Miscibility between Dimesogenic Compounds

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Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer, 8. Mutual Miscibility between the Dimesogenic, Nematic Compounds

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Mutual miscibility between thermotropic, nematic compounds with two terminal mesogenic units and a central spacer was studied by differential scanning calorimetry (DSC) and on a polarizing microscope. It was found that the isomorphous, nematic dimesogenic compounds with wide variety of structures are miscible in mesophases with each other over the whole range of composition and that Schröder-van Laar equation almost correctly predicts the melting temperature and composition of eutectic mixtures. There was a pair of compounds which were exceptional and did not form a eutectic mixture and, instead, revealed a monotonous change in melting (T_m) and isotropic transition temperatures (T_i) as the composition of the mixture was varied. The compounds were of almost same structure in shape and seemed to undergo formation of solid solution.

Introduction

We have been investigating the liquid crystalline properties of a wide variety of series of thermotropic dimesogenic compounds with two terminal mesogenic units and central polymethylene spacers.[1-3] It was found that melting (T_m) and isotropization temperatures (T_i) of this type of compounds (I) show odd-even dependence on the number of carbon atoms in the central spacer and that these compounds can be taken as models for main chain thermotropic polymers (II) with similar mesogenic units and the same spacers.[3]

$$\boxed{\ }\!\!\!\sim\!\!\!\sim\!\!\!\boxed{\ } \qquad (I)$$

$$\sim\!\!\!\sim\!\!\boxed{\ }\!\!\sim\!\!\!\sim\!\!\boxed{\ }\!\!\sim\!\!\!\sim\!\!\boxed{\ }\!\!\sim\!\!\!\sim \qquad (II)$$

$\boxed{\ }$; mesogenic unit

$\sim\!\!\!\sim$; spacer

Other thermodynamic parameters such as change in enthalpy (ΔH_i) and entropy (ΔS_i) for isotropization also showed a regular odd-even dependence on the number of methylene units in the spacers.

On the other hand, it is well known that selective miscibility rule originally developed by Sackmann and Demus[5] is applicable to low molecular weight thermotropic compounds.[6,7] This rule states, "all liquid crystalline modifications which exhibit an uninterrupted series of mixed crystals in binary systems without contradiction can be marked with the same symbol". This rule, however, has been tested up to now mainly for monomesogenic compounds, *i.e.* those with only one mesogenic unit.

It is also well known that Schröder-van Laar equation (III or IV) predicts correctly the eutectic compositions of binary mixtures of monomesogenic compounds.[8,9]

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

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

where ΔH_m's are heats of melting and x's mole fractions. The numbers 1 and 2 stand for each component.

While we were trying to establish the structure-property relationship of dimesogenic compounds of type I, we became interested in their mutual miscibility in mesophase. Whether

Table 1. Structure of the Compounds

COMPOUND 1	COMPOUND 2
E-5	E-8
E-4	P-4
E-9	Y-9
E-9	E-N
E-9	P-3
E-9	P-10

or not Schröder–van Laar equation can be applied to these binary mixture systems was also a point of interests to us. Miscibility of the present systems (see Table 1) was studied by differential scanning calorimetry (DSC) and by the optical observation of the mixture melts on a polarizing microscope equipped with a hot stage.

Results and Discussion

As shown in Table 1 wide variety of combinations of dimesogenic compounds were subjected to the present miscibility study. Combinations include the pairs of compounds with different length of central spacers, with different terminal substituents, and with different mesogenic unit. All of the compounds shown in the table were reported earlier by us and are nematics.

According to the phase diagrams shown in Figures 1-6, all of the nematic pairs studied are mutually miscible and form a single phase over the whole range of mesophasic compositions. They, with the exception of E-9/Y-9 pair (see Figure 3), also are able to form eutectic mixtures, whose compositions varied widely depending on the pairs' structures. The compositions forming eutectic mixtures all revealed five regions (I-V) in the phase diagrams (Figures 1, 2 and 4-6): (I) solid 1 plus solid 2, (II) solid 1 plus nematic phase, (III) solid 2 plus nematic phase, (IV) nematic phase, and (IV) isotropic phase. The E-9/Y-9 pair was unique in that melting point of the mixture changed continuously over the whole range of composition. This is a strong indication that cocrystallization occurs during cooling process. Eutectic formation could not be observed for this pair. As a result, only three regions (I-III) exist in the phase diagram (Figure 3): (I) solid 1 plus solid 2, (II) nematic phase, and (III) isotropic phase.

These two compounds, E-9 and Y-9 are of about the same structure with the only difference being in the order of ester linkages in the mesogenic unit. The reverse order of the linking group is not expected to cause much difference in the stereogeometry of the compounds. Such a structural similarity appears to allow for the two compounds to cocrystallize during solidification. Slight depression of Tm's observed for the mixtures, however, suggests that crystal packing becomes slightly less efficient when the two compounds are cocrystallized.

The isotropization temperature of the mixtures revealed almost linear dependence on the composition as shown in Figures 1-6, which suggests the close-to-ideal nature of the
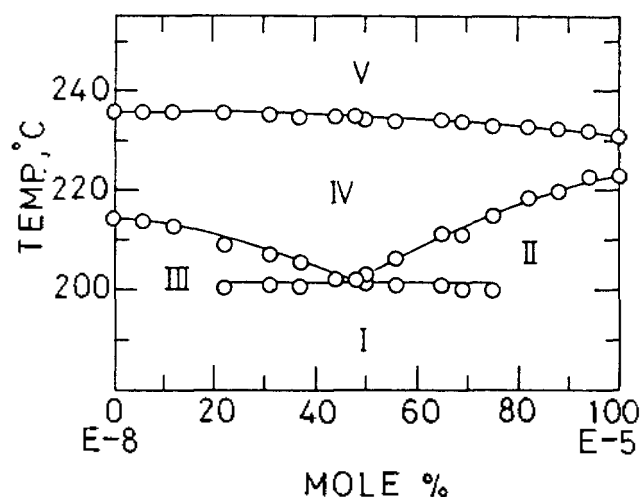

Figure 1. Phase diagram for mixtures of E-5 and E-8 as determined from the DSC heating curves.
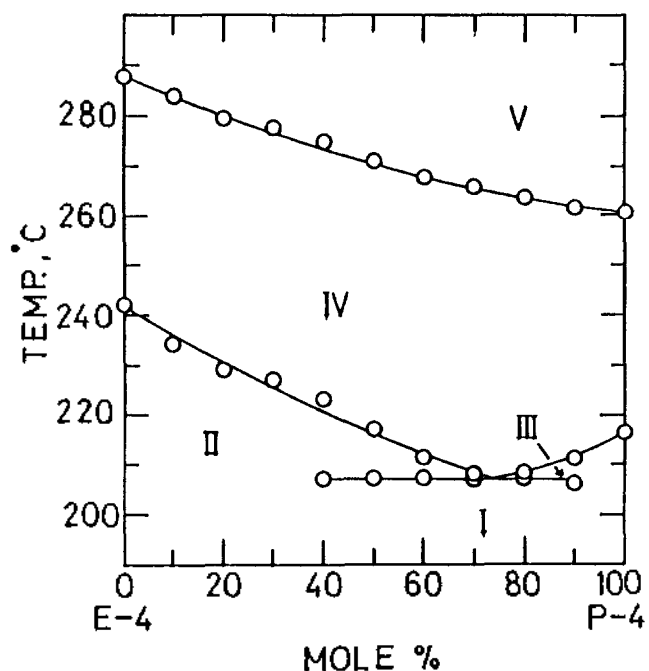

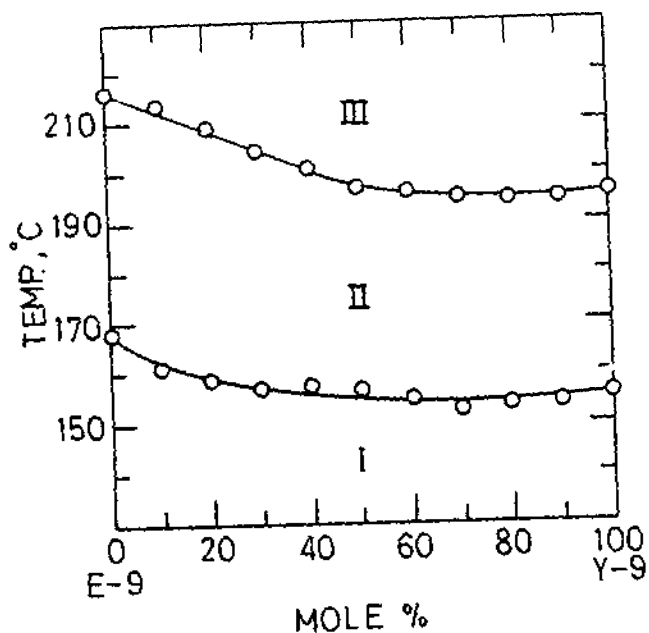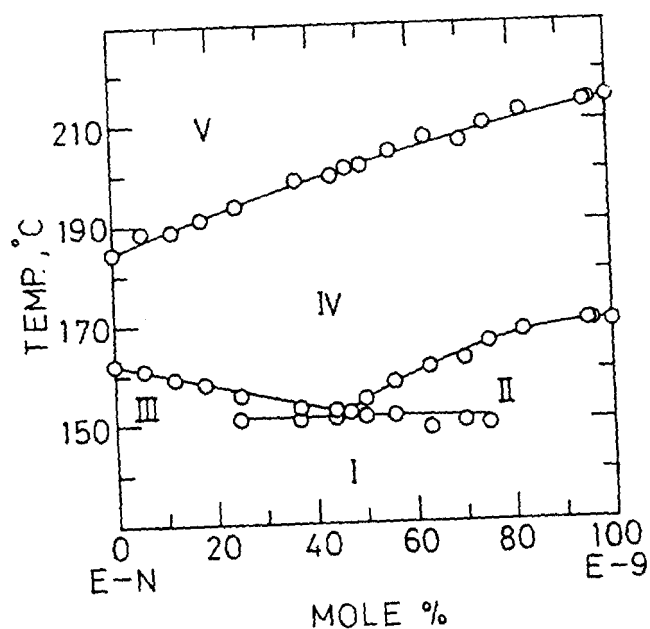**Figure 2.** Phase diagram for mixtures of P-4 and E-4 as determined from the DSC heating curves.

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Figure 3. Phase diagram for mixtures of Y-9 and E-9 as determined from the DSC heating curves.

Figure 5. Phase diagram for mixtures of P-3 and E-9 as determined from the DSC heating curves.

Figure 4. Phase diagram for mixtures of E-9 and E-N as determined from the DSC heating curves.
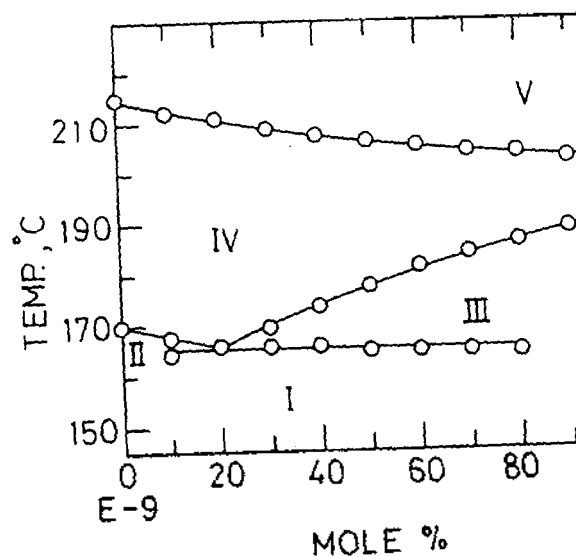
Figure 6. Phase diagram for mixtures of P-10 and E-9 a mined form the DSC heating curves.

mixtures in liquid crystalline phases. There are, however, observed slight negative (Figures 2, 3 and 6) or positive deviations (Figure 4) from the linearity, although the degree of deviations is very small. It should be noted that mesophase temperature range for the mixtures was maximum at the eutectic compositions. Figure 7 shows a representative DSC thermogram of an E-9/P-10 mixture in the mole ratio of 1:4.

It is rather surprising to notice the largest deviation from the ideality was observed for E-9/Y-9 pair which, as discussed above, exhibited cocrystallization in solid. In spite of the slight difference in their structures the intermolecular attraction in mesophase between the same species must be stronger than
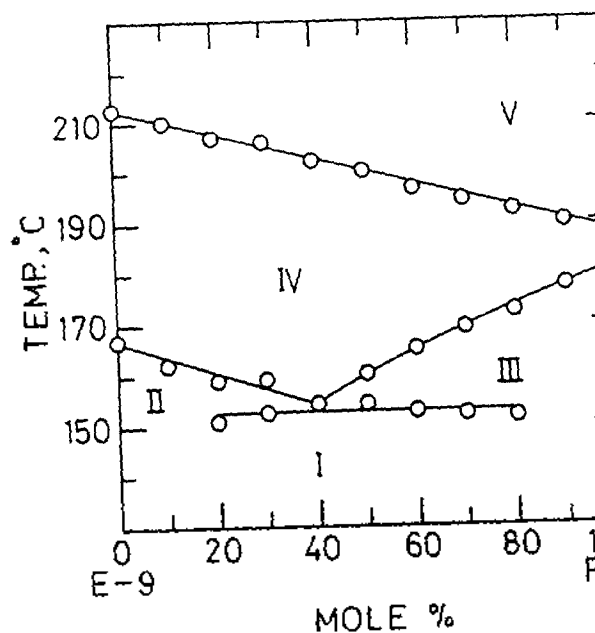
observed for the E-9/E-N pair (Figure 4) is likely to ha originated from the favorable intermolecular interac tween the pair induced by the terminal, dipolar subs (nitrile and phenyl groups) of opposite polarity. As far mal transitions and mutual miscibility of the mixtures cerned, the observations described above could confirmed by visual examination on a polarizing mici Any phase separation and appearance of any new opt tures were not observed.

In order to see whether the pairs of the present stud the Schröder-van Laar relationship we calculated tl tic melting temperatures (T_m) and compositions (X the equations III and IV and the results are tabulated 2. The experimentally obtained values of ΔH_m, T_m and

Table 2. Eutectic Compositions and Eutectic Melting Points

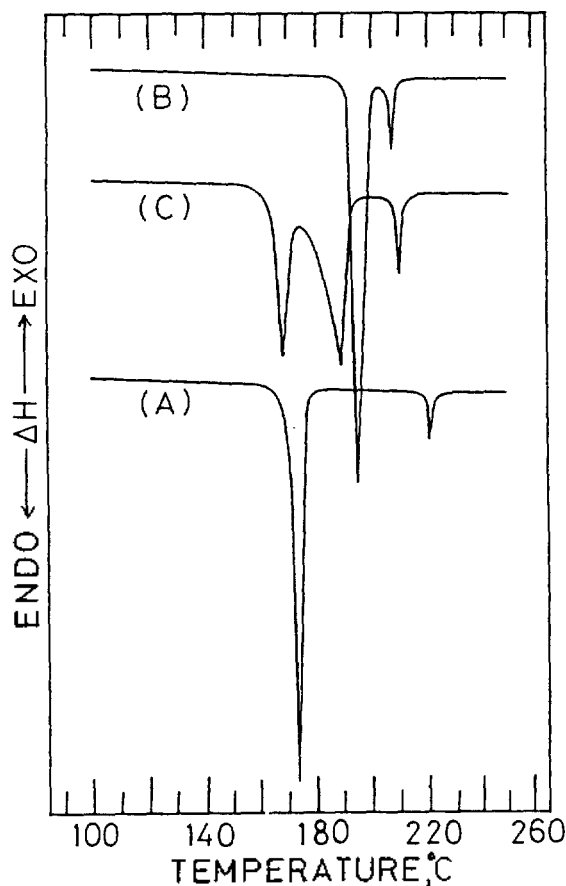| Compound 1	Compound 2	T_m^1 °K	ΔH_m^1 KJ/mole	T_m^2 °K	ΔH_m^2 KJ/mole	Experimental		Calculated	
						T_m °K	X_m* mole %	T_m °K	X_m* mole %
E-5	E-8	496	42.8	488	51.2	475	0.48	465	0.48
E-4	P-4	515	68.2	489	44.4	480	0.27	476	0.27
E-9	Y-9	442	37.2	429	20.2	—	—	414	0.19
E-9	E-N	442	37.2	435	50.1	425	0.53	413	0.51
E-9	P-3	442	37.2	448	38.2	427	0.61	426	0.61
E-9	P-10	442	37.2	463	67.4	438	0.80	436	0.86

*Mole fraction of Compound 1.

Figure 7. DSC thermograms of (A) E-9, (B) P-10 and (C) a mixture of E-9/P-10 in the mole ratio of 1:4.

employed for the calculation. The experimental values of T_m as well as X_m are also included in the table for comparison. In general, the agreement between the experimental values and predicted values is fairly good. We believe that slight deviations of experimental values from the theoretical prediction can be attributed to the non-ideality of the systems as well as to the experimental errors existing in the determination of ΔH_m's and T_m's by dynamic calorimetry. It is well known that several percent error can occur in the determination of ΔH_m by DSC.[10] Moreover, DSC runs in this study were made at the heating rate of 10°C/min, which also must have caused a certain degree of uncertainty in the values of T_m used in the calculation. Theoretically, for thermodynamical

equilibrium, one has to employ extremely slow heating rate, ideally close to 0°C/min, which is certainly impossible to be accomodated in practice.

Conclusion

Following conclusions can be drawn from the present investigation:

(1) All of the pairs of nematic, dimesogenic compounds described are mutually miscible and form eutectic mixtures, with the only exception of E-9/Y-9.

(2) Schröder-van Laar equation was found to be able to successfully predict the composition and melting temperature of eutectic mixtures.

(3) All, but a couple of the pairs, revealed almost perfect linear dependence of clearing temperature on the composition of the mixtures.

(4) The melting temperature of the E-9/Y-9 pair which are of almost the same structure, changed monotonously with compositional change indicating cocrystallization of the two compounds in the solid state.

Experimental

Synthesis of the Compounds. Syntheses of the compounds were described earlier by us[1,3,11] and the same synthetic methods were employed. The compounds were identified by their mp, IR and NMR spectra.

Miscibility Study. Binary mixtures of known compositions were heated above melting temperature and thoroughly mixed. They were then slowly cooled (ca. 40°C/min) to room temperature by allowing them to stand at room temperature. Small quantity (ca. 10 mg) of thus prepared mixture samples was taken for DSC (duPont 910) analysis. Heating rate was 10°C/min. All of the DSC runs were made under a nitrogen atmosphere. The temperature where the endothermic peak maximum appeared on DSC heating curves was taken as a transition temperature. Indium and lead were employed for calibration of temperature scales and the enthalpy changes. The same mixtures were examined on a polarizing microscope equipped with a hot-stage. Any change in optical textures and thermal transitions were closely followed.

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Synthesis of Some Conjugated Polyynes

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Several aryl substituted 1,3,5-hexatriynes were synthesized by the use of aryl containing trimethylsilylated 1,3-butadiyne intermediates. 1-Phenyl-1,3,5-heptatriyne, one of the naturally occurring phototoxic conjugated polyacetylenes, and 1-(1'-naphthyl)-1,3,5-heptatriyne were prepared by the use of 1-trimethylsilyl-1,3-pentadiyne which is a very stable precursor for the 1,3-pentadiyne at room temperature.

Introduction

Certain naturally occurring conjugated polyacetylenes such as 1-phenyl-1,3,5-heptatriyne(PHT) have been reported to be phototoxic to a variety of substrates.[1-5] However, little is known about the photochemistry of conjugated polyacetylenes. In connection with this problem, we needed a variety of conjugated polyynes –especially aryl containing conjugated polyynes which are similar to PHT– and study their photochemical and photophysical properties.

Synthesis of these compounds, therefore, was carried out and the schemes were devided into three parts:

Part-1: Synthesis of diyne units.
Part-2: Coupling of triple bonds(mono or diyne) with aryliodides.
Part-3: Extension of triple bond units and variation of the substituents of triple bond by coupling reactions.

In order to satisfy these purposes, considerably stable and asymmetrically substituted butadiynes such as trimethyl silylated 1,3-butadiynes were required. Generally, the base promoted elimination reaction of 1,4-dichloro-2-butyne was used for the preparation of diyne units.[6-10] But reaction condition is unfavorable for trimethylsilylation[11] and (Z)-1-methoxybut-1-en-3-yne as diyne source was used instead.[12]

Classical synthetic methods for the terminal arylacetylenes in general involve manipulation of preformed, two carbon side chains and include methods such as the Vilsmeier method,[13,14] the halogenation–dehydrohalogenation sequence of vinyl aromatics[15] and ketones,[16,17] and the dehydrohalogenation of β, β-dihalo olefins.[18,19] Terminal aryl butadiynes have also been

prepared by the use of aryl-1,4-butandiol-2-ynes as a precursor through several steps[20] or coupling reactions between aryl acetylenes[11,21] and triethylsilylacetylenes. Trimethylsilyl group cannot be used in this case because of the sensitivity of the trimethylsilyl-acetylene bonds to base.[11] A recent innovation in the synthesis of arylacetylenic compounds has been the use of protecting groups.[22] Acetylenes, protected at one end, can be introduced onto an aromatic nucleus via coupling at the free end. Subsequent removal of the protecting group generates a terminal arylacetylene. The widely accepted procedure for the introduction of an acetylenic substituent onto an aromatic nucleus is the Stephens–Castro methods.[23-25] An elegant alternative to the Stephens–Castro methods rests in the coupling between arylcopper reagents and (iodoethynyl) trimethylsilane below ambient temperatures.[26] Recently, however, it was reported that the palladium–catalyzed coupling reaction between arylhalides and ethynyltrimethylsilane give trimethylsilylated arylacetylenes which yield ethynylated aromatic compounds after removal of the trimethylsilyl group with base, quantitatively.[27,28] These reactions can be proceeded at room temperature. Several trimethylsilyl arylacetylenes and arylbutadiynes were synthesized by the use of this reaction. Moreover various symmetric and asymmetric aryl containing conjugated polynes are synthesized through self or cross coupling reactions of them. Trimethylsilyl group plays an important role in synthesis as a protecting group and as one which enhances the stability of resulting butadiynes.

For the synthesis of the polyynes, present method offers some distinct advantages over methods using a copper acetylides, alkynylzinc, and aryl copper reagents in terms of