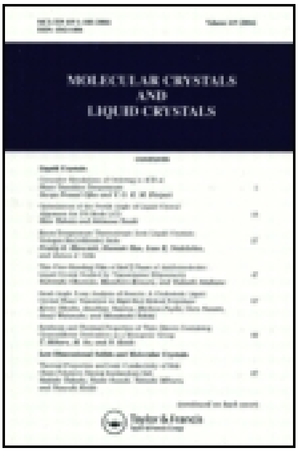

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Interaction between Thermotropic-Liquid Crystalline Polypeptides having Long Alkyl Side-Chains and n-Alkanes

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Interaction between Thermotropic-Liquid Crystalline Polypeptides having Long Alkyl Side-Chains and n-Alkanes

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The behavior of mixtures of derivatives of poly(γ-benzyl L-glutamate) (PBLG) having long alkyl side-chains as pendant groups and n-alkanes was investigated by means of differential scanning calorimetry, wide-angle X-ray diffraction, electron-spin resonance, and observation under crossed polarizers. When the n-alkane was not too long compared with the length of the alkyl side-chains of the polypeptide, the n-alkane molecules intruded into a crystalline texture formed by the polymer side-chains, extending the interval of the rod-like polymer backbones and disarranging the crystalline texture to lower its melting point. The temperature of the crystal-to-liquid crystal transition of the PBLG derivative, caused by the melting of the side-chains crystal lowered accordingly. The critical number of carbons of the n-alkane to lower the transition temperature was 16 when the number of carbons in the alkyl chain was 8, 19 when it was 12, 21 when it was 16, and 27 when it was 22.

Keywords: thermotropic liquid crystal, polypeptide, long alkyl side-chain, n-alkane, interaction

INTRODUCTION

Kasuya and his coworkers[1] first demonstrated that copoly(γ-n-alkyl L-glutamate)s assumed the cholesteric mesophase when two different n-alkyl groups were combined in the ratio of about 50/50 in mol% and the preparations were annealed at 110–190°C. The combinations of the n-alkyl groups were methyl–hexyl, methyl–octyl, and propyl–

octyl. This work was furthered by Watanabe and his coworkers[2] who found that poly(γ-methyl D-glutamate-co-γ-hexyl D-glutamate)s assumed a similar mesophase at any hexyl content between 30% and 70%. Almost at the same time, Hanabusa and his coworkers[3] synthesized poly(4-substituted γ-benzyl L-glutamate)s that assumed mesophases; the preparations had long alkyl side-chains as pendant groups and underwent a crystal-to-liquid crystal transition as a result of the side-chains melting on heating and acting as a solvent in the manner same as in lyotropic liquid crystals of polypeptides including PBLG. Properties of these preparations have been studied in more detail.[4] The transition temperature depends on the length of alkyl side-chains, it is −6°C when the number of carbons in one alkyl chain is 12, 42°C when it is 16, and 69°C when it is 22. When it is 8, a dip corresponding to some structural change such as a glass transition is observed in the DSC curve around 20°C instead. The transition temperatures were determined as rise-temperatures of the DSC curves. PBLG derivatives with a degree of polymerization of 50 or less transit to the cholesteric mesophase directly from a crystalline state, and those with a degree of polymerization 91 or more assume another mesophase prior to assuming the cholesteric mesophase. This interposed mesophase is suspected to be smectic.

All these thermotropic-liquid crystalline polypeptides are composed of a mesogenic (or rigid) backbone and flexible side-chains as pendant groups. They are a kind of comb-like polymers in the architecture; however, they differ from genuine comb-like polymers which have a flexible backbone and rigid pendant groups. These polypeptides should be classified as a new type of thermotropic-liquid crystalline polymers as Watanabe and his coworkers[2] have proposed. The alkyl side-chains of the PBLG derivatives are perpendicular rather than parallel to the backbone helices. Axial ratios of the PBLG derivatives are rather small (0.7–3.2). The feature of liquid crystals of the PBLG derivatives has an analogy with that of columnar phases (see refs. 5 and 6) especially in the supposed smectic phase.

The present study has been carried out in order to clarify in more detail the behavior of alkyl side-chains which play an important role in endowing rigid polymers with the thermotropic-liquid crystalline nature.

EXPERIMENTAL

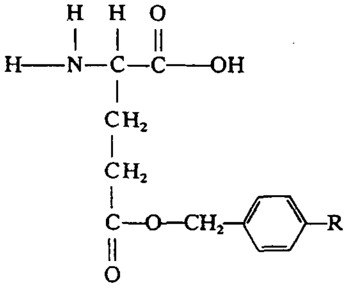
Materials

Table I lists the PBLG derivatives used in this study. All the preparations except one are those used in the previous works;[3,4] the R16 with a mean

TABLE I

PBLG derivatives used

Preparation	R	D.P.	Axial ratio
R8	OC_8H_{17}	91	3.2
R12	$OC_{12}H_{25}$	102	2.9
R16	$OC_{16}H_{33}$	30	0.7
		50	1.2
		60	1.4
R22	$OC_{22}H_{45}$	110	2.1



degree of polymerization (DP) of 60 was newly synthesized. Procedures to synthesize these preparations have been described elsewhere.[3] The number of carbons in one alkyl chain was 8, 12, 16, or 22, and the DP ranged from 30 to 110. The PBLG derivatives were α-helical at least up to 180°C. The alkyl side-chains which extend perpendicular to the backbone helix overlapped a considerable part, say about 2/3 of the whole alkyl length, with those of the neighboring polymer helices.[4] The n-alkanes used were guaranteed reagents and were purchased from Nakarai Chemicals, Ltd. The number of carbons of the n-alkanes ranged from 10 (n-decane) to 30 (n-triacontane).

The polymer samples were mixed with any n-alkane at predetermined ratios through the medium of chloroform which evaporated later in air. Densities of the polymers and of the n-alkanes were assumed respectively to be 1.1 and 1.0, the ratios were expressed in vol%. Those n-alkanes with a small number of carbons evaporated rather quickly in air. It was known, however, that in an aluminum pan for measurements of differential scanning calorimetry (DSC) the solvent chloroform became undetected without any noticeable loss of n-dodecane (n12) 1 hour after being kept in open air at room temperature.

Methods

Thermal analysis was carried out using a Rigaku DSC-8230 differential scanning calorimeter at the scanning rate of 5°C/min. Microphotographs were taken with a Mitamura prism-type melting-point detector under crossed polarizers after the specimens had been kept at each predetermined temperature for 2 hours. The wide-angle X-ray diffraction was measured using a Rigaku geigerflex (Cu-K_α line, 40 kV–30 mA). The electron-spin resonance (ESR) was also measured using a Varian E-109E EPR spectrometer at temperatures between 30 and 100°C. In doing so, the specimens were labeled with 5-doxyl-stearic acid (5SAL) or with 12-doxyl-stearic acid (12SAL) which was purchased from Sigma Chemicals Co., Ltd., concentration of the labeling reagents being 1.3×10^{-4} mol%.

RESULTS AND DISCUSSION

Thermal behavior

Figure 1 shows several DSC curves of R16(DP60) mixtures. When n-cetane (n16) is mixed, the temperature of a strong endothermic transition which is exhibited by pure R16(DP60) at 42°C lowers with increasing n16 concentration. This transition (main) corresponds to the melting of the alkyl side-chains of the PBLG derivative (and of crystals formed by these side-chains) and accompanies the formation of liquid crystals as already mentioned. The melting of free n16 which is expected to occur at about 18°C cannot be observed on the DSC curve when the n16 concentration is 10%. It becomes observable at a n16 concentration of about 30%. This experimental evidence suggests that n16 molecules are incorporated into regions where the alkyl side-chains of the polymer molecules align parallel with each other to form themselves a crystalline texture up to at least about 30% in the volume ratio. Similarity of the structural formula between the alkyl side-chains of the polymer and the n-alkane may enable both components to make a hydrophobic interaction with each other. Incorporation of n-alkane molecules would more or less disarrange the crystalline texture to lower its melting point, which explains the lowering of the crystal-to-liquid crystal transition temperature. The temperature of an additional endothermic transition, which has been suspected to be the smectic-to-cholesteric transition and is exhibited by pure R16(DP60) at 130°C, also lowers (by about 5°C) with 10% n16; this transition disappeared on further addition of n16.

The transition temperatures of R16(DP60) are not controled by the addition of n-octacosane (n28), unlike the foregoing case. The melting of free n28 can be assigned to the DSC curve at its characteristic temperatures around 58 and 61°C even when the n28 concentration is 10%. Both pieces of the experimental evidence suggest

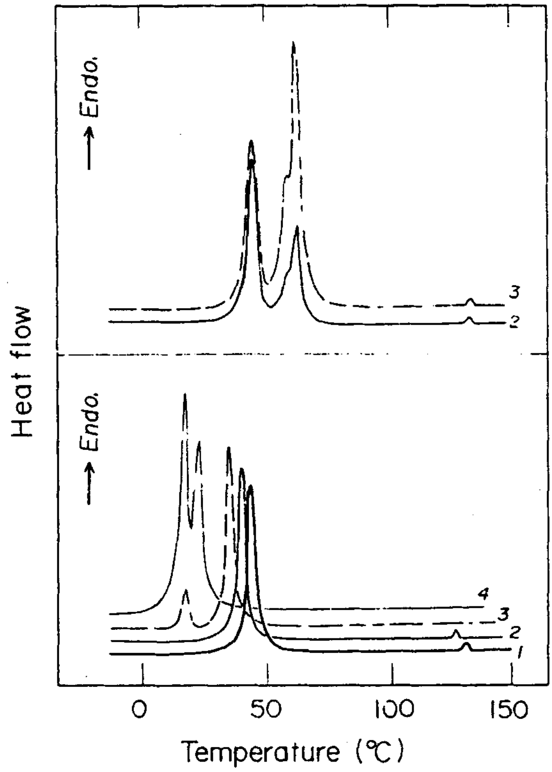


FIGURE 1 DSC curves of mixtures of PBLG derivative and n-alkane. Upper panel, R16(DP60) + n-octacosane; lower panel, R16(DP60) + n-cetane. n-Alkane concentration: 1, 0%; 2, 10%; 3, 30%; and 4, 50%. Scanning rate, 5°C/min.

that n28 does not interact with R16(DP60) unlike n16 and that disappearance of transition of the n-alkane on the DSC curve can be a measure to detect the presence of interaction between PBLG derivative and n-alkane. Incorporation of (extended) n-alkane molecules among the polymer side-chains would cause extension of the interval between the polymer helices which align parallel with each other to form themselves a crystalline texture. To keep this texture stable, the polymer side-chains may have to overlap at least some part with those of the neighboring polymer helices. n28 would be too long to meet such a demand, and the two components of the mixture form themselves crystalline structures separately to minimize the internal energy of the system.

Figure 2 shows DSC curves of mixtures of PBLG derivative and 10% n-alkane, displaying the critical number of carbons of the n-

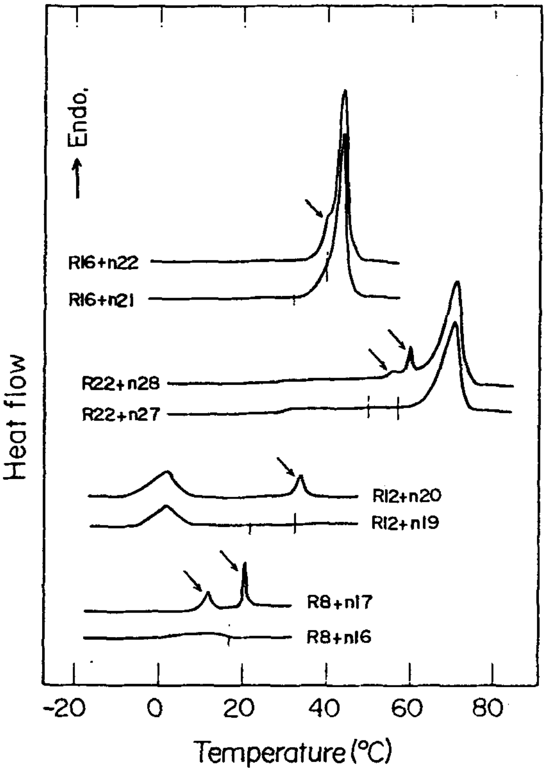


FIGURE 2 DSC curves of PBLG derivatives with 10% n-alkane. The arrows on the lines point out the transitions of the n-alkanes. The short, vertical lines show the peak positions of transitions expected to appear for the n-alkanes.

alkane, n_c, at and below which the n-alkane can interact with the host polymer. It may be seen that n_c is 16 for R8, 19 for R12, 21 for R16, and 27 for R22. This number did not depend on the DP of the PBLG derivative as far as the R16 preparations were concerned.

Figure 3 shows how the temperature of the crystal-to-liquid crystal transition changes with increasing n-alkane concentration for two kinds of mixtures, R16(DP60) plus n16 and R22 plus n-tridecane (n13, m.p., −6°C). In both kinds of mixtures, the corresponding temperature lowers when the n-alkane concentration is increased. The lowering of the transition temperature slows down in the R16-n16 mixture, or almost comes to a standstill in the R22-n13 mixture, both at an n-alkane concentration of about 50%. At this n-alkane concentration, the transition temperature of R16(DP60) is 23°C which is

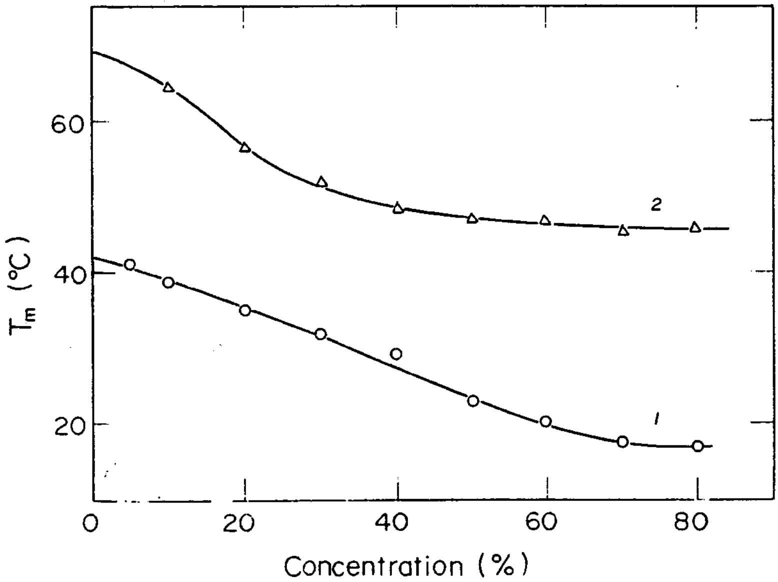


FIGURE 3 Crystal-to-liquid crystal transition temperature vs. concentration of n-alkane for mixtures of PBLG derivative and n-alkane. 1, R16(DP60) + n-cetane; 2, R22 + n-tridecane.

19°C lower than that of pure R16(DP60) and the transition temperature of R22 is 47°C which is 22°C lower than that of pure R22.

Dependence of the main transition temperature on the number of carbons of the n-alkane, n, is shown in Figure 4 for three kinds of PBLG derivatives, R12, R16(DP60), and R22, in which the n-alkane concentration is fixed at 50%. Lowering of the transition temperature of R12 may be seen, though slightly only when n is 19 or less. This number naturally coincides with n_c as determined from the DSC curve of the mixture with 10% n-alkane. n-Nonadecane (n19) melted at 21 and 31°C. These temperatures are higher than the transition temperature of pure R12 (−6°C). It thus is known that the transition temperature of the PBLG derivative lowers whether the melting point of the n-alkane is higher or lower than the transition temperature of the host polymer. This suggests that disarrangement of the polymer side-chains crystals is the cause for the lowering of the transition temperature.

The transition temperature of R16(DP60) lowers markedly when n is 17 or less. With the increase of n-value lowering of the transition temperature of the host PBLG derivative becomes less, suggesting

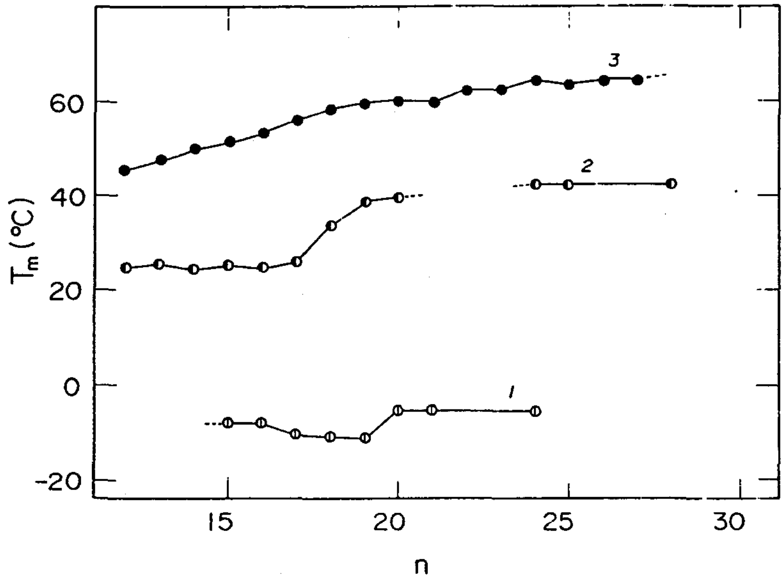


FIGURE 4 Crystal-to-liquid crystal transition temperature vs. number of carbons of the n-alkane for mixtures of PBLG derivative and n-alkane. PBLG derivative: 1, R12; 2, R16(DP60); 3, R22. Concentration of the n-alkane, 50%.

that the difference between the melting point of the n-alkane and the transition temperature of the host polymer is involved. Because of overlapping of the transitions of both components, the transition temperature of R16 could not be specified in mixtures with n-alkane having 21, 22, or 23 carbons. The transition temperature does not lower any more when n is 24 or more. Therefore, n_c is known to be 21, 22, or 23, which is compatible with the already mentioned result. A sign of the odd-even effect seems to be present. As for the transition temperature of R22, it lowers with the addition of n-alkanes having 26 or less carbons. This is again compatible with the already-mentioned result.

Observation under crossed polarizers

When the DP was 91, a R16 sample started to become decomposed at about 200°C before it turned to an isotropic liquid.[4] Those preparations, of which the DP is 60 or less exhibit a liquid crystal-to-isotropic liquid transition at a certain temperature that depends on the preparation as may be seen in Figure 5, for instance. The image under crossed polarizers changes drastically with increasing temper-

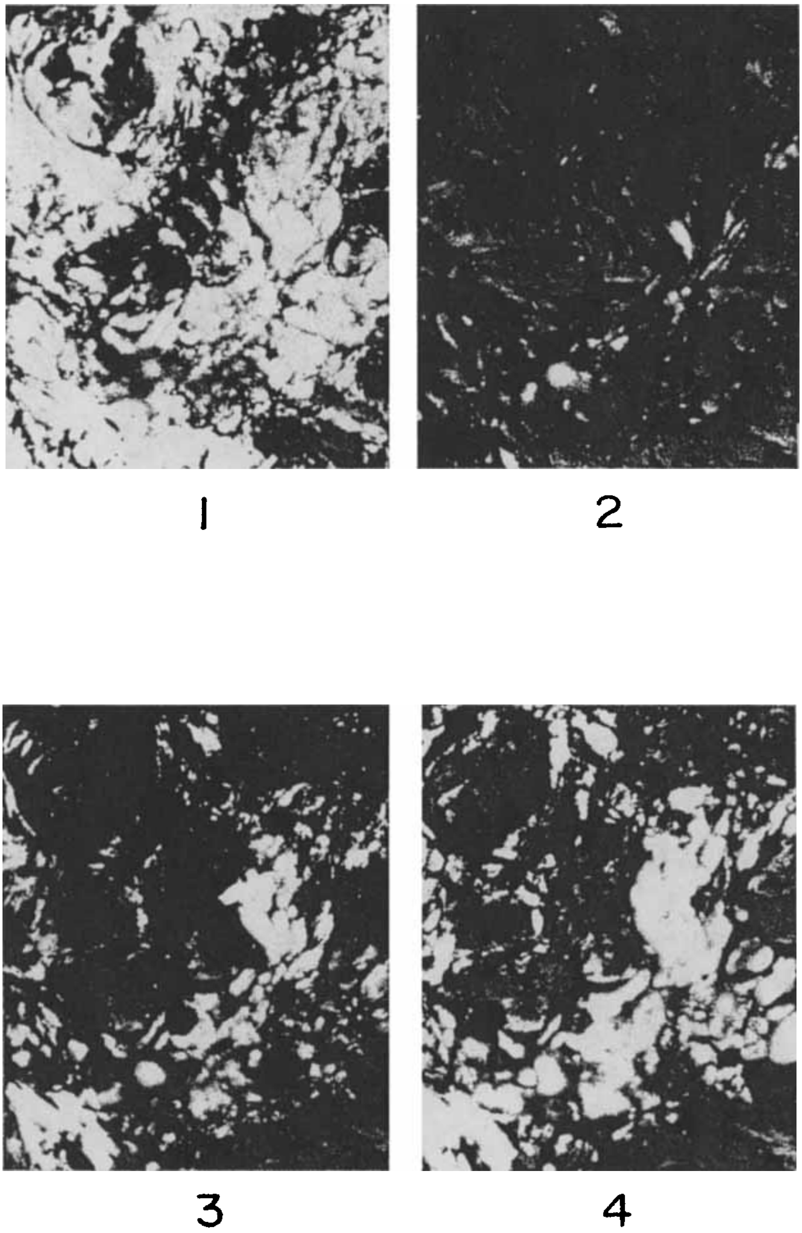
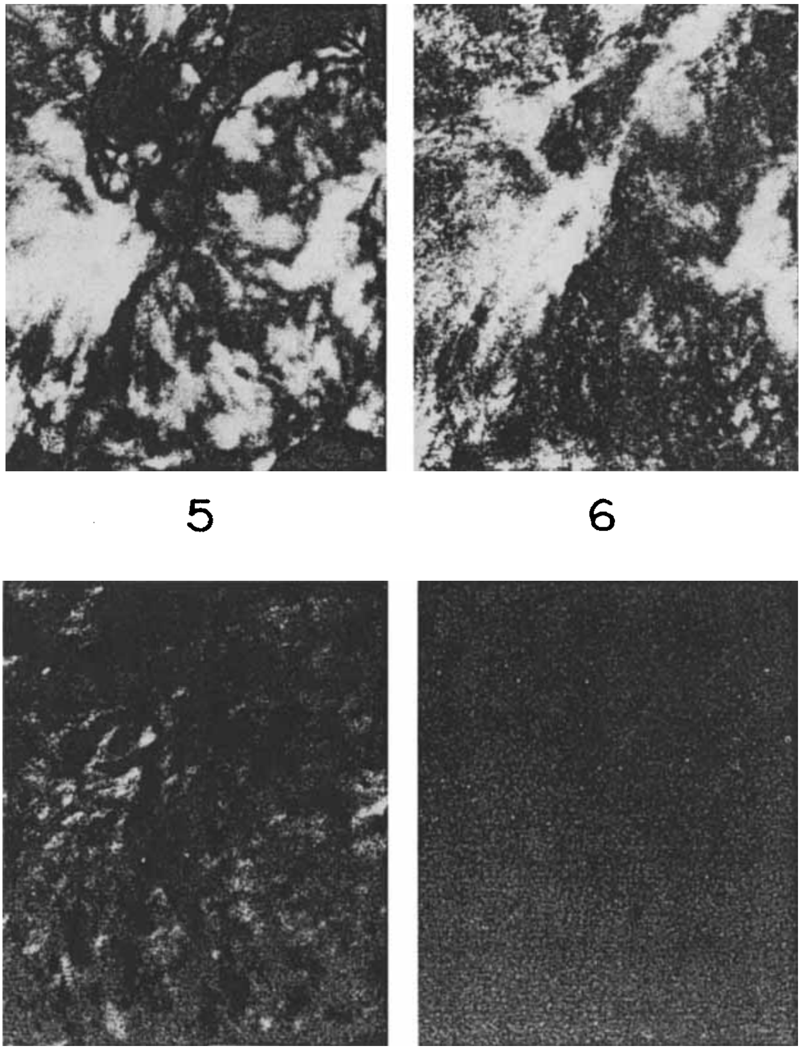


FIGURE 5 Microphotographs of a mixture of PBLG derivative and n-alkane under crossed polarizers at various temperatures. Mixture, R16(DP60) + n-cetane. Concentration of the n-alkane, 5%. Measured at: 1, 30°C; 2, 50°C; 3, 80°C; 4, 100°C; 5, 120°C; 6, 130°C; 7, 140°C; 8, 160°C.



5 6

7 8

FIGURE 5 (continued)

ature; it becomes temporarily dark with a slight change in the pattern when passing through the crystal-to-liquid crystal transition (41°C for R16(DP60) plus 5%-n16) and changes its pattern completely at the cholesteric temperature (128°C). Furthermore, it becomes disappeared at about 160°C, indicating that the specimen becomes an isotropic liquid. The transition to an isotropic liquid could not be detected on the DSC curve, which suggests that this transition proceeds gradually upon heating through a successive increase of the cholesteric pitch, exhibiting no explicit heat transfer on the DSC curve.

Figure 6 shows that the isotropic temperature falls monotonically with increasing n-alkane concentration for the mixture of R16(DP60) and n16. At a n16 concentration of 90%, it becomes 50°C which is as much as 110°C lower than that of pure R16(DP60) and is rather close to the melting point of the guest n-alkane. This suggests that n-alkane molecules are continuously taken in by the host polymer molecules when the n-alkane content is increased. As may be seen in Table II, the isotropic temperature falls when the DP of the PBLG derivative decreases. However, the temperature of the crystal-to-liquid crystal transition was independent on the DP at least when it was 30 or more.

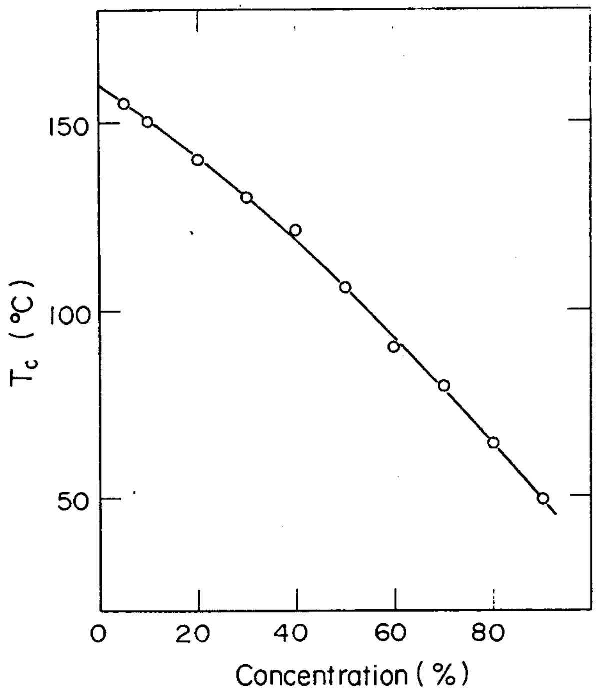


FIGURE 6 Liquid crystal-to-isotropic liquid transition temperature vs. concentration of the n-alkane for a mixture of PBLG derivative and n-alkane. Mixture, R16(DP60) + n-cetane.

TABLE II

Temperature of the liquid crystal-to-isotropic liquid transition vs. degree of polymerization for the mixture of R16 and n-cetane

Alkane concn. (%)	Degree of polymerization		
	30	50	60
0	112	122	160
20	101	116	142
60	77	88	91
		Temperature in °C.	

X-ray diffraction

Figure 7 shows X-ray diffraction photographs of mixtures of R8 and n-alkane. The innermost Debye–Sherrer ring is due to a lattice plane that relates to the interval between the backbone helices of the polymer. The corresponding Bragg angle decreases when n16 is mixed, indicating an increase of the spacing of the lattice plane. This suggests that n16 molecules intrude into interstices between the alkyl side-chains of the polymer molecules to extend the backbone interval. The Bragg angle in question is not affected by the addition of n28, suggesting that this n-alkane cannot extend the backbone interval. These experimental evidence agree with the idea obtained based on the DSC measurements that those n-alkanes of which the molecular lengths are too long, compared with that of the alkyl side-chains of the host molecule, cannot be received by the host polymer.

When n16 is mixed, sharp Debye–Scherrer rings are seen in the outer portion of the photograph distinctly only at a n16 concentration of 40% or more and at a temperature which is lower than the melting point of n16 (18°C). This suggests that these sharp diffraction rings come from crystals formed by surplus n16 molecules that are not accepted by the polymer and is consistent with the DSC result that the heat transfer of free n-alkane starts to appear at a certain n-alkane concentration. (In the mixture of R16(DP60) and n16, the corresponding concentration is about 30%.) The Debye–Scherrer rings due to the side-chains crystals cannot be identified for pure R16(DP60). They are broad probably because the size of the crystals are small. The mixture of R8 with n-octadecane (n18) displays sharp Debye–Scherrer rings, at the outer portion of the photograph, even at a n18 concentration of 10%. This indicates that n18 does not interact with R8, which agrees again with the DSC result.

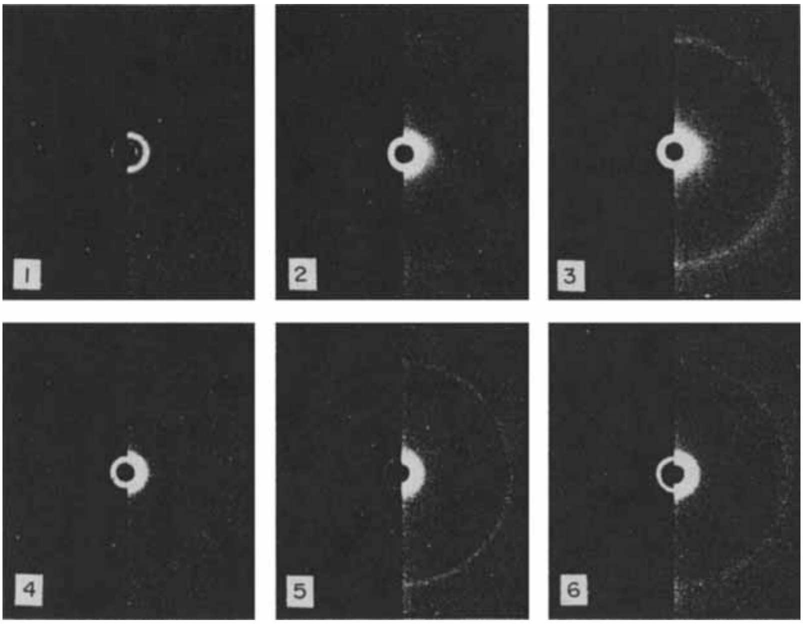


FIGURE 7 X-ray diffraction photographs of mixtures of PBLG derivative and n-alkane. 1–4, R8 + n-cetane. n-Alkane concentration: 1, 0%; 2, 30%; 3, 40% (1–3, measured at 15°C); 4, 50% (27°C). 5 and 6, R8 + n-octadecane. n-Alkane concentration: 5, 10%; 6, 30% (5 and 6, 22°C).

Figure 8 shows the value of the spacing related to the backbone interval of a PBLG derivative as a function of n-alkane concentration for the mixture of R8 and n16 at two temperatures, one above and the other below the melting point of n16. It increases with increasing n16 concentration up to 20–30% addition of the n-alkane. This corresponds to the DSC result concerning the appearance of the heat transfer of free n-alkane. The value of the spacing are somewhat smaller at the higher temperature because of shrinkage of the n-alkane molecules. At n-alkane concentrations of 50% or more, the Debye–Scherrer ring became too diffuse to read the Bragg angle.

Figure 9 shows how this spacing depends on the number of carbons of the n-alkane for three kinds of PBLG derivatives, R8, R12, and R16(DP60), all at an n-alkane concentration of 30%. The PBLG derivative R22 was not tested since the corresponding Bragg angle is too small to be accurately measured. The value of the spacing for pure PBLG derivative is 27 Å for R8, 33 Å for R12, and 41 Å for R16(DP60) at room temperature. It increases when n-alkane is mixed

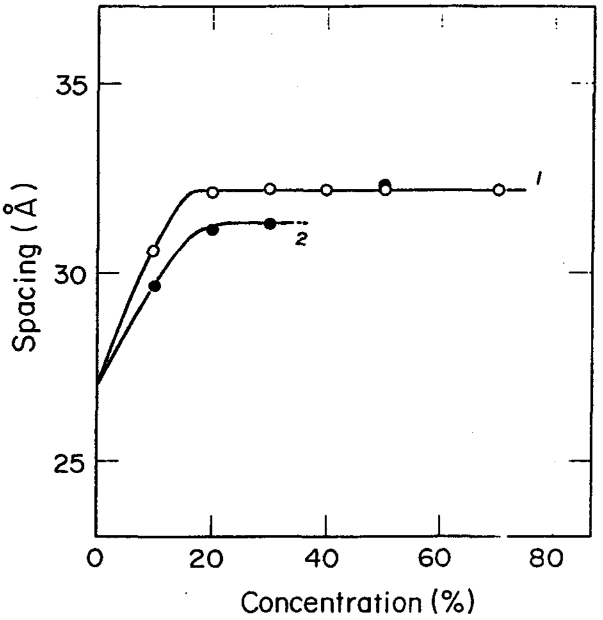


FIGURE 8 Spacing corresponding to a lattice plane which is related to the interval of backbone helices of the polymer vs. concentration of the n-alkane for a mixture of PBLG derivative and n-alkane. Mixture, R8 + n-cetane. Measured at 1, 15°C; 2, 27°C.

unless the number of carbons of the n-alkane exceeds a certain value that depends on the PBLG derivative. This critical value is 16 for R8, 19 for R12, and 21 for R16(DP60). Beyond these critical values, the value of the spacing is not affected by the addition of n-alkane any more. This experimental evidence is in complete agreement with the DSC result as far as R8, R12, and R16(DP60) (and the other R16s as well) are concerned. As for R22, the experimental results obtained by the DSC measurements will also be granted to be true since no disagreement between the DSC results and the X-ray diffraction results are found in the other PBLG derivatives. The amount of spacing increase is independent of the number of carbons of the n-alkane in any PBLG derivatives tested; it is 5.6 Å for R8, 3.3 Å for R12, and 4.2 Å for R16(DP60). It was also independent on the DP of the R16 preparation. The interval of the polymer helices is regulated only by the amount of the n-alkane. This requires an explanation; however, it is still not given.

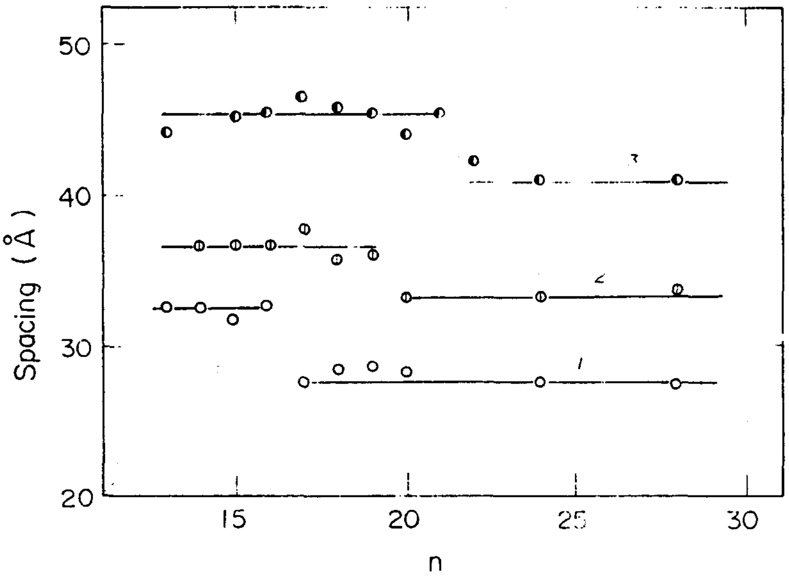


FIGURE 9 Spacing corresponding to a lattice plane which is related to the interval of backbone helices of the polymer vs. number of carbons of the n-alkane for mixtures of PBLG derivative and n-alkane. PBLG derivative: 1, R8; 2, R12; 3, R16(DP60). n-Alkane concentration, 30%.

Electron-spin resonance

Figure 10 summarizes temperature dependence of the empirical motion parameter, $\tau_c^{(m)}$, for mixtures of R16(DP60) and n16. The $\tau_c^{(m)}$-value of pure R16(DP60) shows a sharp decrease at about 40°C, which corresponds to melting of the alkyl side-chains of the polymer molecules. The temperature at which such a sharp decrease takes place falls with increasing n16 concentration (and with lowering of the melting temperature of the polymer side-chains). At 20°C where the host polymer is in the crystalline state, the $\tau_c^{(m)}$-value becomes smaller with increasing n16 concentration. The labeling molecules may be introduced among the alkyl side-chains of the polymer molecules, aligning parallel with the side-chains. Therefore, mobility of the labeling reagent reflects that of the alkyl side-chains. It thus is known that the crystalline texture formed by the polymer side-chains is disarranged by the n-alkane molecules. The decrease of $\tau_c^{(m)}$-value occurs mostly at the first 20% addition of n16. All these experimental evidence are consistent with the DSC and X-ray diffraction results.

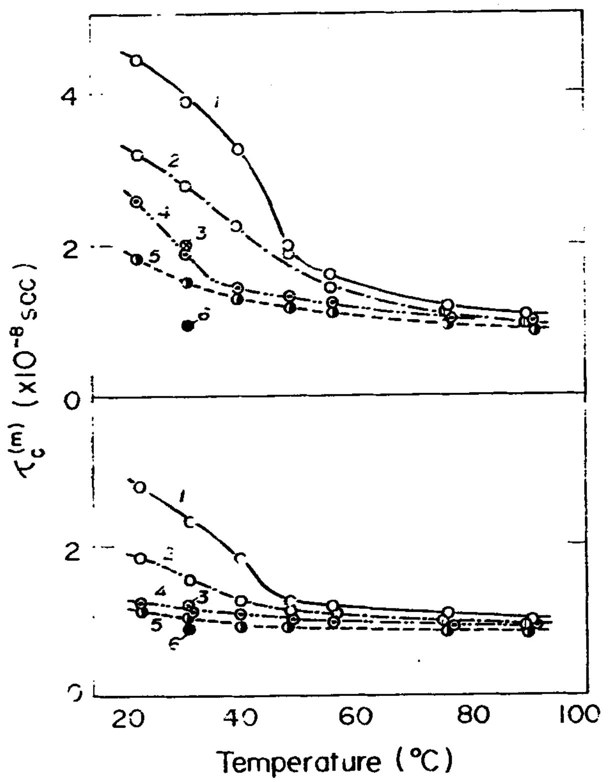


FIGURE 10 Empirical motion parameter as a function of temperature for a mixture of PBLG derivative and n-alkane. Mixture, R16(DP60) + n-cetane. Concentration of the n-alkane: 1, 0%; 2, 10%; 3, 20%; 4, 40%; 5, 80%; 6, 100%. Spin-labeled with 5SAL (upper panel), or with 12SAL (lower panel).

In the temperature range tested, the τ_c -values are smaller when 12SAL is used as the labeling reagent than when 5SAL is used and the values for the mixtures are always larger than those for pure n16. Therefore, the alkyl side-chains of the PBLG derivative are more or less restricted to rotate at all times and that the restriction is stronger toward the bottom of the alkyl chain. This means that the shorter side-chain is more restricted to rotate than the longer side-chain as a whole.

CONCLUSION

n-Alkane molecules are incorporated into a crystalline structure formed by the alkyl side-chains of the PBLG derivative up to at least about

30% by volume only when the number of carbons of the n-alkane does not exceed a certain value that depends on the PBLG derivative. The corresponding critical numbers of carbons are respectively 16, 19, 21, and 27 for PBLG derivatives having alkyl side-chains with 8, 12, 16, and 22 carbons. When n-alkane molecules are incorporated, the interval of backbone helices of the PBLG derivative becomes larger with increasing n-alkane concentration up to about 30%. The amount of increase is independent on the number of carbons of the n-alkane. The crystalline structure of the alkyl side-chains of the PBLG derivative becomes more or less disarranged and its melting temperature falls accordingly. Thus, the temperature of the crystal-to-liquid crystal transition of the PBLG derivative, caused by melting of the side-chains crystal, falls with the addition of n-alkane when its length is not too long compared with that of the alkyl side-chains of the PBLG derivative. The amount of temperature drop increases with increasing n-alkane concentration and the temperature of the liquid crystal-to-isotropic liquid transition also becomes lower simultaneously.

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