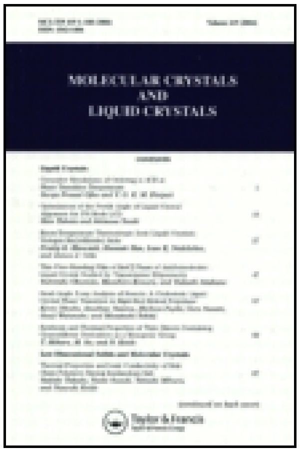

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Molecular Structural Effects on Mesophase Behavior of Monomers and Polymers : Azo vs Olefinic

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Molecular Structural Effects on Mesophase Behavior of Monomers and Polymers: Azo vs Olefinic

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Two monomers containing two phenylene rings, two linking units, and one phenyl group have been synthesized. The linking units were ester and azo functionalities for one of the monomers, and ester and olefinic for the other. Phase transitions, range of mesophase stabilities, textures, enthalpy, and/or entropy changes of the two mesogens are compared for the monomeric and polymeric forms. Thermal transitions observed by differential scanning calorimetry were confirmed by optical microscopy. The results reveal that while there are markedly different structural effects in the monomers, such effects are considerably diminished in the polymers. However, the polymers had substantially different textures as confirmed by a solution-cast miscibility study. The data illustrate that mesogenic systems containing three phenyl rings and two linking units as opposed to two phenyl rings and one linking unit do allow one to better assess molecular structural effects on mesophase behavior.

Keywords: comblike polymers, liquid crystals, structure-mesophase relationships

INTRODUCTION

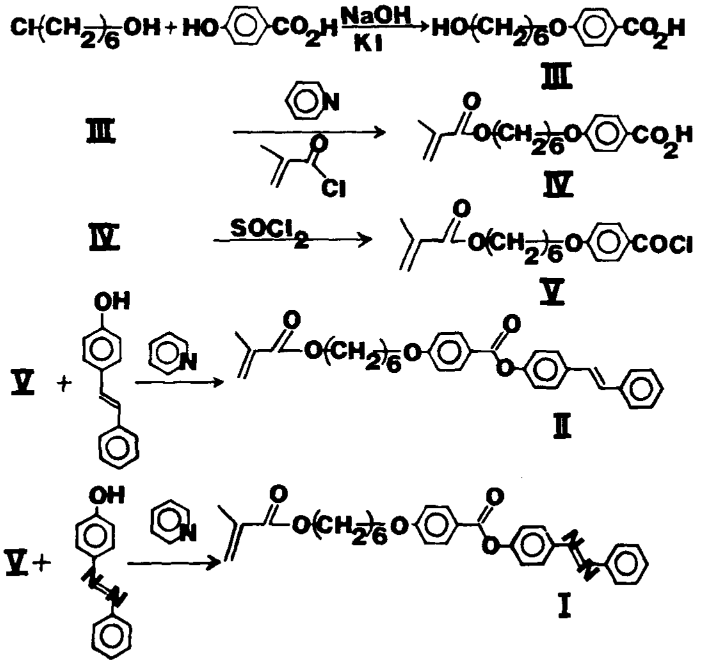
In comblike liquid crystalline (LC) polymers, the mesogenic group is linked to the main chain polymer, as a pendant group, by a flexible spacer. Despite the considerable amount of work undertaken in this area,[1-3] there are still several problems that need to be addressed. Liquid crystalline property in these polymers is attributed to decoupling of the motions of the mesogen from that of the main chain.[4] Linking of the mesogens to a main chain by flexible spacers, however, restricts rotational and translational motions of the mesogens in the polymer.[5] The precise role, at the molecular level, played by this motional restriction and the degree of decoupling of the motion is not clearly understood. Comparative studies using monomers and polymers should give some insight into this problem. Similarly, there is no common view on the thermal changes of LC order in polymer systems.[6] Correlation of LC order, obtained by direct methods such as NMR, and thermal properties should be very helpful in this case. The extent of mixing of LC polymers at the molecular level and the role played by chemical structure is another area of not only fundamental but also technological and industrial interest. It is obvious that further work is warranted in this area.

The above, and related problems require molecular interpretation of mesophase behavior. We have, therefore, recently initiated work in our laboratories in molecular structure-mesophase behavior relationships using comblike polymeric LC systems. We have chosen mesogenic systems containing three phenyl rings and two linking units (Scheme 1) for our initial work. The rationale for this choice, as opposed to mesogens of two phenyl rings and one linking unit, is based on the expectation that such mesogens would give two mesophases thus allowing one to assess the molecular structural effects on mesophase behavior. In this report, we will compare the mesophase behavior (phase transitions, mesophase stability, enthalpy and entropy changes) of two mesogens, which vary in only one linking unit (azo vs olefinic), in their monomeric and polymeric forms. Preliminary results on the miscibility of the polymers which confirm textural differences will also be reported. The results show that molecular structural effects are less pronounced in the polymeric forms, a result which we interpret to be due to the translational and rotational motional restriction imposed on the pendant mesogens by the polymer backbone.

EXPERIMENTAL

Synthesis

The synthesis of monomers I and II were accomplished by the following standard reactions (Scheme 1).[7]



Scheme 1. Sequence of reactions used for the syntheses of monomers I and II.

All the products were purified by recrystallization from methanol several times. The purities of the monomers were checked by proton FT NMR spectroscopy. The free radical polymerization of the monomers was carried out in 20% DMF solutions (degassed with N_2 for four hours). The monomer to initiator (AIBN) ratio was 300:1. A precipitate was obtained by adding boiling ethanol to the reaction mixture which was heated at 70–80°C for 24 hours under N_2. The residue, washed several times with boiling ethanol to remove unreacted monomer, was dried under vacuum at 110°C and was characterized by proton and ^{13}C FT NMR spectroscopy. Preliminary ^{13}C NMR analysis of the polymers showed predominantly syndiotactic microstructures for both polymers.

Measurements

The monomers, polymers, and blends of the polymers (prepared by casting from chloroform solutions) where characterized by differential scanning calorimetry (DSC) on a Du Pont 990 thermal analyzer and a Perkin Elmer DSC-4 system (ΔH values were calculated using the

DSC-4 software). Both annealed and quenched (from isotropic phase) samples were analyzed at different heating and cooling rates to assess the effect of thermal history and recrystallization behavior. Thermogravimetric analysis was done on a DuPont 951 TGA system. Optical polarization microscopy was performed on a Leitz Laborlux 12 Pol microscope fitted with an automatic camera and a Mettler FP 80/82 hot stage. All phase transitions observed by DSC were confirmed by optical microscopy. Both proton and carbon-13 NMR spectra were obtained on a Bruker WM-250. Molecular weight data were obtained by gel permeation chromatography (Waters 150-C ALC/GPC) using a polystyrene standard (at room temperature in tetrahydrofuran).

RESULTS AND DISCUSSION

Listed in Table I are the T_m's and T_g's of the monomers and the polymers, their mesophase transition temperatures (T_{12} and T_{2I}) and ranges of mesophase stabilities (ΔT). The data for monomer and polymer III are taken from the literature.[8,9] Table II lists the enthalpy and entropy changes of the monomers, and their respective polymers.

Comparison of monomers

The three monomers differ, chemically, only in the nature of one linking unit: azo (monomer I), olefinic (monomer II), and none (bi-

TABLE I

Thermal properties and mesophase textures[a] of monomers and polymers I, II, and III

	$T_m(T_g)$	T_{12}^{b}	T_{2I}^{c}	$\Delta T_1(\Delta T_2)^{d}$
Monomer				
I	K90S†	†94N†	†N99I	4(5)
II	K99S	S144†	†165I	45(21)
III[e]	K64S	S68N	N92I	4(24)
Polymer				
I	135H	S172SS	SS188I	37(16)
II	135H	S172N	N212I	33(40)
III[e]	132H	S164N	N184I	32(20)

[a] S = smectic, N = nematic, SS = schlieren smectic C, K = crystal, H = homeotropic, I = isotropic. † indicates that the assignment is tentative, or that the exact texture has not been assigned.

[b,c] First and second phase transition temperatures in °C.

[d] Range of mesophase stability for first (ΔT_1) and second (ΔT_2) mesophases.

[e] Taken from Reference 8.

TABLE II

Enthalpy and entropy changes[a,b]

	ΔH_1	ΔH_2	ΔH_3	ΔS_1	$\Delta S_2 \times 10$	$\Delta S_3 \times 10$
Monomer						
I	9315		94	25.66		2.62
II	10367	48.4	85	27.87	1.2	1.94
III	6579		115	19.52		3.15
Polymer						
I		136	194		3.06	4.21
II		40	102		0.76	2.1
III[c]		86	252		2.03	5.54

[a] Enthalpy changes are in cal/mole for monomers and cal/(mole of mesogen) for polymers.

[b] Entropy changes are in cal/mole.deg for monomers and cal/(mole of mesogen.deg) for polymers.

[c] Taken from Reference 9. ΔH_1 and ΔS_1 are for the K to LC transitions of only the monomers. ΔH_2 and ΔS_2, and ΔH_3 and ΔS_3 are for the first and second mesophase transitions of the monomers and polymers. GPC data were: $M_w = 1.7 \times 10^4$, $M_n = 1.1 \times 10^4$ and $M_w/M_n = 1.5$ for polymer I; $M_w = 2.4 \times 10^4$, $M_n = 8.8 \times 10^3$ and $M_w/M_n = 2.7$ for polymer II. Both polymers were fractionated (by precipitation) once using hot dimethylformamide and methanol.

phenyl, monomer III). Some of the effects of the differences in molecular structure on the mesophase behavior of the three monomers can be discerned from the data in Table I. The apparent similarities are (1) all the monomers appear to have two mesophases, (2) the ΔT_1's of monomers I and III, and the ΔT_2's of monomers II and III are about the same, and (3) the T_{2I}'s of monomers I and III are also about the same. There are however a number of differences among the monomers: (1) the T_m, T_{12}, and T_{2I} of monomer III are consistently lower than those of monomers II (by 35, 76 and 73° respectively), and I (by 26°, 26° and 7° respectively); (2) the ΔT_1 of monomer II is about ten times that of monomers I and III; (3) the ΔT_2 of monomer I is substantially lower than that of monomers II and III (5° vs 21° (monomer II) and 24° (monomer III)); (4) the overall ranges of mesophase stability are 8°, 66°, and 28° for monomers I, II, and III, respectively; (5) the textures of monomer III have been assigned to be smectic and nematic;[9] but the textures of monomer I and II are not easily assignable (vide infra), except for the first mesophase of monomer II which is smectic.

When monomer II was heated, while being irradiated with polarized light, no mesophase behavior was observed above 145°C. The DSC thermogram, on the other hand, showed an endotherm at 165°C (Figure 1). It must be emphasized, that the observability of this second endotherm is very dependent on sample history and instrumental

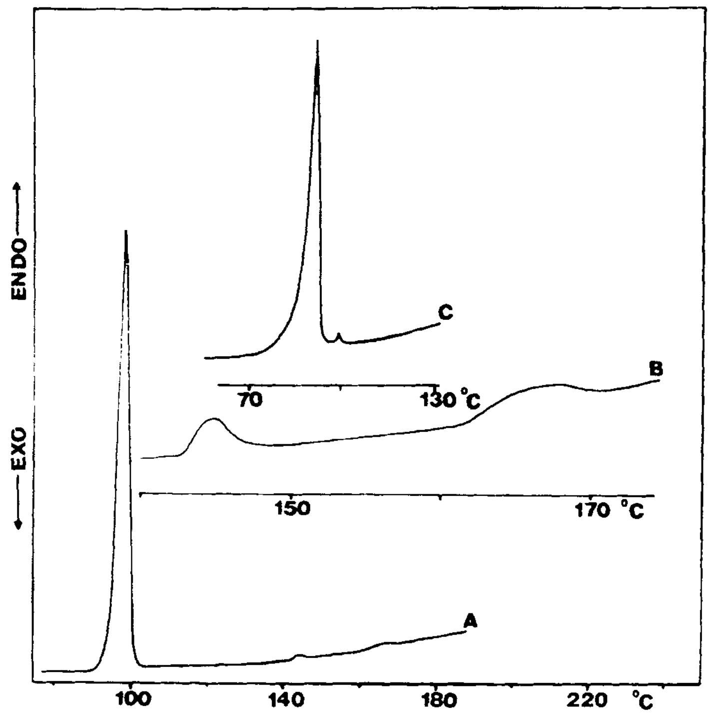


FIGURE 1 DSC thermograms of monomer I (C) and monomer II (A). The expanded curve B shows the two transitions of monomer II in the fluid state.

sensitivity. When the material was heated without being irradiated, to a temperature >145°C, a mesophase, albeit thermodynamically unstable, that became isotropic at about 165°C (this corresponds to the transition temperature observed by DSC) was observed. The cis-isomer of monomer II is not probably conducive to LC formation, and can accumulate on exposure to light due to photochemical isomerization,[10] thus making the mesophase unobservable. As alluded to earlier, depending on sample history we have also observed in the second mesophase region (145–165°C), a continuous phase with a nematic-type texture coexisting with another phase, consisting of small spherical oriented domains (some actually interspersed in the nematic-type continuous phase), the texture of which we have been unable to assign. This, we believe, is due to the trans → cis isomerization process.[11] If it were not for this process, the second mesophase of monomer II, we reason, would have been a stable nematic phase.

The case of monomer I is even more intriguing. This monomer has a fluid state which is apparently biphasic, with the range of this biphasic mesophase stability being roughly 10° (approximately 5° per mesophase). The "first" phase, because it occurs in a narrow range which overlaps with the melting transition, does not develop its full texture. The "second" mesophase showed points of singularities with four brushes ($|s| = 1$). Again, before this material develops its true texture, the material becomes isotropic. The disinclinations in the structure (singularities) with $|s| = 1$ suggest schlieren textures.[12] Whether these textures are nematic or smectic C could not be determined from the optical microscopic examination.

The extent of supercooling and crystallization were compared for monomers I and II using data obtained from DSC cooling curves (10°C/min). The enthalpy of recrystallization (LC to crystal (K) transition at 64°C) of monomer I is about 89% of the melting enthalpy change obtained from the heating curve (K to LC transition at 94°C). The supercooling effect was found to be about 30°C. For monomer II (LC to K transition at 50°C) on the other hand, the enthalpy of recrystallization was only 25% of the melting enthalpy (K to LC transition at 98°C). The supercooling effect in this case was about 48°C. These results suggests that the kinetics of recrystallization in monomer I is probably considerably faster than in monomer II. At a cooling rate of 10°C/min the LC to K transition was not observed for monomer III. These results can be explained by the greater anisotropic "molecular" polarizability in monomer I. While attractive London forces can be operative in all the monomers, the magnitude of the London forces (due to instantaneous, induced, and permanent dipoles) should be greater in monomer I because of the greater polarizability of the azobenzene unit, compared to that of the stilbene and biphenyl units.

The first mesophase transitions are clearly observable in the cooling curves for both monomer I and III (at 75°C and 67°C, respectively, cooling rate of 10°C/min). They were not, however, observable upon heating. This suggests that these mesophases are either "monotropic" or their mesophase transition temperature ranges overlap with those of the crystal melting. In any case, these two monomers seem to behave similarly, but differently from monomer II for which neither a monotropic behavior nor an overlap of the crystal melting and the first mesophase transition temperatures were observed. On the other hand, the behavior of monomers II and III during cooling appears to be similar, but different from that of monomer I, i.e., either the LC to K transition enthalpy change is very small (monomer II, cooling rate of 10°C/min) or not observed at all (monomer III, when cooled to 40°C at a rate of 10°C/min), unlike for monomer I. This supports the argument that the driving force for the higher degree of packing in monomer I during cooling must be anisotropic "molecular" polarizability.

Mesogenic units comprising of phenylene rings typically are linked by multiple-bond units such as —CH═CH—. Such units can conjugate with phenyl rings. Since rotation is restricted about such linking units, the rigidity and elongation of the mesogen is preserved. The breakdown of a mesophase can therefore be explained by the onset of thermally induced rotational motion and/or thermophotochemical isomerization about such linking units. The behavior of monomers I and II observed under the polarizing microscope and discussed above may be explained by such processes.

The mesophase of monomer II is nevertheless exceptionally stable (ΔT_1 of 45° vs 4° for monomers I and III). The ΔT_2's of monomers II and III are comparable but still about five times as broad as that of monomer I. Since the ΔT_1 of monomer III is only 4°, the biphenyl benzoate unit thus gives primarily a nematic texture. The rather narrow range of mesophase stability of monomer I is somewhat surprising. Two phenyl rings linked by an ester-functionality are known to give rise to LC property (particularly a nematic texture),[13] and by extending the two-phenyl system to a three-phenyl system (by introducing an additional azophenyl unit), one would have expected some enhancement of the LC behavior as a result of molecular elongation. That this was not observed suggests that the mesogenic unit of monomer I assumes a substantially different molecular shape from those of monomers II and III with probably a substantially different axial ratio.

In summary, when all the data for the three monomers is considered, no clear correlation exists among the thermal properties and mesophase behavior of the mesogens. Consideration of the T_{2I} values may suggest a thermal stability order of —CH═CH— > —N═N— > biphenyl.[14] Comparison on this basis alone, as the data presented here indicated, does not however present a meaningful picture of the differences in textures and thermooptical behavior of the monomers which result from the molecular structural differences.

Comparison of polymers I and II

The markedly different structural effects observed in the monomers were less evident in the polymers. The diminishment of the molecular structural effects observed in the monomers can be illustrated by comparing polymers I and II. Both polymers assumed homeotropic, probably "glassy liquid crystalline," textures at room temperature and slightly above the Tg's. Both attained a fluid state at about 150°C, and had the same T_{12}'s (Figure 2 and Table I). These two observations are expected to be dependent on certain ranges of molecular weight and are probably accidental. There is a substantial difference (24°) between the T_{2I}'s of the polymers, but compared to the difference between those of the monomers (66°), this differential is diminished. There are also two other differences that are noteworthy: (1) the

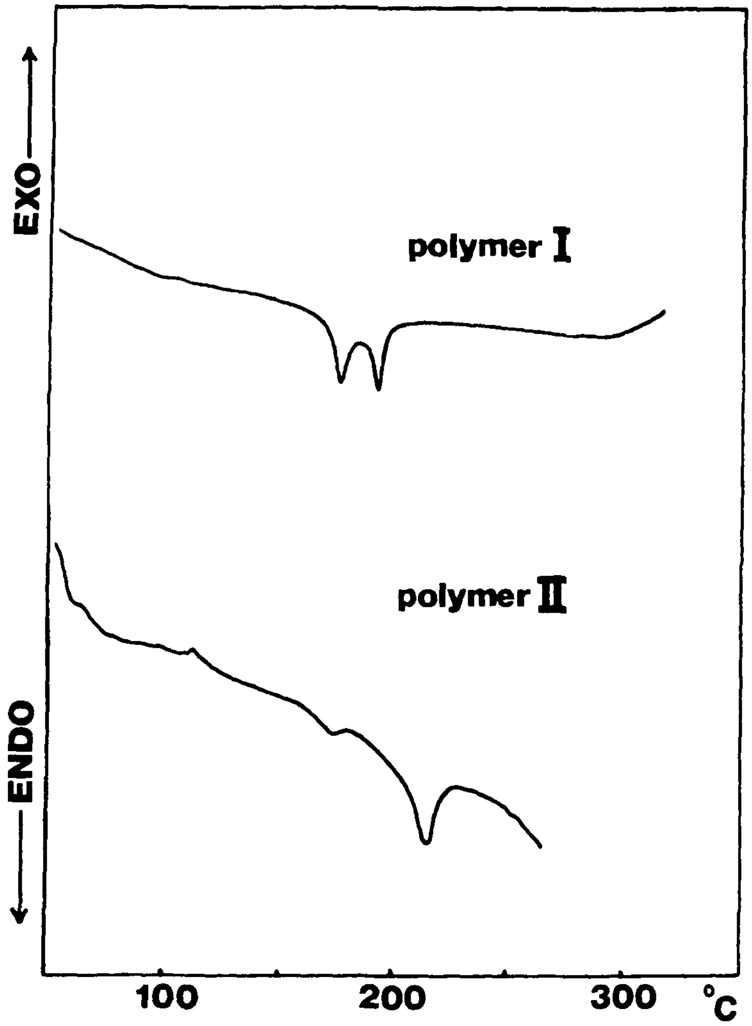


FIGURE 2 DSC thermograms of polymers I and II.

ΔT_2's of monomers I and II are 5° and 21°C respectively, while those of polymers I and II are 16° and 40°C, (2) the textures of the second mesophases of the two polymers (Table I and Figures 3 and 4) are different; this has been confirmed by a miscibility study (vide infra). A similar comparison between monomers II and III and polymers II

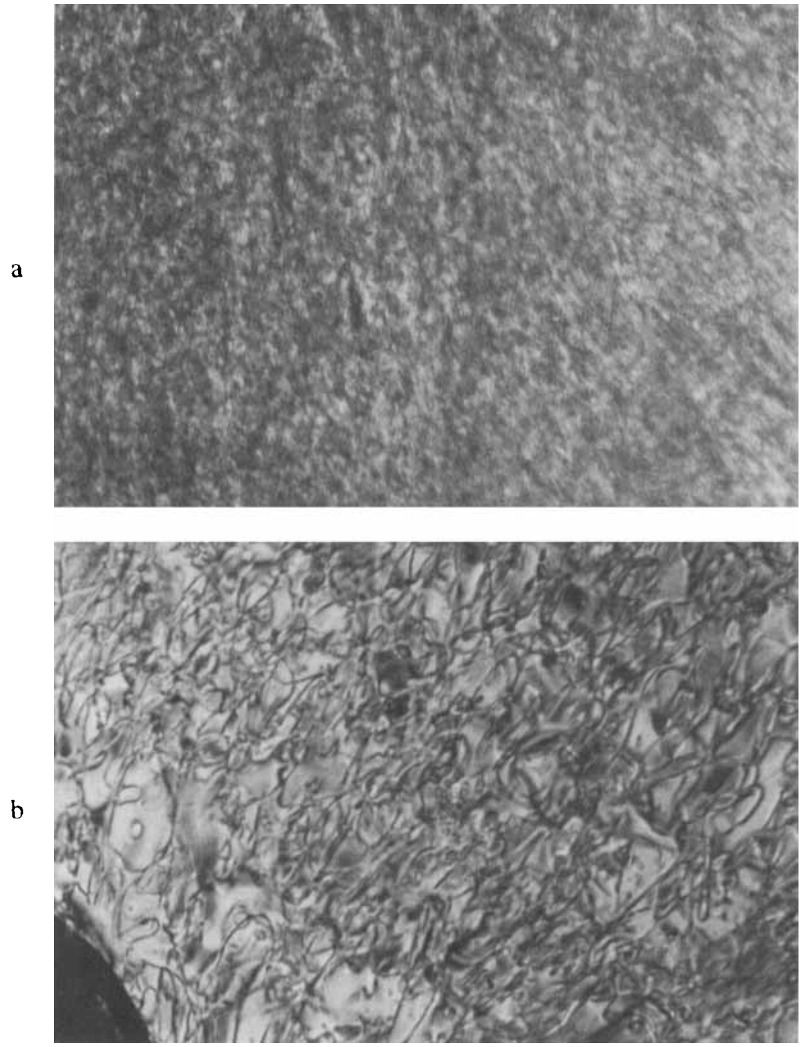


FIGURE 3 Optical textures of polymer I between crossed polarizers: a) 168°C, smectic phase, b) 182.2°C, schlieren texture. See Color Plates II a and b.

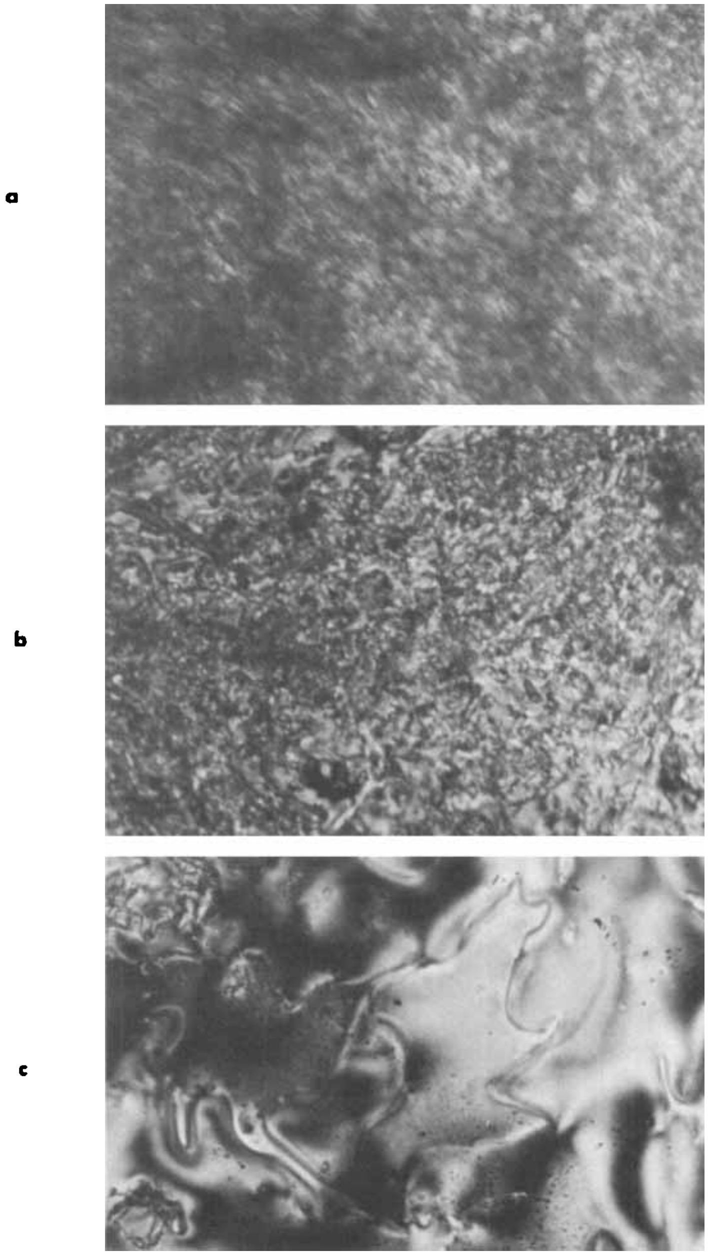


FIGURE 4 Optical textures of polymer II between crossed polarizers: a) 159.4°C, smectic phase, b) 165.7°C, and c) 183.4°C nematic phase. See Color Plates III a, b and c.

and III can also be made. Here again a noteworthy point: the ΔT_2's of monomers II and III are 21° and 24°C, while the corresponding values for the polymers are 40 and 20°C. The second mesophase of polymer II, compared to that of III, is stable over a significantly broader range of temperatures.

Despite these differences, on the bases of the data in Table I and the optical microscopic examinations, we conclude that there are more similarities than there are differences in the polymers, particularly among the first mesophases. The converse seems to hold for the monomers: there are more differences than there are similarities. Furthermore, the differences among the polymers seem to be mostly among the second mesophases. This conclusion may suggest that structural effects are more pronounced when the polymers are heated to high temperatures, i.e., when the polymers attain motions of certain ranges of frequencies.

The effect of thermal history on the enthalpy changes of polymer I and II has been investigated thoroughly. Table III shows some relative enthalpy changes at various heating and cooling rates, and thermal histories. The data in each row are for a given sample, while those in a column are for different samples. Column one demonstrates the effect of heating rates (different samples). The values in parentheses (Column 1) are percentages of the enthalpy changes with the enthalpy change for the 5°C/min heating rate set to 100. For both polymer I and II, there is an increase in enthalpy change as the heating rate increases. The reheating columns represent data for samples cooled (Rate 1) at 20°C/min (polymer I) and 2°C/min (polymer II) or quenched with dry ice from the isotropic phase (Rate 2). The numbers in parentheses, across a given row represent the percent increase or decrease in enthalpy changes, compared to the corresponding enthalpy changes of the initial heating rates (column 1) in each case. The minus sign denotes a decrease in enthalpy change. The decrease range up to about 40%, except for the quenched sample of polymer II (5°C/min heating rate) which is about 56%. Comparison of the data in column 3 (Rate 1) and 4 (Rate 2) shows that the enthalpy changes of the cooled and quenched samples are about the same.

Two conclusions can be made on the basis of the data in Table III: (1) the effect of heating rate has a similar trend in both polymers, and the dependence of the enthalpy change on heating rate implies that some crystallization (molecular orientation) does occur in both polymer samples during the heating; (2) the density of packing or order is not significantly different in the cooled and quenched samples. A simple explanation for this later observation is probably the

TABLE III

Relative enthalpy changes at various heating and cooling rates[a,b]

Heating rate	Cooling rate	Reheating rate 1	Reheating rate 2
Polymer I (annealed at 150°C)			
5(100)	20	5(−8)	5(−13)
20(114)	20	20(−2)	20(−7)
40(125)	20	40(−14)	40(−19)
Polymer II (annealed at 165°C)			
5(100)	2	5(−28)	5(−37)
20(113)	2	20(−15)	20(−17)
40(147)	2	40(−21)	40(−23)
Polymer II (annealed at 190°C)			
20(100)	20	20(−28)	20(−26)
40(118)	5	40(−36)	40(−56)

[a] A given sample was subjected to the following thermal treatment: first heated at the respective heating rate (column one) to above the clearing temperature, then cooled at 40°C at the cooling rate of column two, followed by reheating at Rate 1 to above the clearing temperature, followed by quenching with dry ice and then reheating at Rate 2. Data in each row are for a given sample, while those in a given column are for different samples. Each entry represents an average of three runs in most cases. All samples were annealed at the temperatures indicated for 48 hours and cooled to room temperature before the DSC runs. No significant dependence on annealing temperature was observed.

[b] Both polymers were fractionated (by precipitation) three times using hot dimethylformamide and ethanol; GPC data were: $M_n = 3.7 \times 10^4$, $M_w = 5.8 \times 10^5$, and $M_w/M_n = 15$ for polymer I; $M_n = 5.1 \times 10^3$, $M_w = 2.5 \times 10^4$ and $M_w/M_n = 4.9$ for polymer II. The fractionation was not very effective to further narrow the molecular weight distribution.

inability to supercool the isotropic phase even by the thermal shock (quenching) treatment. This phenomenon of inability to supercool the isotropic phase to any significant extent has been observed in main chain polymers.[15]

In the various annealing, heating and cooling studies, no evidence of appearance of new endothermic or exothermic peaks, or multiple peaks, was observed for both polymers. Although, the data suggest that some crystallization/recrystallization takes place at the reasonably slow heating/cooling rates, the molecular orientation phenomenon does not appear to be complex. However, some changes in transition temperatures, shapes and areas of the endothermic/exothermic peaks were observed. These may be explained, at least in part, by the long relaxation times of polymers and the lack of positional "memory" of polymer segments during different heating/cooling cycles.[16] Comblike polymers prepared by free-radical polymerization are likely to have some random microstructure (tacticity). This may lead to a fair number of polymer segments with different mobilities and environments. Such segments will probably respond very differently to a given thermal treatment. Free-radical polymerization is also likely to result in considerable polydispersity (preliminary GPC data confirm this). The variation of the enthalpy changes of either polymer with thermal histories may also therefore be partly attributable to tacticity and polydispersity of the polymers.

For both polymers, the enthalpy changes of the second mesophase to isotropic phase transitions were found to be relatively insensitive to thermal history. Compared to that of polymer I, the magnitude of the enthalpy change of the first phase transition of polymer II is, however, very dependent on thermal history and heating rate. This may imply that the kinetics of recrystallization in polymer II is considerably different. The higher degree of recrystallization in polymer I implied by the data may be due to the anisotropic molecular polarizability of its mesogenic units. Despite such salient differences between the polymers, the effects of heating and cooling rates do not indicate, unlike in the monomers, substantial differences in the thermal behavior of the polymers. This observation further demonstrates that molecular structural effects are more pronounced in the monomers as opposed to the polymers.

Comparison of monomers with polymers

LC property in comblike polymers has been attributed to decoupling of the motions of the mesogen from that of the main chain, although the degree of the decoupling of the motion is not clearly understood.[4] Some observations, albeit only instructive, can be made from this study. The overall range of mesophase stability is only 9° for monomer I while that for polymer I is 53°. The ΔT_1 of monomer III is only 4° while the corresponding value for polymer III is 32°.[8] Similarly, the ΔT_2 of monomer II is 21° while that of polymer II is about 40°. These observations strongly suggest that intermolecular forces which are expected to be more pronounced in the polymers, and restricted molecular motion must stabilize the mesophases by stabilizing the rigid core structures of the mesogens. The degree of the restriction of the motion will depend partly on the strength of the intermolecular forces which in turn depend on the molecular structure. Further evidence for this conclusion comes from comparison of the mesophase behavior of polymers I and II with their respective monomers. The thermo-photochemical effects observed in the monomers were not observable in the polymers, i.e., the first and second mesophases of polymer I, and the second nematic mesophase of polymer II can be observed even under constant light irradiation.

The nature of the interactive forces that might be operative (dispersion, induction, dipole-dipole, etc.) is such that the interactions fall off rapidly with distance (r^{-6} dependence on the distance), a fact that makes the energetics very sensitive to volume changes.[17] Polymers in the fluid state are more viscous materials, compared to monomers, and the volume (or viscosity) changes as a function of temperature are much less. Thus motions in polymers are much more restricted, and this motional restriction necessarily leads to stabilization of a mesophase over a broader range of temperatures in LC polymers as opposed to monomers. We suggest here that the degree of motional restriction is also partly dependent on molecular structure. Support for this conclusion can be gleaned from the data in Table I on the ranges of overall mesophase stabilities: 9° vs 53° for monomer I vs polymer I; and 66° vs 73° for monomer II vs polymer II, respectively. That the stabilization is greater in the azo system (as opposed to the olefinic) may be attributed to the enhancement of anisotropic polarizability by the —N=N— group leading to increased random dipole-induced dipole type interactions.[17]

Solution-cast blends

Preliminary investigations of solution-cast blends of polymers I and II (see Tables I and II for data on the polymers) were done on two compositions (percent by weight) of 50/50 and 75/25 (polymer I/II). The 50/50 blend started to phase separate at 180°C with two continuous phases being observed as the principal type of morphology (Figure 5). The extent of the minor phase in each of the two phases could not be determined by the optical microscopic examination. The observation (immiscibility of the polymers) confirms that the textures of the polymers are different. The 75/25 blend, on the other hand, gave one continuous phase throughout which was dispersed a second phase in the temperature range of 117–207°C (Figure 6). The actual phases may be regions or domains within which there are microdomains of separate compositions. Although both polymers give smectic first mesophases in the temperature range 137–172°C, and hence may be expected to be miscible, optical microscopy does not appear to be sensitive enough to confirm molecular mixing.[18] More direct spectroscopic methods such as NMR should be helpful in this regard.

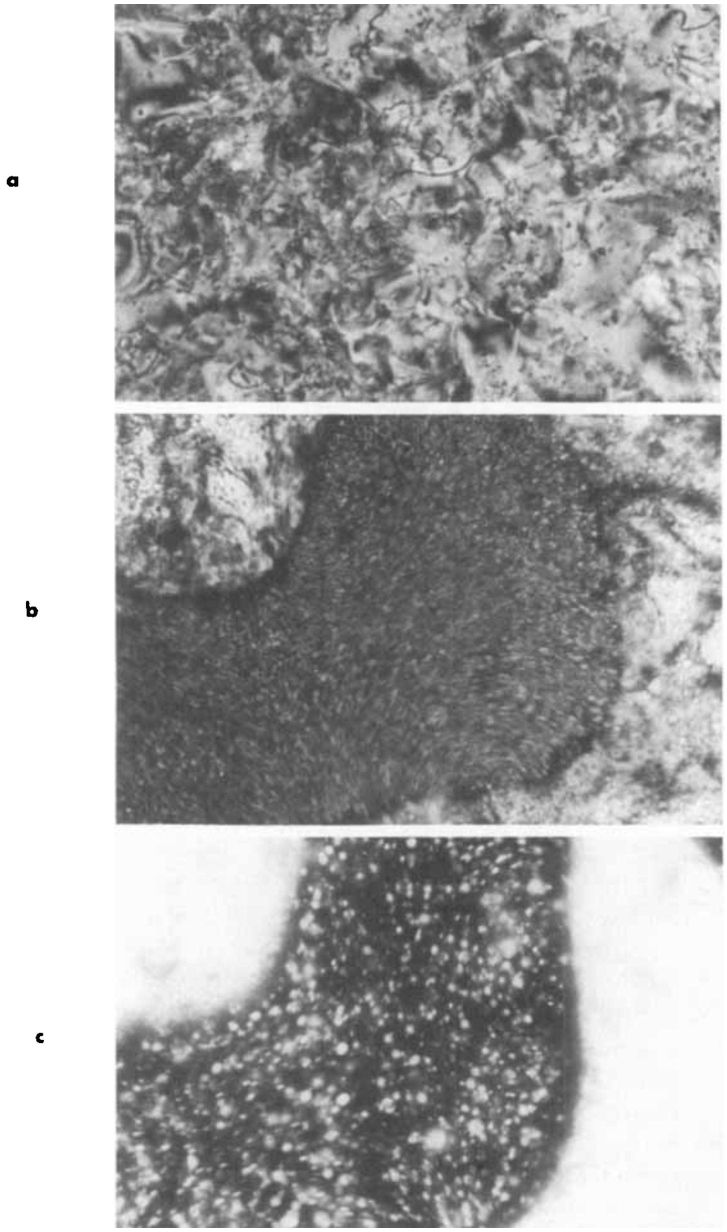


FIGURE 5 Optical textures of 50/50 (percent by weight) solution-cast blend of polymers I and II between crossed polarizers: a) 180.1°C, b) 189.7°C, and c) 205.1°C. See Color Plates IV a, b and c.

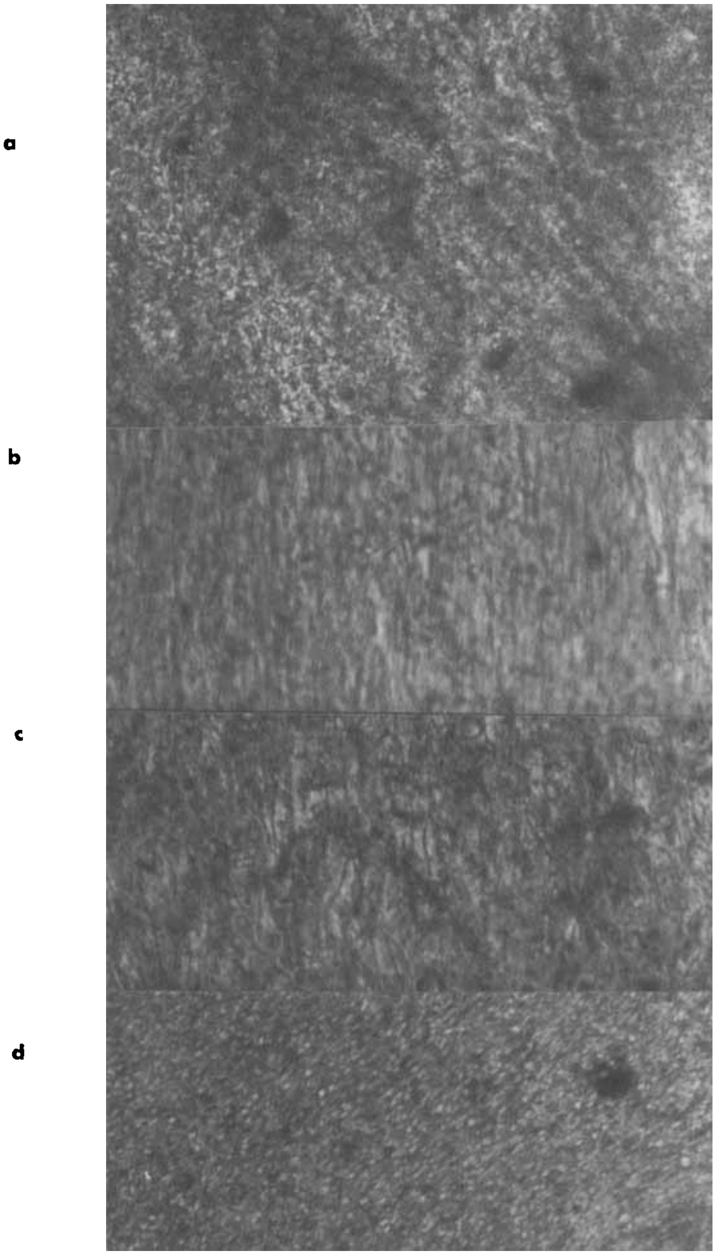


FIGURE 6 Optical textures of 75/25 (percent by weight) solution-cast blend of polymer I/polymer II between crossed polarizers: a) 160.1°C, b) 171.8°C, c) 179.5°C, and d) 200°C. See Color Plates V a, b, c and d.

CONCLUSION

In both the monomers and the polymers the olefinic linking unit gives a broader range of mesophase stability and a higher clearing temperature. The first mesophase of monomer I appears to be monotropic. The azo unit favors smectic textures while the olefinic unit gives both smectic and nematic textures. The effects of heating and cooling show significant differences in the monomers; the cooling DSC curve particularly manifests clearly that the degree of recrystallization is much greater in monomer I. This is interpreted in terms of molecular interactive forces arising from enhanced anisotropic molecular polarizability due to the azo unit. From the heating and cooling experiments, it was determined that the thermal behavior of the polymers had a very similar trend, unlike in the monomers. Comparison of the range of mesophase stability in the monomers and the polymers clearly shows that the stabilization (over that of the monomer), is greater in polymer I than in polymer II. This is interpreted as a direct consequence of the anisotropic molecular polarizability. By and large, there are more similarities in the polymers than in the monomers. The data illustrate that mesogenic systems containing three phenyl rings and two linking units as opposed to two phenyl rings and one linking unit do allow one to better assess molecular structural effects on mesophase behavior as well as to better compare monomers and polymers. Further work using this approach is currently in progress.

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