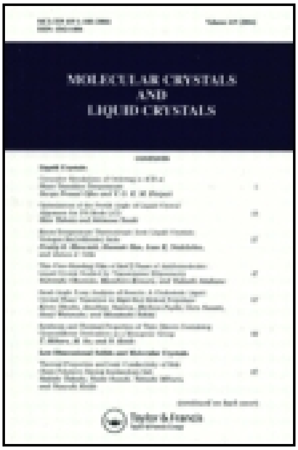

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Phase Studies of Liquid Crystalline Side Chain Polymers Mixed with Low Molar Mass Liquid Crystals of Similar Structure

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Phase Studies of Liquid Crystalline Side Chain Polymers Mixed with Low Molar Mass Liquid Crystals of Similar Structure

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Low molar mass liquid crystals exhibiting the same mesomorphic structure are miscible over the whole range of concentration. The applicability of this rule has been examined for mixtures of nematic liquid crystalline side chain polymers with low molar mass nematic liquid crystals. The liquid crystalline side chain polymers are polysiloxanes, characterized by nematogenic units attached as side chains to the polymer backbone, which are miscible with chemically analogous low molar mass liquid crystals. It has to be emphasized, that at high polymer concentrations the mixtures do not crystallize and the nematic region is substantially enlarged towards lower temperatures (plasticizing effect). By further cooling the mixtures freeze yielding anisotropic glasses.

INTRODUCTION

Extensive studies have been made on binary mixtures[3-6] of low molar mass LC-phases. The results of these measurements always obey the rule of Arnold and Sackmann,[3] according to which liquid crystalline phases of the same phase structure are miscible over the whole range of concentration.

Recently liquid crystalline polymers have been prepared by connecting low molar mass LC-units with flexible polymer chains.[1] These "LC side chain polymers" show the same liquid crystalline behavior as the low molar mass systems. The question is, whether LC-polymers and low molar mass LC-materials are completely miscible and whether the phase rule of Arnold and Sackmann[3] is applicable to those mixtures. It is of great interest for technological applications whether these systems show an equivalent enlarging of the range of the LC-phase as is well known for mixtures of two low molar mass LC-components. The main subject of this paper therefore is the investigation of the miscibility of polymers and low molar mass materials exhibiting the same liquid crystalline structure. Detailed phase diagrams of LC-monomers and their corresponding polymers have been reported by Cser *et al.*[7] Their phase diagrams are, however, complex, because no defined LC-state has been observed for the pure polymer component. Therefore these mixtures cannot prove the existence of direct similarities in the miscibility of LC-polymer systems and the application of the rule of Arnold and Sackmann.[3] For our investigations, we therefore started with polymer systems for which the LC-state has been well defined by different methods.[1,2]

Recently measurements on LC-polymers/LC-low molar mass components have been reported by Griffin and Havens.[8] Both components show liquid crystalline behavior with a nematic structure. Contrary to our systems, their LC-polymers are polymers with the mesogenic group incorporated into the polymer backbone. These LC-polymers exhibit a phase transformation crystalline–nematic, but no glass transition, as can be seen for LC side chain polymers. Therefore their mixtures show nearly the same phase diagrams as those known for binary liquid crystalline low molar mass systems.[3-7]

EXPERIMENTAL PART

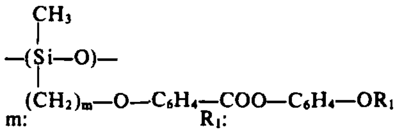
For our investigations on binary mixtures we used well-defined liquid crystalline polymers and chemically related low molar mass materials which exhibit a nematic phase (Table I). The polymer components P1 and P2 are poly-(methylsiloxanes) with phenyl benzoate side chains connected by flexible spacers to the main chain.

In contrast to M1 and M2, the LC-polymers P1 and P2 do not crystallize at normal cooling rates, but P2 crystallizes when the polymer is annealed at temperatures below $T = 330$ K. At the glass transition points T_{g-n} and T_{g-s} the LC-phases are converted on cooling into the glassy state.

To obtain mixtures, the monomers and polymers were dissolved in chloroform. Then the solvent was removed *in vacuo*. The phase transitions were determined by differential scanning calorimetry (Perkin Elmer, DSC-2) and polarizing microscopic measurements (Ortholux

TABLE I

Phase transitions of the pure components of the mixtures

Monomer (y_1)	$R_2O—C_6H_4—COO—C_6H_4—OR_1$ R_2:	R_1:	*Phase Transitions*
M1	$—C_6H_{13}$	$—CH_2—CH{=}CH_2$	*k* 333 *n* 360 *i*
M2	$—C_6H_{13}$	$—C_6H_{13}$	*k* 327 *n* 368 *i*
Polymer (y_2)	 $—(\underset{(CH_2)_m—O—C_6H_4—COO—C_6H_4—OR_1}{\overset{CH_3}{Si}}—O)—$ m:	R_1:	*Phase Transitions*
P1	4	$—CH_3$	*g* 287 *n* 370 *i*
P2	6	$—CH_3$	*g* 276 *s* 319 *n* 383 *i*

Pol.Bk.II). By microscopic observations, the phase transformations crystalline-nematic and nematic-isotropic can be observed, while with DSC, the glass transition additionally is detected. All DSC-measurements were performed with the same rates of cooling and heating (10 K/min). For some samples, annealing experiments were carried out to get more detailed information. Comparison of the results indicates that the transformation temperatures T_{n-i} and T_{k-n}, determined by polarizing microscopic measurements, agree with the peak maxima of the transformations determined by DSC. The phase diagrams show the transition and transformation temperatures T_{g-n}, T_{g-s} and T_{n-i} as functions of the concentration of mixtures indicated by the weight fraction of the low molar mass component y_1.

RESULTS

The components of mixture I (P1/M1) exhibit nematic phases. Their transformation temperatures are listed in Table I. The phase diagram (Figure 1) indicates the miscibility of the liquid crystalline components in the isotropic and the nematic state over the whole range of concentration y_1. This indicates that the rule of miscibility for LC-phases of binary low molar mass mixtures is applicable for this system.[3] Starting from M1 ($y_1 = 1$) the transformation temperature T_{n-i} only slightly changes until a polymer concentration $y_2 = 0.5$ is reached. At higher polymer concentrations the transformation temperature increases more strongly. Heating and cooling experiments do not lead to different results in the transformation temperature T_{n-i} within the limits of error (±1 K). This means, that the isotropic and the liquid crystalline phases have nearly the same composition. Detailed measurements by polarizing microscopy carried out for one mixture show a small heterogeneous region of about 0.6 K difference in the temperature of the liquidus- and solidus-curve. Calculation of these curves as described by Haase[9] verify the experimental results. The existence of a small heterogeneous region is featured as a dotted line in the Figures 1, 4 and 5.

The homogeneous nematic phase is identified by polarizing microscopic measurements. Starting from M1 with $y_1 = 1$, the texture does not change over the whole range of concentration. At lower temperatures, the nematic phase is limited by the crystallization of M1 or the

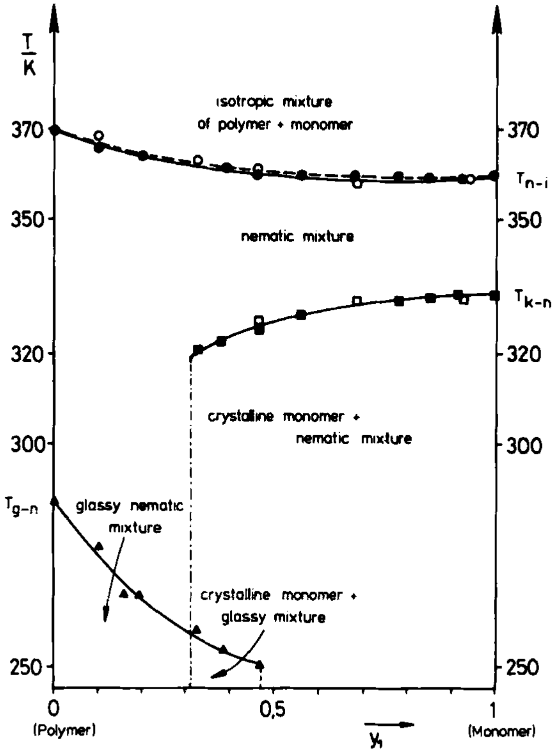


FIGURE 1 *Phase Diagram of Mixture I (P1/M1)* (Transition- and transformation temperatures were determined by heating experiments on mixtures cooled from the isotropic to the glassy state; see also Figures 4, 5 and 6) ▲ (T_{g-n}), ■ (T_{k-n}), ● (T_{n-i}): DSC-measurements; □ (T_{k-n}), ○ (T_{n-i}): Polarizing microscopic measurements.

glass transition of the polymer P1 in the case of higher polymer concentrations.

The transformation temperature $T_{k\text{-}n}$ decreases very slightly from pure M1 to a monomer concentration of nearly $y_1 = 0.7$. With higher polymer concentrations, the transformation temperature decreases more strongly. Below a low molar mass content of $y_1 = 0.31$, no crystallization could be observed (possibly due to kinetic reasons) and the nematic phase is enlarged. By lowering the temperature below $T_{g\text{-}n}$, the nematic structure becomes frozen in.

Starting from the pure polymer P1, the glass transition temperature decreases from 287 K to 250 K at a low molar mass content of $y_1 = 0.47$. The decrease is caused by the effect of *plasticizing.* Further increase of M1-content leads to a suppression of the freezing in process. In a small range of concentration ($y_1 = 0.31$–0.47) both effects—the crystallization and freezing—occur on lowering the temperature. First the low molar mass component crystallizes and then a mixture freezes in at lower temperatures.

Measurements in this range are extremely time dependent. The transition points in the phase diagram were determined by the process described in the experimental part. At the chosen cooling rate, the crystallizable low molar mass component does not crystallize completely and does not have its equilibrium value. Heating a cooled mixture from the glassy to the liquid crystalline state, causes a recrystallization because the glass transition temperature is passed. Annealing experiments above $T_{g\text{-}n}$ lead to a further crystallization of M1. Another well-known effect of annealing, is the reduction of the "jump" value Δc_p (c_p = specific heat) at the glass temperature and the increase of $T_{g\text{-}n}$. This effect does not influence the transformation temperature $T_{k\text{-}n}$. The heat of transitions $\widehat{\Delta H}_{k,n}$ and $\widehat{\Delta H}_{n,i}$ depend linearly on the concentration y_1 (Figures 2 and 3).

The polarizing microscopic measurements gave no information about the state of the mixture below the transformation temperature $T_{k\text{-}n}$. The calculations of the heats of the transformations and their linear decrease with increasing polymer content indicate however that the mixture below the melting point is heterogeneous, consisting of a mixed nematic phase and a crystalline monomer phase. Addition of LC-polymers to low molar mass LC-molecules decreases the degree of crystallization. Reaching a polymer content of $y_2 = 0.69$, the crystallization is completely suppressed and a homogeneous nematic phase exists. This means that the low molar mass LC-crystals do not induce a crystallization of the mesogenic groups of the LC polymers.

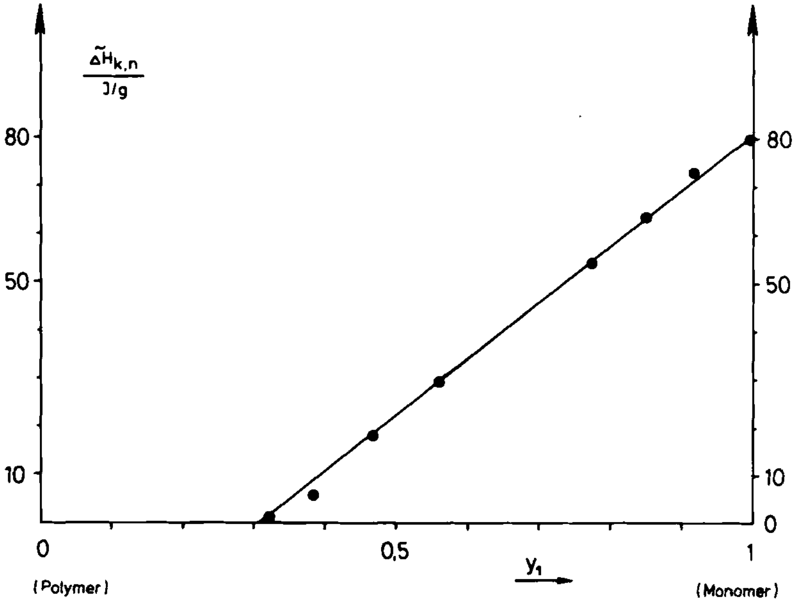


FIGURE 2 *Heat of Transformation* $\Delta\tilde{H}_{k\text{-}n}$ (Mixture I, related to the mass of monomer).

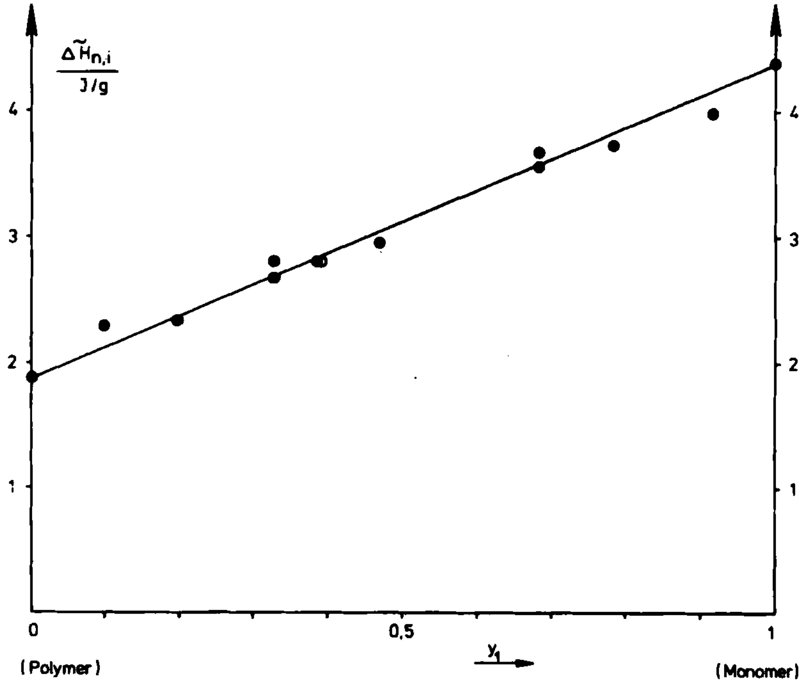


FIGURE 3 *Heat of Transformation* $\Delta\tilde{H}_{n\text{-}i}$ (Mixture I, related to the mass of mixture).

Another phase diagram, the mixture system II (P1/M2), giving nearly the same results is shown in Figure 4. Both liquid crystalline components are nematic, but M2 differs from M1 in the substituents of the mesogenic moiety.

Starting from M2 the transformation temperature T_{n-i} changes slightly because the difference in the transformation temperatures of the pure components is only about 2 K. In contrast to the phase system I, crystallization is suppressed at a higher polymer content $y_2 = 0.77$. The transformation temperature T_{k-n} only slightly decreases to $y_2 = 0.4$ and then in the same way as that shown in phase diagram I (Figure 1). The homogeneous phase is extended over a temperature interval of 90 K. The glass transition temperature decreases in the same way as shown in phase diagram I by adding the plasticizing low molar mass

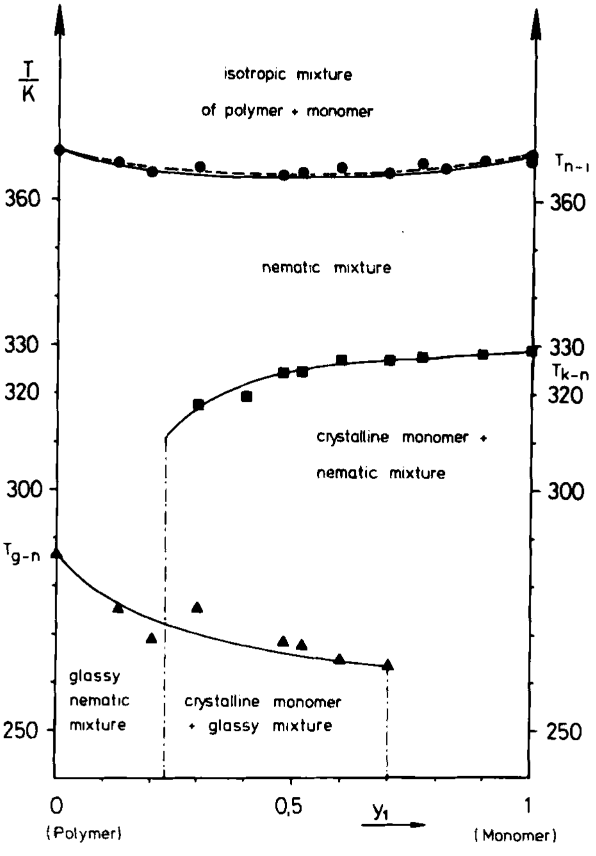


FIGURE 4 *Phase Diagram of Mixture II (P1/M2)* ▲ (T_{g-n}), ■ (T_{k-n}), ● (T_{n-i}): DSC-measurements.

component. Within a range of $y_1 = 0$ to $y_1 = 0.7$, the glass transition temperature decreases from 287 K to 264 K. It is remarkable that the glass transition still occurs at a concentration of $y_1 = 0.7$. Consequently, a broad range for both transitions, crystallization and glass transition, appears ($y_1 = 0.23$–0.7). The calculations of the heats of the transformations are similar to the results obtained for the mixed system I. Below the transformation temperature T_{k-n}, the mixture is heterogeneous consisting of a crystalline M2-phase and a nematic mixture. Above the melting point, the system is homogeneous throughout the whole range of concentration.

In mixture III (P2/M1) (Figure 5), a liquid crystalline polymer with a smectic–nematic transition is used (see Table I). The smectic state is metastable and crystallizes by annealing above the glass transition temperature.

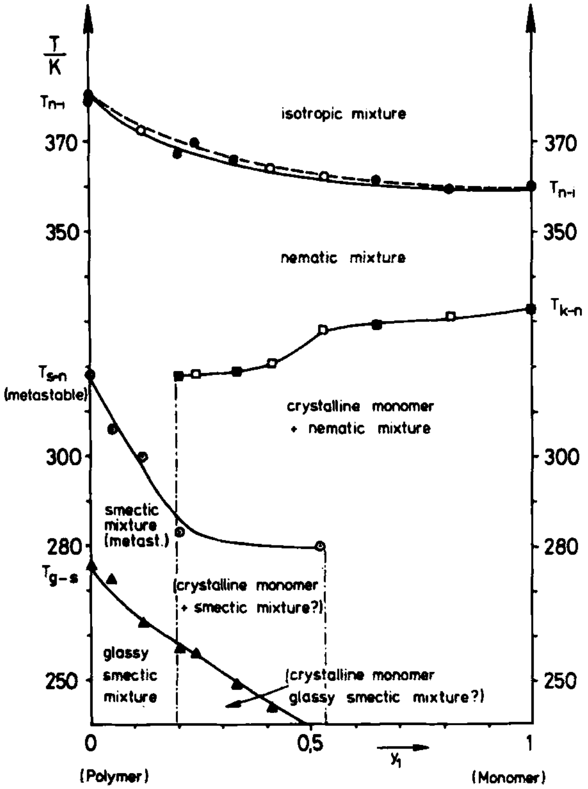


FIGURE 5 *Phase Diagram of Mixture III* (*P2/M1*) ▲ (T_{g-s}), ⊙ (T_{s-n}), ■ (T_{k-n}), ● (T_{n-i}): DSC-measurements; □ (T_{k-n}), ○ (T_{n-i}): Polarizing microscopic measurements.

The components are miscible over the whole range of concentration in the nematic and isotropic states. The shape of the transformation curve T_{n-i} (y_l) of the mixture is the same as expected from the other measurements. Starting from M1 ($y_l = 1$), the transformation temperature T_{k-n} decreases slightly over a wide range of mixtures and then decreases more strongly. This is in agreement with the measurements described before. In the range of concentration $y_l = 0.65$–0.33, there is a splitting of the DSC-peak of crystallization (see Figure 9), but there is no explanation of this effect at present. The transformation temperatures in Figure 5 relate to the greater peaks.

Looking at the transformation T_{s-n} of the LC polymer component, a strong decrease of the transformation temperature from 319 K for the pure polymer to 283 K for a mixture with $y_l = 0.2$ is observed. A further increase of the low molar mass content only slightly influences the transformation temperature. At concentrations greater than $y_l =$ 0.6, the DSC-curves show no phase transformation smectic–nematic.

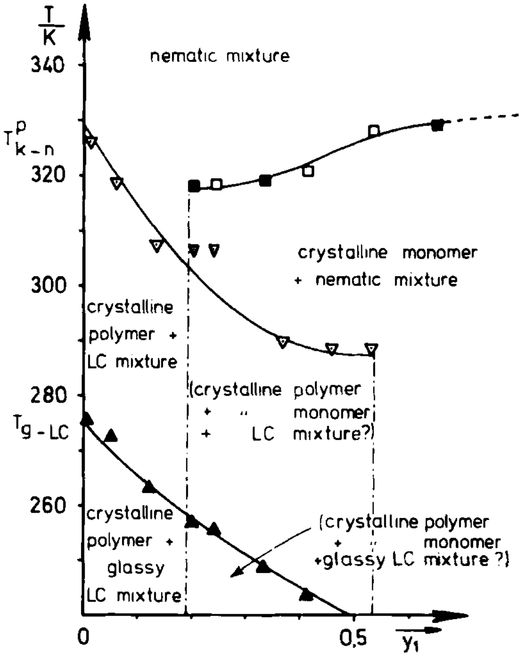


FIGURE 6 *Partial Phase Diagram of Mixture III (P2/M1)* ▲ ($T_{g\text{-}LC}$), ▽ (T^p_{k-n}), (■, □ see Figure 5). (T^p_{k-n} is the transformation temperature (crystalline–nematic) for the metastable smectic polymer component annealed at temperatures above the transformation curve (T_{s-n})(y_l) in Figure 5).

The effects in the DSC—diagrams become too small and the transformation of the smectic mixture between $y_l = 0.6$–1.0 may be suppressed for kinetic reasons. It is not easy to evaluate the DSC-curves in relation to the smectic-nematic transformation. This transformation in a mixture is only recorded by a broad peak in the DSC-curve with a small area representing a small heat of transition ($T_{s\text{-}n}$ in Figure 9). The glass transition temperature decreases from 276 K for the pure LC-polymer to 237 K at a low molar mass content of $y_l = 0.53$. In contrast to the measurements for mixtures I and II showing a glass transition glassy-nematic, this system shows a transition glassy–smectic.

The heats of transitions $\Delta\tilde{H}_{k\text{-}n}$ and $\Delta\tilde{H}_{n\text{-}i}$ are shown in Figure 7 and 8. They are not linear functions of the concentration y_l but slightly curved in the case of the transition crystalline-nematic (Figure 6) and more characteristic in the case of the transition nematic–isotropic (Figure 7).

To get more detailed information about the smectic–nematic transition, annealing experiments were carried out (40 h at 288 K, some degrees above $T_{s\text{-}n}$). Figure 9 shows as an example the DSC-curve for an annealed mixture with the low molar mass content $y_l = 0.41$.

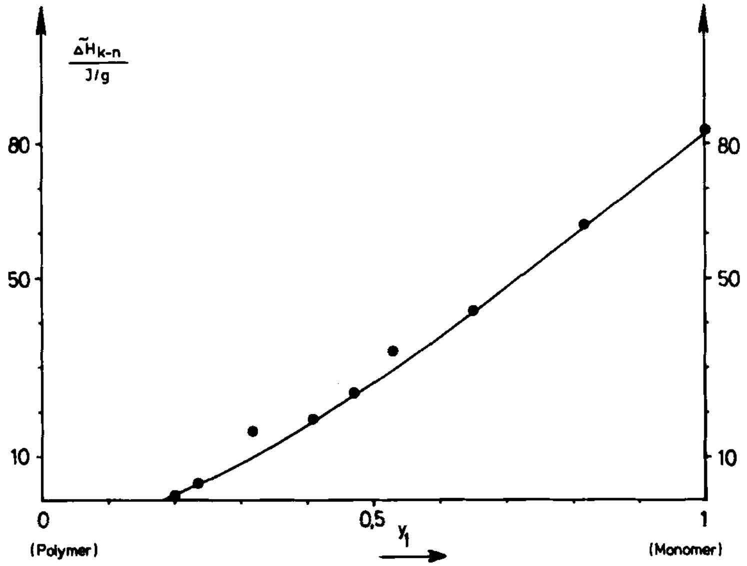


FIGURE 7 *Heat of Transformation* $\Delta\tilde{H}_{k\text{-}n}$ (Mixture III, related to the mass of monomer).

For comparison with this DSC-curve (b), the DSC-curve (a) for the non-annealed mixture is shown (Figure 9). Annealing of the sample above the glass transition temperature does not affect the transformation temperature T_{k-n} substantially. In contrast to this observation, the transformation smectic–nematic is replaced by a transformation crystalline–nematic at a temperature $T = 290$ K. The DSC-peak (Figure 9) can be assigned to the crystallization of the metastable smectic phase of the LC-polymer. The transition temperatures of this crystalline phase differ from the transition temperature T_{s-n} by about 10 K. On the other hand, annealing leads to a decrease in the "jumping" value Δc_p and to an increase of $T_{g-\mathrm{LC}}$.

The phase diagram of the annealed mixture III is partially shown in Figure 6.

In contrast to the phase diagram in Figure 5, the $T_{s-n}(y_1)$-curve is diminished, and a further crystallization curve $T^{p}_{k-n}(y_1)$ appears, which represents the crystallization of the metastable smectic LC-polymer.

A precise classification of the different phase regions is not possible in all cases, because the courses of the transition curves $T^{p}_{k-n}(y_1)$ and

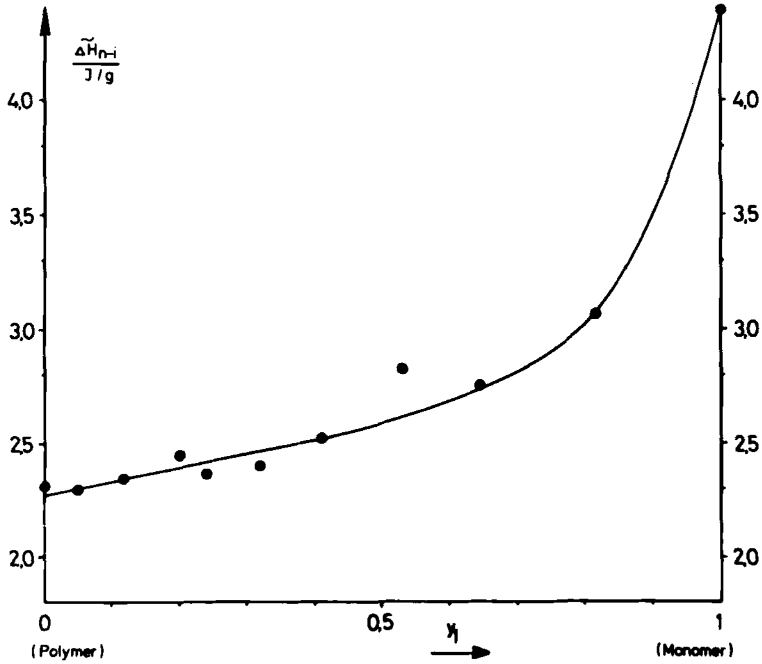


FIGURE 8 *Heat of Transformation* $\tilde{\Delta H}_{n-i}$ (Mixture III, related to the mass of mixture).

$T_{k\text{-}n}$ (y_l) below $y_l = 0.53$ and $y_l = 0.19$ respectively are not known.

The dash-dotted lines in Figure 5 and Figure 6 only indicate the disappearance of an endothermal peak in the DSC-measurements at the concentrations mentioned above, obtained by extrapolation of the heat of transformation.

The process of annealing in the range of $y_l = 0.2$–0.3 is more complicated than described above. The DSC-curve (Figure 10) of the sample which was not annealed shows smectic–nematic transitions ($T_{s\text{-}n} = 281$–287.5 K), crystalline-nematic ($T_{k\text{-}n} = 316.8$ K) and nematic- isotropic ($T_{n\text{-}i} = 369$ K curve (a) in Figure 10). As described above, annealing effects a crystallization of the metastable smectic phase. At higher annealing times [curve (b)], two maxima in the melting peak appear. The higher one corresponds to the transition crystalline-nematic for the low molar mass component, while the lower one indicates the melting of the crystalline polymer phase.

Higher annealing times as reported in this paper have no further influence on the shape of the DSC-curve. It is remarkable that the transi-

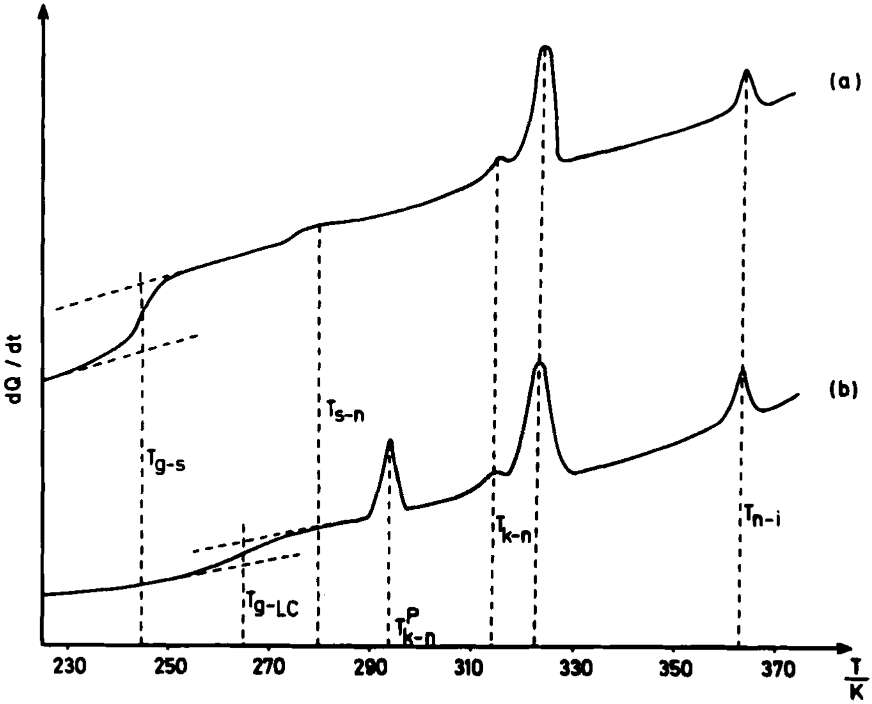


FIGURE 9 *DSC-curve of Mixture III* ($y_l = 0.41$) (curve b: annealed at $T = 288$ K for an annealing time t of 40 h).

tion temperatures T_{k-n} in this range of concentration do not lie on the transition curve $T^{p}_{k-n}(y_1)$ (see Figure 9). The glass transition temperature T_{g-LC} increases from 255 K to 260 K after annealing for 240 hours and the "jumping" value Δc_p decreases approximately 75 percent.

SUMMARY

The investigations indicate the miscibility of LC-side chain polymers and chemically related LC-low molar mass components in the nematic state. These mixing systems obey the rule of Arnold and Sackmann[3] as reported up to now for binary low molar mass mixtures. Contrary to most low molar mass mixtures, our systems show a glass transition in a certain range of concentration.

The presence of a low molar mass component reduces the glass transition temperature of the pure polymer component (plasticizing effect of the monomer) and leads to a broadening of the nematic phase. On the other hand, by adding a certain amount of the LC-polymer, the crystallization of the low molar mass component is suppressed and leads to a broadening of the nematic phase as well. Both effects exist in mixtures of LC-polymers and LC-low molar mass materials. If a suit-

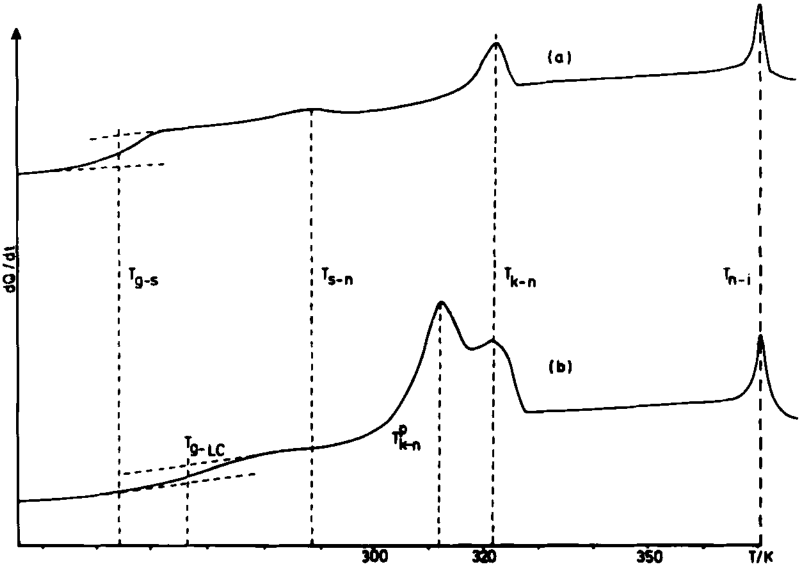


FIGURE 10 *DSC-curve of Mixture III* ($y_1 = 0.24$) (curve b: annealed at $T = 288$ K for an annealing time t of 240 h).

able concentration of the mixture is chosen, a large broadening of the temperature range of the nematic phase can be attained. Further investigations must be made to clarify the extent to which the results obtained can be generalized for other liquid crystalline polymer-monomer mixtures.

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