

유연격자 양단에 메소겐기를 갖고 있는 열방성 화합물. 9.
디메소겐성 네마틱 화합물과 네마틱 혹은 콜레스테릭
폴리에스테르와의 혼합성

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(1986년 6월 24일 접수)

**Thermotropic Compounds having Two Terminal
Mesogenic Units and Central Spacers. 9. Miscibility
between Dimesogenic, Nematic Compounds and Nematic
or Cholesteric Polyesters**

Dedicated to Prof. R. W. Lenz on his 60th birthday

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(Received June 24, 1986)

Abstract: Miscibility of dimesogenic, nematic compounds with main chain nematic or cholesteric polymers having flexible spacers was examined by differential scanning calorimetry and on a polarizing microscope. The four pairs studied in the present investigation revealed complete miscibility in mesophases. In solid state, however, they showed more complicated behavior. When the structures of a polymer and a dimesogenic compound were similar, eutectic formation was observed. No eutectic formation was detected when the structures of the pair were not similar. The Schröder-van Laar equation was able to approximately predict both the composition of eutectic compositions and the eutectic melting temperatures only for two systems among the four pairs of mixtures studied.

INTRODUCTION

Examination of miscibility between the liquid crystalline compounds is an often used indirect method for the identification of the mesophase formed by a newly synthesized liquid crystalline compound. Many multicomponent mixtures of liquid crystalline compounds also find important technical applications in the various electronic devices because of their widened temperature range of mesophases compared with those of each

component.

In the previous paper¹ we described the mutual miscibility of dimesogenic, nematic compounds of various structures. The isomorphous compounds not only exhibited miscibility in mesophases, but also agreed with Schröder-van Laar equation's (equations I and II) prediction in the eutectic composition and eutectic melting temperatures².

$$-\ln x_1 = \frac{\Delta H_m^1}{R} \left(\frac{1}{T} - \frac{1}{T_m^1} \right) \quad (\text{I})$$

$$-\ln x_2 = -\ln(1 - x_1) = \frac{\Delta H_m^2}{R} \left(\frac{1}{T} - \frac{1}{T_m^2} \right) \quad (\text{II})$$

where ΔH_m 's are heats of melting and x 's mole fractions. The numbers 1 and 2 stand for each component. It also was found that Demus and Sackman's selective miscibility rule³ is applicable to the miscibility between the dimesogenic compounds subjected to our earlier study.

There have appeared several papers on the miscibility between liquid crystalline polymers and low molar mass, monomesogenic compounds⁴⁻⁶. The selective miscibility rule seems to be applicable to these low molar mass-polymer liquid crystalline mixtures. Schröder-van Laar equation, however, was not successful in the prediction of their eutectic temperatures and compositions⁵.

Since it was found that the dimesogenic compounds with central spacers are better models than monomesogenic compounds for the semiflexible main chain mesomorphic polymers with the same spacers⁷, we became interested in the miscibility between dimesogenic compounds and liquid crystalline polymers.

The polymers and dimesogenic compounds chosen for this study are listed in Table 1. Three among the four polymers are nematic compositions^{7, 8} and the remaining one is cholesteric⁹. Properties of the dimesogenic compounds were earlier reported by us and they are nematics^{7, 10, 11}. It was also our interest to see if Schröder-van Laar relationship can be applicable to such binary systems. Differential scanning calorimetry (DSC) and visual observation of the mixtures on a polarizing mi-

croscope are the two methods employed in the present investigation.

EXPERIMENTAL

Synthesis and Properties of Liquid Crystalline Polymers and Dimesogenic Compounds All of the polymers and compounds chosen for this study were earlier reported by us⁷⁻¹⁰. Either newly or previously prepared samples were utilized in the present study. Characteristics of the polymers and the compounds pertinent to this investigation are summarized in Table 2.

Miscibility Study Examination of miscibility of the pairs given in Table 1 was conducted by DSC analysis and by visual observation of the mixture melts on a polarizing microscope. Phase diagrams were constructed based on the calorimetrically determined transition temperatures.

Accurately weighed mixtures of the two components were vigorously mixed in a mortar and heated to their isotropic states. The mixtures were then cooled to room temperature at a rate of ca. 10°C/min. Several milligrams of each mixture were taken in a DSC pan followed by sealing. The capped pan was placed on a duPont DSC 910 and thermal analysis was conducted under nitrogen atmosphere at a heating rate of 20°C/min. The maximum point of the heating endotherm was taken as the transition temperature. Enthalpy changes for transitions was calculated from the area of en-

Table 1. The Structure of LC Polymers and Dimesogenic Compounds^a

LC polymers		Dimesogenic compounds	
Description	Structure	Description	Structure
P-7, 10		Y-7	
P-5, 10		K-NO ₂	
P-Br		E-10	
P-Chol		E-5	

^aLC stands for 'liquid crystalline'.

Table 2. Eutectic Compositions and Eutectic Melting Points

LC Polymers	Dimesogenic Compounds	ΔH_m^a , KJ/mole	T_m^a , °K	ΔH_m^b , KJ/mole	T_m^b , °K	Experimental		Calculated	
						T_{eu} , °K	X_{eu}^c , mole%	T_{eu} , °K	X_{eu}^c , mole%
P-7, 10	Y-7	22.6	423	21.8	434	414	0.70	420	0.78
P-5, 10	K-NO ₂	7.70	442	7.20	449	423	0.70	410	0.85
P-Br	E-10	7.84	426	58.1	461	—	—	404	0.89
P-Chol	E-5	14.9	432	42.8	496	—	—	415	0.16

^aThe values for LC polymers.^bThe values for dimesogenic compounds.^cMole fractions of LC polymers expressed in moles of repeat-units.

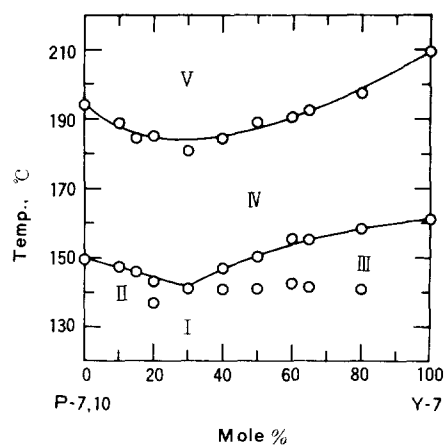
dothemic peaks obtained from the heating runs of DSC analysis. Indium was employed for calibration.

The same binary mixtures were placed on a hot-stage (Mettler FP-5) of a polarizing microscope (Leitz, Orthoplan) and possible phase separations were closely observed.

RESULTS AND DISCUSSION

In our earlier studies we found that all of the polymers and compounds described in this study (Table 1) were thermotropic, nematic compositions with the exception of cholesteric P-Chol⁷⁻¹⁰. The phase diagrams constructed for the four pairs are given in Figs. 1–4. All of the data points are calorimetrically determined ones. Although all of the four pairs exhibited complete mutual miscibility in their mesophases, they can be divided in two groups depending on the capability of forming eutectic mixtures. As shown in Figs. 1 and 2 the two pairs of P-7, 10/Y-7 and P-5, 10/K-NO₂ formed eutectic mixtures, while the pairs of P-Br/E-10 and P-Chol/E-5 pairs did not as presented in Figs. 3 and 4.

Unfortunately we do not yet have enough experimental facts which would enable us to give a definite reason for such a difference between the two groups. We, however, should take it into our account that the structural similarity between the pairs forming eutectic mixtures is far greater than

**Fig. 1.** Phase diagram for mixtures of P-7, 10 and Y-7 as determined from the DSC heating curves.

that between the non-eutectic forming pairs. The structural similarity certainly would favor the formation of eutectic mixtures. It is also interesting to note that the eutectic compositions of both P-7, 10/Y-7 and P-5, 10/K-NO₂ pairs are about the same, i.e., 70 polymer/30 dimesogenic compound (mole/mole).

Figs. 1 and 2 separate five distinguishing regions: region I of solid mixtures, region II with polymer solid plus nematic mixture, region III of low molecular weight solid plus nematic mixture, nematic region IV consisting of homogeneous mixture of two nematic components and the isotropic

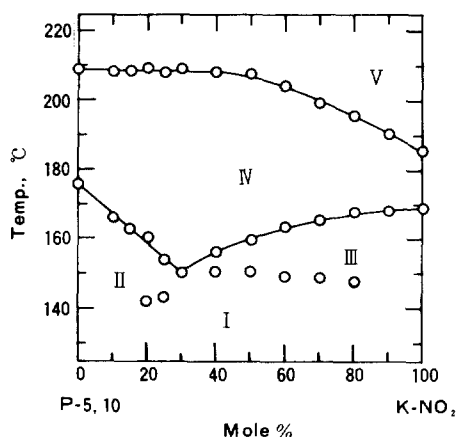


Fig. 2. Phase diagram for mixtures of P-5, 10 and K-NO₂ as determined from the DSC heating curves.

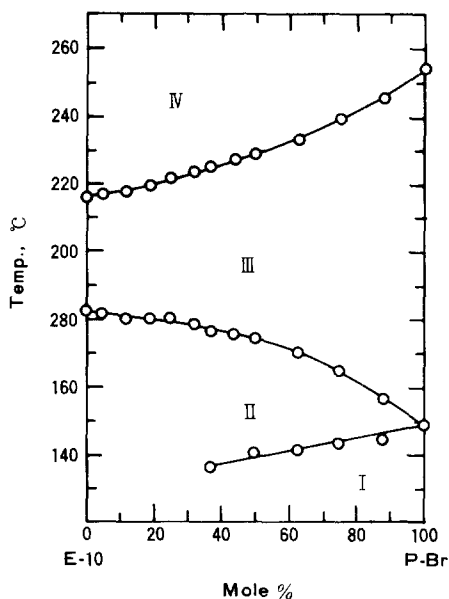


Fig. 3. Phase diagram for mixtures of P-Br and E-10 as determined from the DSC heating curves.

region V. The isotropic transition temperatures, T_i 's, of the mixtures changed smoothly and continuously depending on the composition. The isotropization curves, however, were not exactly linear revealing a non-ideal behavior. The first pair displayed a negative deviation from the linearity

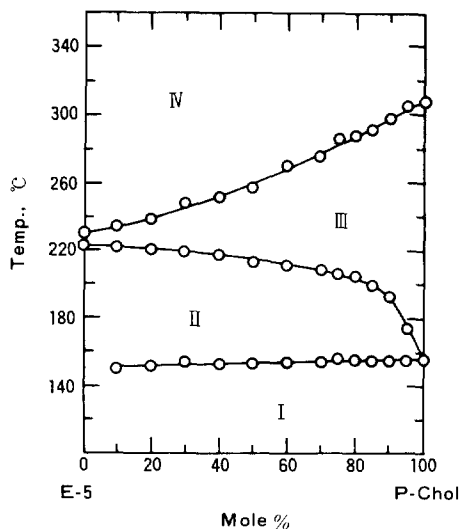
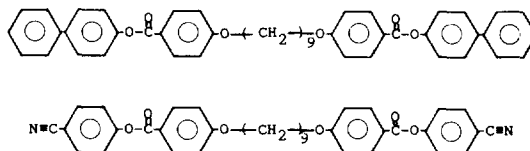


Fig. 4. Phase diagram for mixtures of P-Chol and E-5 as determined from the DSC heating curves.

while the second a positive deviation.

It is apparent that the nitro groups in K-NO₂ exert a significant degree of polar interaction resulting in enhanced intermolecular attraction between the molecules of K-NO₂ and the polymer P-5, 10, which would result in higher stability of mesophasic ordering. Such an interaction is not expected to occur in the first pair of P-7, 10/Y-7. We earlier observed a similar phenomenon in a miscibility study of dimesogenic, nematic compounds. For example, the following pair revealed a positive deviation¹,



although the extent of the deviation was less than that observed for the P-5, 10/K-NO₂ pair. On the contrary, analogous molecular interaction is not possible between P-7, 10 and Y-7, and the presence of the second component in the liquid crystalline phase significantly destabilizes the mesophase thermal stability.

The two systems whose phase diagrams are presented in Figs. 3 and 4 are much different from

those described above. The two diagrams show four, instead of five, distinctive regions: region I of solid mixtures, region II consisting of polymer mesophasic melt and dimesogenic solid, region III of mesophasic mixture and isotropic region IV. These two pairs of mixtures reveal very similar behavior in their dependence of transition temperatures on composition. The melting temperatures (T_m 's) of both components in the mixture slowly decreases as the content of the opposite component increases. These systems formed homogeneous mixtures in the mesophase reflecting a mutual miscibility between the two components involved. The P-Br/E-10 pair formed nematic phases while P-Chol/E-5 pair cholesteric states. It is an interesting observation that the low molar mass, nematic compound is freely miscible with cholesteric polymer. This implies that cholesteric pitch of a cholesteric polymer can be varied simply by mixing with different amount of a low molar mass, nematic compound. Noel et al.⁶ recently reported an observation very closely related to this. They observed that the nematic phase of liquid crystalline polyester could be transformed to the cholesteric one by dissolving an optically active compound in it.

Isotropization temperature curves of the binary mixtures of P-Br/E-10 and P-Chol/E-5 pairs are almost linear (Figs. 3 and 4), suggesting close-to-ideal behavior. Slight negative deviations are observed as shown in Figs. 3 and 4. It appears to be general that the binary mixtures of liquid crystalline polymer and a low molecular weight compound exhibit negative deviation from the ideal transition line for nematic→isotropic change^{5, 6}, unless there exists a specific molecular interaction as observed above for P-5, 10/K-NO₂ pair.

The miscibility of the four pairs in mesophase could be confirmed not only by DSC studies discussed so far, but also by the visual observation of the optical textures formed by the mixture melts.

As described above, only the first two pairs, i.e., P-7, 10/Y-7 and P-5, 10/K-NO₂, could form eutectic mixtures. In order to see if the eutectic compositions and melting points agree with prediction made

by the Schröder-van Laar equation, we calculated the values, see Table 2. As one can see from the results given in the Table 2, none of the systems followed the Schröder-van Laar equation. This discrepancy is probably due to a combination of various reasons. First of all, the enthalpy change for polymer melting transition, ΔH_m , is highly dependent of the thermal history of the sample or the degree of crystallinity. Moreover, the polymers which we are dealing with are polydisperse, which causes a certain degree of uncertainty in the measured value of melting point, T_m . It is also possible that fractionation of the polymer occurs by the presence of a low molecular weight, dimesogenic compound. Such a discrepancy was earlier observed also by Griffin and Havens⁵, and it seems to be a general rule than an exception for the mixtures composed of polymers and low molecular weight compounds. It is however worthwhile to note that the compositions of eutectic mixtures and the values of eutectic melting points of the first two pairs (P-7, 10/Y-7 and P-5, 10/K-NO₂) are not too far from those predicted by Schröder-van Laar equation.

CONCLUSIONS

The following conclusions can be drawn from the present investigation:

- 1) The four pairs of liquid crystalline compositions are mutually miscible in mesophases over the whole range of compositions.
- 2) The Schröder-van Laar equation does not seem to be applicable to the mixtures of liquid crystalline polymers and low molecular weight compounds, although eutectic compositions and melting temperatures are not too far from those theoretically predicted when the structures of the pair are similar.
- 3) Demus and Sackmann's selective miscibility rule seems to be applicable to polymer/low molar mass compound mixtures of liquid crystalline nature.

Acknowledgement: We thank the Korea Science and Engineering Foundation for support.

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