and the nature of the orientation (homeotropic or planar) is dependent on the frequency of the applied voltage and the dielectric anisotropy of the mesogenic core.[4] The possibility of manipulating the mesogenic alignment of these materials makes them candidates for applications such as electrically, thermally, or laser addressed information storage devices[5] or in nonlinear optics.[6]

To cause electrical realignment it is generally necessary to apply the voltage to the sample in the isotropic state (above the clearing point) and slowly cool through the biphasic region (where isotropic material and liquid crystalline material coexist) while maintaining the electric field. In SCLCP's this biphasic region is broader than that of low molar mass mesogens and demonstrates interesting effects such as template behavior of the aligned portion of the biphasic region[7] and hysteresis of the biphasic region.[8] It is necessary to better understand the behavior of material in this region, particularly if the materials are to be used as field-assisted erase/write optical information systems in which continual cycling and annealing under the influence of electric fields in or near the biphasic region may be required.[7,9] In addition, as part of the process of mesophase identification, it is often necessary to hold a SCLCP film for an extended period of time below the clearing point in a hot-stage microscope to obtain the developed textures.[10] Both of these examples involve annealing in or near the biphasic region, and it is of scientific interest to further investigate the biphasic region and the effect of thermal treatment upon it. In this paper we show that annealing of SCLCP's in this temperature regime results in phase separation.

Biphasic annealing phenomena have been reported by Kim et al.[11] in copolyester main-chain liquid crystalline polymer (MCLCP) systems. In their work, annealing within the biphasic region led to splitting of the melting and isotropization DSC endotherm peaks (formation of two distinct peaks in each instance), and this was explained as the demixing of low and high molecular weight chain fractions. More recently, work by Laus et al.[12] involved synthesis of semiflexible MCLCP polyesters with differing molecular weights and molecular weight distributions. By mixing together samples with well-defined size and distribution characteristics, it was found that these parameters influenced both the position and effect of annealing on the phase separation process. The biphasic segregation was most obvious at intermediate values of average molecular weight and polydispersity.

Phase segregation behavior by annealing has been rarely reported in side-chain liquid crystalline polymers. In one recent paper by Galli et al.,[13] however, it was reported that acrylate side-chain liquid crystalline systems which initially show a single, broad clearing endotherm by DSC techniques can be annealed at temperatures just below the clearing point and that the DSC thermogram, on rescanning, showed the endotherm being split into two peaks—evidence of thermoreversible, annealing-induced

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® Abstract published in *Advance ACS Abstracts,* January 1, 1994.

0024-9297/94/2227-1603$04.50/0

phase separation in the biphasic region. This was ascribed to demixing of phases that coexist in the nematic–isotropic region with different phase temperatures. Such demixing was proposed to be due to material of differing molecular weight and molecular weight distribution becoming phase separated (although no direct evidence for this was presented). Such a hypothesis is in line with that described above by Kim et al.[11] and Laus et al.[12] for MCLCP's. Galli et al.[13] found that subsequent annealing above the isotropic temperature removed evidence of phase separation.

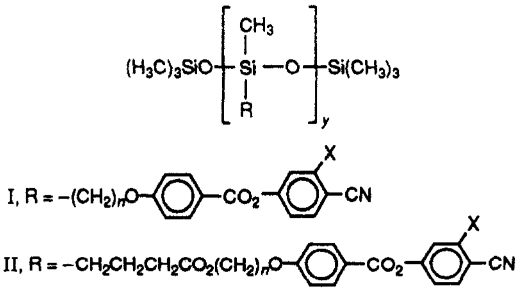
Other than the Galli paper,[13] no work has been done concerning a detailed examination of the effect of annealing of SCLCP's in the biphasic region and its influence on demixing and none at all in side-chain liquid crystalline polymers in which the mesogens are attached to flexible polysiloxane main chains. These materials represent an important and widely studied class of SCLCP materials.[1–5,7–9,14]

In this work we present a detailed study of annealing of siloxane side-chain liquid crystalline polymers in the biphasic region with materials containing differing mesogenic groups and spacer units. We examine the effects of the number of polymer precipitations following synthesis as well as the thermal treatment.

Experimental Section

Synthesis. The polymers were synthesized by grafting of vinyl monomer onto polysiloxane chains in a monomer/SiH ratio of 1:1. Small amounts of 1-octene were used to ensure complete reaction of all SiH units. Further details of the synthesis of the monomer and grafting procedure are described elsewhere.[15,16] The siloxane material used was Petrach PS120 (DP = 40 ± 3). The SCLCP product was precipitated from a solution of dichloromethane by adding a fivefold excess of methanol. The number of precipitations was either 3 or 10. A paper by Gray et al.[17] indicated that T_g and T_{cl} could be a function of the number of reprecipitations. Three precipitations were found to be sufficient to remove materials such as cyclic siloxanes that have been shown to occur in commercially obtained hydrogenmethylsiloxane samples.[18,19] Grafted cyclic siloxanes have thermal properties quite different from those of linear polysiloxanes (for example, much higher values of the isotropization endotherm).[20] The effects of the precipitation on the molecular weight distribution of the remaining linear polymers will be discussed later in the text, since this is one of the variables which is examined.

The polymers synthesized in this work were of the following formulas:



with $y = 40 \pm 3$ and various values of n and X summarized with the results in Table 1. The difference between structures I and II is the vinylacetic acid-based spacer in II compared to a more conventional polymethylene-based spacer in I such as reported by Ringsdorf et al.[21] As described elsewhere, the vinylacetic acid-based spacer was synthesized largely in an effort to produce a flexible spacer unit which would allow electrical alignment in the liquid crystalline state.[16] In this work we used SCLCP's with different spacers and mesogen units to determine the influence of chemical structure on the annealing behavior.

Measurements. Superambient DSC data were obtained using a Perkin-Elmer DSC7. All thermograms were run at 10 K/min and calibrated with indium. Subambient runs were performed on a similar system cooled by liquid nitrogen and calibrated with dodecane. Thermal history of the material is an important aspect of this work, and all samples were prescanned to above the clearing point into the isotropic phase prior to observing annealing behavior to eliminate any thermal prehistory. Therefore the unannealed data presented in Table 1 represent second thermal scans. All annealing was done on these second thermal run samples within the DSC chamber, allowing accurate and extended temperature control.

Table 1. Thermal Data for Unannealed Side-Chain Liquid Crystalline Polymers

no.	type	n	X	no. of precip	T_g (°C)	T_m (°C)	ΔH_{KS} (J/g)	T_{SI} (°C)	ΔH_{SI} (J/g)
1	I	6	H	3	*a*	50	11.5	176	3.7
2	I	11	H	3	*a*	56	8	189	5.7
3	I	6	F	10	–4.8	*b*	*b*	148	2.8
4	I	11	F	10	–7.4	33	8.2	171	5.5
5	II	6	H	3	–3.8	*b*	*b*	40	3.4
6	II	8	H	3	–7.9	*b*	*b*	97	5.1
7	II	11	H	3	–3.7	*b*	*b*	106	6.5
8	II	8	F	3	–15.4	*b*	*b*	65	3.8
9	II	8	F	10	–14.0	*b*	*b*	66	3.7

[a] No glass transition observed. [b] No crystalline melting point observed.

Features observed on the DSC thermograms and measured were the glass transition (T_g), the melting peak (crystalline–smectic transition) (T_{KS}), and the clearing point (smectic–isotropic transition) (T_{SI}). The position of these latter two peaks was taken as the temperature at peak value, and the enthalpy of the transition was the area under the DSC endotherm. The biphasic region was taken as the lower and upper limits of the isotropization endotherm.

Optical microscopy was performed with an Olympus petrological microscope fitted with a Mettler FP-80 hot stage. Standard crystalline materials were used to ensure that its temperature calibration was the same as that of the DSC.

Results

Liquid Crystalline Properties. The thermal data in Table 1 characterize the materials used in annealing studies. The data presented describe polymers with a range of side chains (differing spacer units and mesogenic cores) and various numbers of polymer precipitations following synthesis. All of these variants are examined to understand the behavior of SCLCP's in the biphasic region and the effect of annealing upon it.

Before discussing the annealing experiments, we will make some general comments about the structure/property relations evident in Table 1. All materials showed smectic textures in the liquid crystalline state, as demonstrated by the appearance of conical fans under cross polars in the hot stage microscope and by the magnitude of enthalpies of the smectic–isotropic transition.

Most of the samples showed no melting point, the exceptions being samples 1, 2, and 4. Presence of a fluorine rather than a hydrogen atom ortho to the cyano group was found to decrease the melting and clearing points. None of the vinylacetic acid-based SCLCP's (type II) showed crystallinity. The glass transitions of the SCLCP's synthesized were all below 15 °C, in keeping with the flexible nature of the siloxane backbones. In series I as the flexible spacer increases in length, the T_g decreases in magnitude due to internal plasticization of the polymer chain. The flexible vinylacetic acid spacer (type II) showed subambient T_g's for all polymers. These values decreased further with increasing spacer length. Glass transitions could not be observed in some of the crystalline materials, and this can be ascribed to the low concentration of the amorphous phase and the action of the crystalline units as "physical cross-links", restraining the extent of motion the siloxane polymer backbone can experience at T_g.

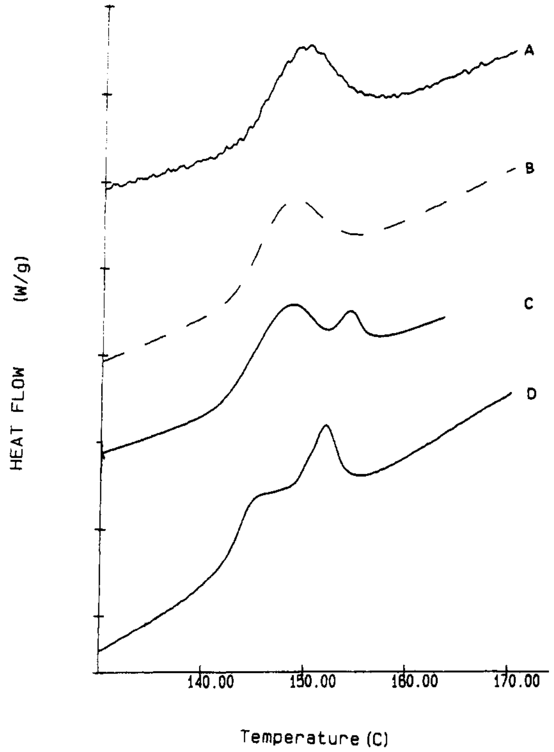


Figure 1. DSC heating curves for sample 3: (A) unannealed; (B) annealed at 1.5 °C above the peak temperature; (C) annealed at the peak temperature; (D) annealed at 1.5 °C below the peak temperature. All DSC curves are normalized with respect to sample weight and are scanned at 10 °C/min. The peak temperature is taken as the position of the maximum of thermogram A—the unannealed polymer with thermal history removed. Unless otherwise stated, all annealing times are 16 h.

General Biphasic Annealing Phenomena. Annealing experiments were carried out in most cases by first eliminating sample prehistory by scanning the sample into the isotropic state, holding for 2 min, and rapidly quenching (at 200 °C/min) to room temperature, well below the clearing point. The samples were then rapidly taken to the desired annealing temperature near the clearing point (T_{SI}) region and held there to anneal the sample for the desired time. By using the position of the clearing point from the DSC data presented in Table 1, samples were accurately annealed within the DSC apparatus at a number of temperatures—the clearing temperature (peak of the DSC thermogram), just above (+1.5 °C) the clearing point, and just below (−1.5 °C) the clearing point. All samples (unless stated otherwise) were annealed overnight (16 h) similarly to the experiments of Galli et al.[13] and under a nitrogen atmosphere within the DSC. Thermal stability of these samples over 16 h was confirmed by thermogravimetric analysis (TGA) studies. As further evidence of sample stability, experiments described later in this paper showed the thermoreversibility of the annealing in some systems. Typical behavior of a sample annealed in its biphasic region was shown by sample 3 with the polymethylene spacer chain and fluorine moiety in the ortho position to the cyano group. The unannealed sample had a clearing point maximum of 148 °C and a ΔH_{SI} of 2.8 J/g. Figure 1 shows the DSC thermograms for unannealed material and smaples annealed at 1.5 °C above and 1.5 °C below the clearing maximum (150.9 and 146.8 °C, respectively) as well as at the clearing maximum.

Annealing at the clearing point produced two peaks at 147.2 and 153.4 °C, split around the unannealed peaks. The total area under the split curve remained 2.8 J/g. Annealing 1.5 °C below the temperature maximum resulted in a wider separation of the two peaks although still centered on the unannealed exotherm peak temperature with peak positions of 145.2 and 151.9 °C and the same total endothermic energy (2.9 J/g). Annealing above the clearing point (but still well within the high-temperature tail of the endotherm) showed no change to the subsequent thermogram compared to that of the unannealed sample. Importantly, however, the peak position and magnitude of endothermic energy of this latter sample remained the same as that of the unannealed material, confirming that negligible degradation of the sample had occurred, even at the higher temperature. Repeated temperature scans up and down in temperature through the biphasic region were not found sufficient in themselves to cause annealing.

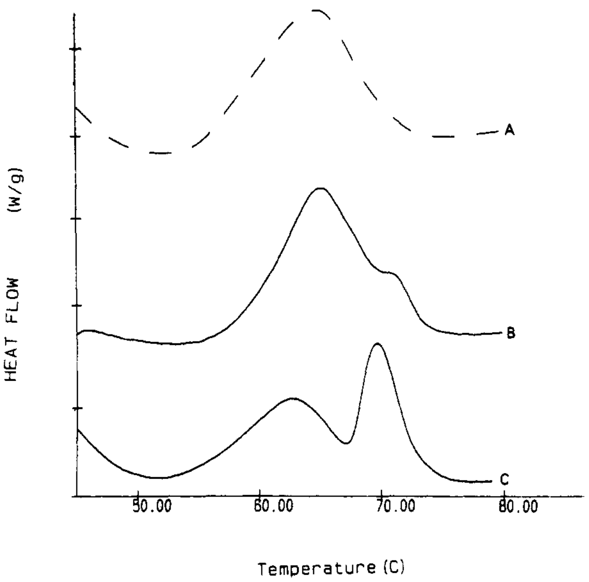


Figure 2. DSC heating curves for sample 8: (A) unannealed; (B) annealed at the peak temperature; (C) annealed at 1.5 °C below the peak temperature.

All the SCLCP's annealed at temperatures at or just below the clearing point showed double peaks upon rescanning of the annealed samples while samples annealed above the clearing point maximum but within the biphasic region showed no signs of splitting. The split peaks were further apart for annealing below the T_{SI} maximum. The total endothermic area remains the same. These general observations were found to be true, independent of the chemical nature of the mesogenic unit or spacer or the number of precipitations and were observed with other SCLCP materials of ours not reported here.

Although most materials followed the above rules, the degree of splitting varied between samples. In some systems (samples 1, 3, 4, and 6) substantial splitting was obtained upon annealing at the peak temperature. In some other cases (for example, samples 5, 8, and 9) annealing at the peak temperature only resulted in the development of a shoulder on the endotherm. By contrast, two peaks always occurred in samples annealed below T_{SI}. This behavior was demonstrated by sample 8 (Figure 2) and contrasts with that shown by sample 3 (Figure 1). No correlation of this behavior was found with polymer structure I or II, *n*, or X.

Effect of the Annealing Temperature. A more detailed study on the temperature dependence of the degree of sub-T_{SI} annealing was performed on sample 6, which showed an endothermic peak of 96.7 °C prior to annealing. The material was annealed at the peak temperature, 1.5 °C, 3 °C, and 4.5 °C below the peak temperature 16 h as described before. The lowest temperature chosen (92.2 °C) was still within the biphasic region, and the results are shown in Figure 3. The temperature peaks of the two demixed phases were found to be independent of the annealing temperature. However,

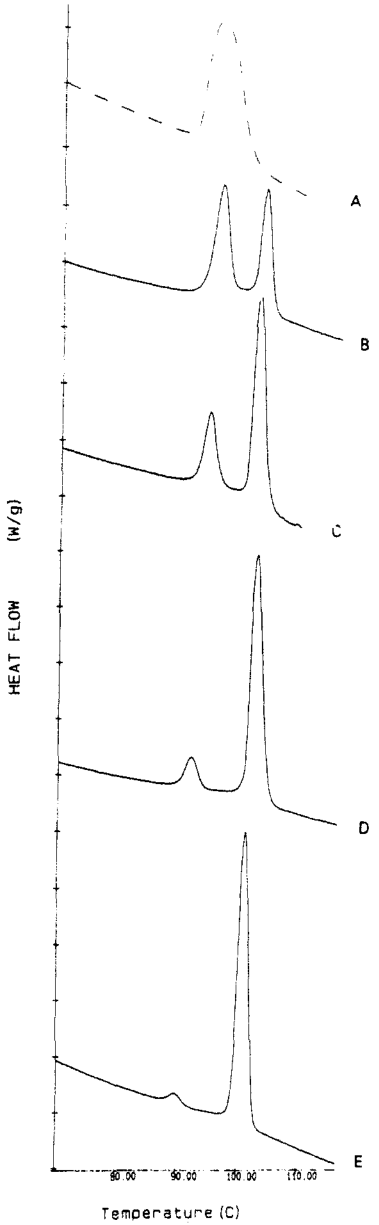


Figure 3. DSC heating curves for sample 6: (A) unannealed; (B) annealed at the peak temperature; (C) annealed at 1.5 °C below the peak temperature; (D) annealed at 3 °C below the peak temperature; (E) annealed at 4.5 °C below the peak temperature.

the lower the annealing temperature, the greater the amount of the higher temperature fraction (as judged by the energy under the split peaks).

Effect of Length of Time of Annealing. The length of time to anneal a sample was arbitrarily set at 16 h in this work (10 h was used in the work of Galli et al.[18] with acrylate SCLCP's and 16 h was used by Laus et al.[12] in MCLCP's). Figure 4 is a comparison of the system (sample 6) annealed at 1.5 °C below the peak temperature for both 16 h and 60 h. The longer annealing time showed a greater degree of splitting (the two peaks were further apart) than for 16-h annealing (and still no sign of decomposition) with the difference between peak positions of 19 °C rather than 8 °C. In addition, extended annealing increased the amount of the high clearing point temperature phase. Although the energy of the varying melting endotherms decreased slightly upon extended annealing, this was not ascribed to decomposition because of the TGA results.

Effect of Number of Precipitations. Direct comparison of the effects of precipitation on annealing behavior can be made between samples 8 and 9, which are the same polymer reprecipitated three and ten times, respectively. Previous work reported by us[19] using gel permeation and thermal characterization methods in these systems indicated that three precipitations were sufficient to rid the grafted siloxane material of any low molecular weight, grafted cyclic siloxanes and any residual 1-octene. However, increasing the number of precipitations above three was found to further increase the average molecular weight of the linear polysiloxanes by removal of some low molecular weight, linear materials. The data from Table 1 indicate that the transition temperatures (T_g and T_{SI}) are similar for three and ten times precipitated material. This differs from work by Gray et al.,[17] who found that the number of precipitations can alter the clearing point by up to 9 °C, or by Attard et al.,[22] who found an increase of 8 °C upon repeated reprecipitation. It is difficult to compare the effects of the number of precipitations on SCLCP's by different workers as the result may depend on the details of the preparative method (such as the mole ratio of monomer to reactive siloxane site) as well as the precise technique of the reprecipitation. For example, Gray et al.[17] indicated that differences observed by his group for various numbers of precipitations were due to removal of trace amounts of residual alkene. In our work[19] we demonstrate that no alkene is present after three precipitations.

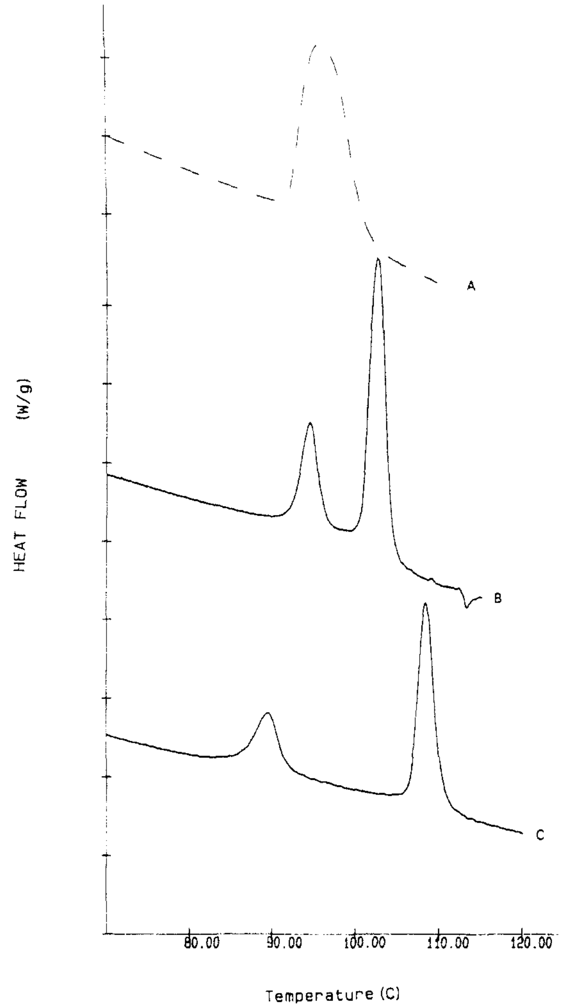


Figure 4. DSC heating curves for sample 6: (A) unannealed; (B) annealed for 16 h at 1.5 °C below the peak temperature (standard heat treatment); (C) annealed at 1.5 °C below the peak temperature for 60 h.

The annealing behavior at temperatures 1.5 °C below the clearing point is quite different for samples 8 and 9 (three and ten precipitations, respectively). Figure 5 shows the annealing data for samples precipitated ten times

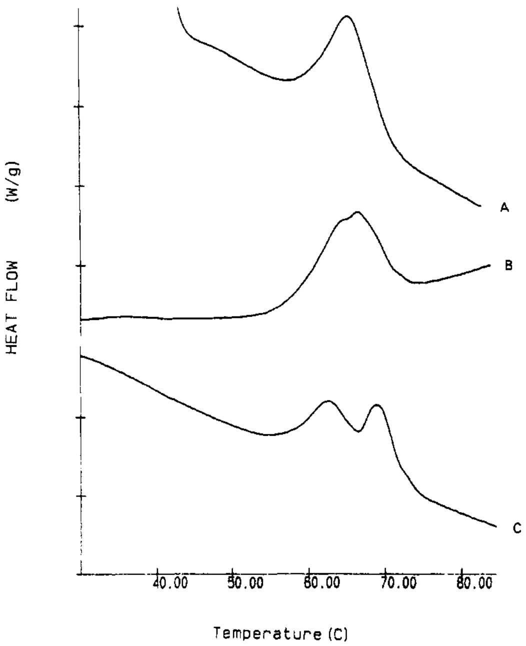


Figure 5. DSC heating curves for sample 9 (10 precipitations): (A) unannealed; (B) 16 h at 1.5 °C below the peak temperature; (C) annealed at 1.5 °C below the peak temperature for 48 h. These data should be compared with data of sample 8 in Figure 2, which was precipitated 3 times.

(sample 9) compared with material precipitated three times (sample 8 in Figure 2) at the same temperature and for the same length of time (16 h). In the ten times precipitated material little splitting occurred after 16 h, with only a shoulder visible on the high-temperature side of the DSC peak. However, after continued annealing for another day, the ten times precipitated sample peaks split to the same degree as the three times precipitated material. That is, further reprecipitations of SCLCP in this system inhibited the rate of phase separation but not the final, attainable level of splitting. The magnitude of the split peak endotherms was more equal in the case of the ten times precipitated sample 9 material than in the three times precipitated sample 8 in which the higher temperature peak endotherm was of much greater energy.

Effect of Annealing in the Biphasic Region on the Melting Point and Glass Transition Temperature. Other than the clearing point, the main features in some SCLCP DSC thermograms are the melting points and glass transition temperatures. Since there appears to be some phase separation induced by annealing in the biphasic region, the influence of annealing above the glass transition and crystalline melting regions on T_m and T_g is of interest. If annealing these materials above these transitions causes a change to the lower temperature transitions, it is confirmation of demixing of mesogenic units, possibly due to differences in siloxane molecular weight. Kim et al.[11] made similar conclusions in their annealing work with main-chain thermotropic liquid crystalline polymers where they found that the crystalline melting peaks were split after holding the material near the liquid crystalline clearing point, the memory of the annealed biphasic behavior clearly being "locked-in" during the rapid sub-melting point quench. This annealing effect should be differentiated from that usually observed in polymers where the crystalline regions are annealed between T_g and T_m. In the work by Galli et al.[13] with SCLCP acrylates, splitting in the melting region was not reported. We now present the effect of biphasic annealing on the crystalline melting point in some of our samples.

The three systems in Table 1 that show melting points are samples 1, 2, and 4. All are of type I with polymethylene

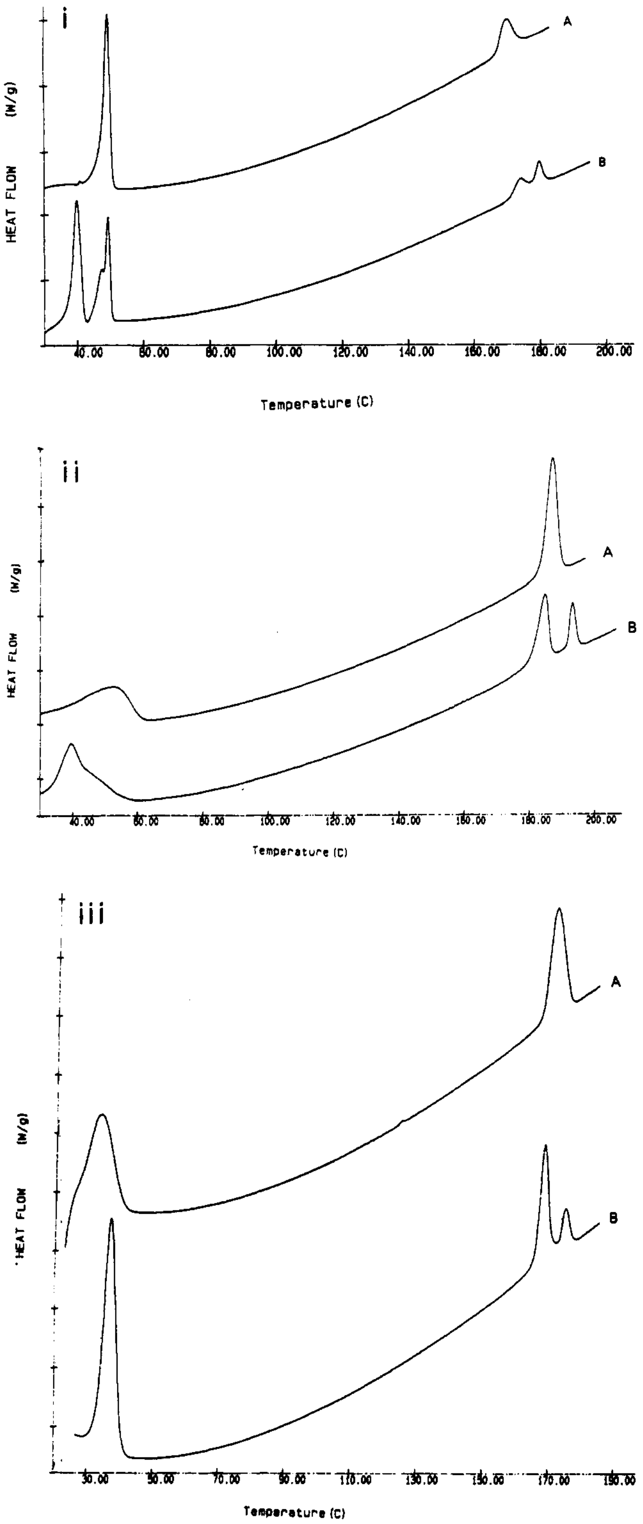


Figure 6. (i) DSC heating curves for sample 1: (A) unannealed; (B) annealed at 1.5 °C below the peak temperature. (ii) DSC heating curves for sample 2: (A) unannealed; (B) annealed at 1.5 °C below the peak temperature. (iii) DSC heating curves for sample 4: (A) unannealed; (B) annealed at 1.5 °C below the peak temperature.

spacer units. The thermal scans of material annealed at 1.5 °C below the clearing temperature for 16 h for samples 1, 2, and 4 are presented in Figure 6i–iii with scans of unannealed material presented for comparison. In all cases the clearing transitions showed clearly split peaks while the melting endotherm was split only in the case of sample 1. A high-temperature shoulder developed in the case of sample 2 and a slight peak shift in the case of sample 4. In the case of sample 1 (Figure 6i) the unannealed peak position coincides with the high-temperature peak of the two peaks resulting from annealing rather than splitting

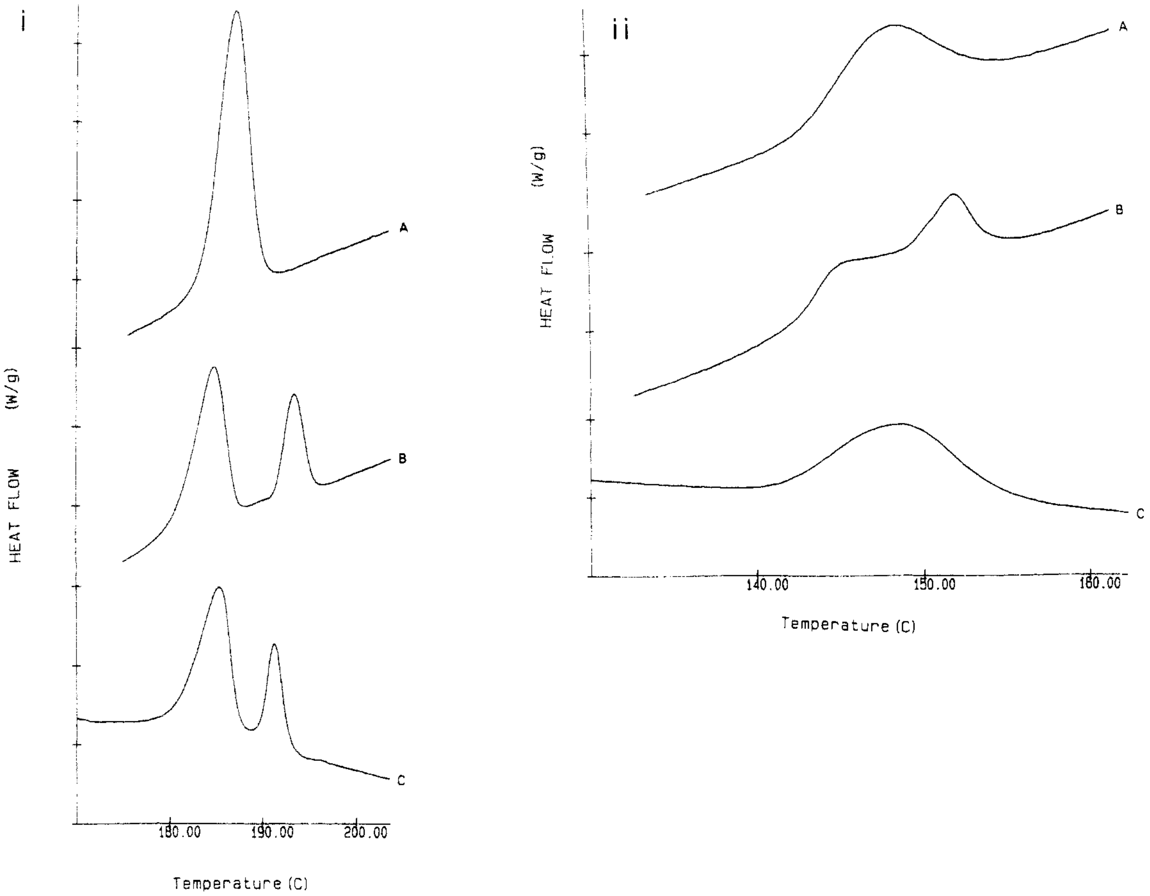


Figure 7. These curves show the effect of holding annealed material 20 °C above the clearing point in the isotropic region for various lengths of time. The annealing conditions involved holding the material at 1.5 °C below the peak temperature for 16 h. (i) DSC heating curves for sample 2: (A) unannealed; (B) after annealing at 1.5 °C below the peak value; (C) after holding the annealed sample in the isotropic for 20 min. (ii) DSC heating curves for sample 3: (A) unannealed; (B) after annealing at 1.5 °C below the peak value; (C) after holding the annealed sample in the isotropic for 60 min.

either side of the unannealed peak as in the clearing point region. In addition, the endothermic energy of melting is much *greater* in the case of all three annealed samples compared to the preannealing state. This is different from the magnitude of the actual clearing point endotherms, the total energy of which, despite being split, remains the *same* as those of the annealed sample.

The subambient DSC thermograms for a range of annealed SCLCP materials were run to determine whether T_g was influenced by annealing. Unlike the melting point, the glass transition temperature remained unchanged upon annealing. Due to the similarity of the DSC traces they are not presented in figure form in this paper.

Reversibility of the Annealing Process. To further examine the thermal reversibility of the annealing process, a number of different samples were annealed, held above the clearing point for various lengths of time, cooled, and rescanned. Two types of behavior were observed. The first is seen in samples 2, 4, and 7, an example of which is shown in Figure 7i for sample 2. Holding these samples for 1 h at 20 °C above the clearing point resulted in only partial recovery from the split peaks typical of the annealed state. Other samples (numbers 1 and 3) reverted back to single peaks after periods of 5–10 min above the clearing point. This is demonstrated in Figure 7ii with sample 3. Although only a few examples have been presented here, it appears as though samples with the shorter spacer units (samples 1 and 3) are able to revert much more rapidly to the preannealing state than those with the longer spacers (samples 2, 4, and 7).

Optical Microscopy. Optical microscopy texture was observed for a number of the systems and correlated with annealing effects measured on the DSC. We present only the results and photographs for sample 1. Figure 8i shows expanded clearing point endotherms for unannealed and annealed sample 1 material. Figure 8ii–vii shows a series of photographs taken at various temperatures before and after annealing. An unannealed sample heated from room temperature to 174 °C (near the unannealed DSC maximum) showed very fine texture (Figure 8ii). Upon taking the sample up into the isotropic region and quenching again to 174 °C, the material shows a larger, poorly developed conical fan texture (Figure 8iii). If the sample is allowed to anneal at 174 °C (2 °C below the endotherm maximum) and photographed at this temperature, black regions can be seen among very well developed conical fans (Figure 8iv). The dark regions are due to liquid crystalline material in its isotropic state. Reference to curve B in Figure 8i indicates that annealed material at 174 °C is between the two, split endothermic peaks. Upon cooling the polymer film to a temperature below the low-temperature peak, 172 °C (Figure 8v), it can be seen that the previously black region is now below its clearing point and shows a very fine conical fan texture. That is, annealing results in material undergoing demixing into two phases—one which has a more highly developed texture and a higher clearing point while the other phase has a lower clearing point and finer texture. Lowering the temperature of the material further to 100 °C resulted in the two-phase structure being maintained (Figure 8vi). Reheating to 174 °C again showed the melting of the fine texture (Figure 8vii) as demonstrated by the appearance of the black regions. Since the endothermic energies of isotropization of these two phases are roughly equal from DSC (±25%) and the regions are of similar volume fraction (by examination of the optical micrographs), it can be

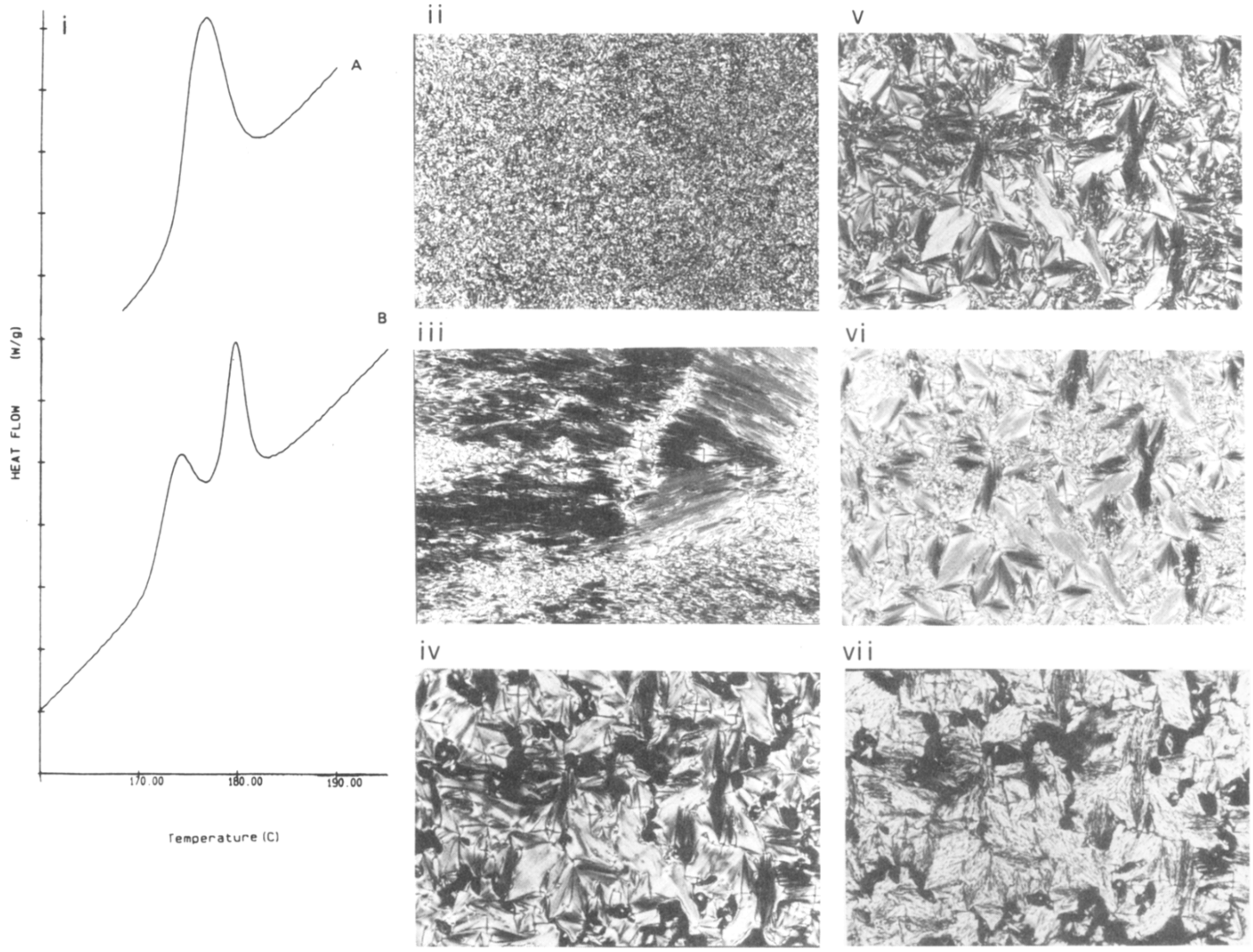


Figure 8. Series of thermal and optical micrographs of sample 1. In all photographs the magnification is such that 1 cm = 6 μm. (N.B.: All photographs have been reduced to 45% of their original size for publication purposes.) All annealing is done at 174 °C (about 1.5 °C below the peak clearing point endotherm. (i) DSC thermogram of (A) an unannealed and (B) annealed sample 1. (ii) sample 1 heated from room temperature to 174 °C. (iii) sample 1 heated to the isotropic and quenched to 174 °C. (iv) Annealed for 16 h at 174 °C and photographed at that temperature. (v) Annealed sample of (iv) cooled to 172 °C. (vi) Annealed sample of (v) cooled to 100 °C. (vii) Sample of (vi) reheated to 174 °C.

concluded that the material is divided roughly equally between the two phases.

Discussion

The common features found in annealing of a large number of SCLCP's in the biphasic region were as follows:

(1) All SCLCP materials show splitting of the endothermic DSC trace after annealing in the biphasic region, independent of the nature of the spacer and mesogenic unit.

(2) Annealing just below the peak endotherm temperature was always more effective in producing two peaks than annealing either at the peak temperature or at temperatures lower than 1.5 °C below. Annealing above the peak value was totally ineffective at causing splitting.

(3) An increase in annealing time led to an increase in the degree of splitting.

(4) The total magnitude of the sum of the enthalpy of the split peaks was similar to that of the endotherm of the unsplit single peak in the unannealed material.

(5) The predominant effect of more precipitations (ten compared to three) seemed to be to delay the onset of biphasic separation. However, the same ultimate degree of splitting was possible upon continued annealing of ten times precipitated material. GPC results[19] indicated continued precipitation resulted in loss of low molecular weight fractions of material (increase in the average molecular weight).

(6) Annealing of crystalline SCLCP samples in the biphasic region was effective in causing splitting in the crystalline melting endotherm.

(7) There is no effect on the glass transition temperature upon annealing in the biphasic region.

(8) In all cases, the phase separation due to annealing was reversible to some degree if the sample was held in the isotropic state. The degree of phase remixing seemed to depend on the length of the spacer, samples with shorter spacer groups showing more rapid remixing.

(9) Optical microscopy indicated two types of smectic phases following annealing—a phase with a larger conical fan texture and another phase with a less developed, finer texture and a lower clearing point. The volume fraction of both phases seemed to be similar.

The observations of phase separation for SCLCP's upon annealing can be explained by a proposal similar to that of Kim et al.[11] and Laus et al.[12] for MCLCP's and Galli et al.[13] for acrylate SCLCP's i.e., that of separation of fractions with differing molecular weights and molecular weight distributions upon annealing. As in the work of Galli et al.,[19] insufficient material could be annealed accurately to allow this theory to be checked directly with use of characterization techniques such as GPC. The attribution of this annealing phenomenon to the molecular weight distribution of the polymer backbone (as opposed to the chemical nature of the side chain) seems clear since the effect was observed in materials with different mesogenic units. This is not to say, however, that aspects of the demixing are not influenced by the type of mesogenic unit or spacer group used.

By comparison with the results of Gray,[22] the higher clearing point polymer fraction separated upon annealing would most likely consist of the higher polymer chain MW. It appears that continuing precipitation, which has the effect of reducing the concentration of the low molecular weight fraction and increasing the molecular weight average, does not change the overall mechanism of the separation process but does seem to delay it (requiring longer annealing times to reach similar levels of endotherm peak splitting). The reason for such behavior is unclear. Laus et al.[12] found in MCLCP's that the degree of splitting of the biphase demixed components was mainly dependent on the *width* of the molecular weight distribution whereas the position of the biphasic region was dependent on the *magnitude* of the average molecular weight. Laus et al.[12] found that, by changing the temperature of annealing, the peak temperatures of the two peaks changed, indicating that different molecular weights could be fractionated dependent on the annealing temperature. Our work in SCLCP's showed different results in that, although the relative energies of the two peaks changed with variations in annealing temperature, the actual positions of the peaks did not (Figure 3).

Interestingly, although the melting point of the semicrystalline SCLCP samples showed peak splitting due to biphasic annealing, the value of T_g in amorphous SCLCP's was invariant to annealing history. It appears that even though the separation is due to polymers of different siloxane backbone lengths becoming demixed, their difference in chain length is insufficient to register dual glass transition behavior using DSC. This is perhaps not surprising given the low T_g of siloxane material associated with their great flexibility and associated high free volume.

The demixing process is reversible to different degrees in various samples upon heating into the isotropic region. Kim et al.[14] found that there was little reversibility in main-chain LCP's; samples which were demixed remained separated. In this work longer spacer groups inhibited remixing of the two phases when the annealed samples were held above the clearing point. Materials with mesogens attached to the siloxane chains by short spacer systems were able to totally remix. These observations (as well as the reuslts presented for samples with differing molecular weights) seem to suggest that annealing causes a diffusion-based separation which resists remixing, particularly in materials with either higher molecular weight siloxane backbone chains or longer covalent spacer groups. Clearly, a sample with a long spacer group and a high molecular weight backbone (and thus higher viscosity) would require greater time to phase separate and, once separated, persist longer in this demixed state upon reheating.

The appearance of different textures of the two phases by optical microscopy (well-developed conical fans with a rather less developed texture in the interstitial regions) at temperatures below the biphasic region is probably due to the fact that the higher temperature phase with more developed texture has been annealed below its clearing point and the material with the lower clearing point has been quenched. We have not attempted to anneal the finer, lower temperature texture, so it is unclear whether this would show similar developed texture with annealing at an appropriate temperature below that phase's clearing point.

Clearly, despite sufficient siloxane/side-chain decoupling, which allows the anisotropic liquid crystalline phase to exist in these SCLCP polymer systems, the polymer backbone still plays a crucial role in the behavior of the mesogenic units. That is, the polymer backbone is more than a host matrix in which the mesogens are embedded but retains an influential connectivity with the mesogens. Similar demonstrations of the existence and importance of siloxane backbone/mesogen connectivities can be seen with other techniques such as in dielectric and dynamic mechanical relaxation experiments[23] and in recent work by Moura-Ramos et al.,[24] who examined the influence of pressure on the dielectric relaxation in SCLCP systems.

An important conclusion from this study is that this annealing phenomenon appears to be generic to SCLCP's (as well as MCLCP's) of different polymer backbones, such as the biphasic annealing of the acrylate SCLCP's of Galli et al.[13] The comparison between polysiloxane and acrylate backbones is important because acrylate and methacrylate materials also have the possibility of possessing distributions of differing tacticities in a given sample which could also be a potential explanation for demixing upon annealing in those systems. The study and control of stereochemistry in siloxane chemistry is a new and promising area (for example, see Saam et al.[25]), and the role that it plays in biphasic demixing phenomena is not yet clear.

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