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Ferroelectric properties of mixtures of a liquid crystalline polymer and its side-group mesogen

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We present the results of our studies of the ferroelectric properties of mixtures of a high polarization, ferroelectric liquid crystalline copolymer and its side-group antecedent, a high polarization, low molecular weight, ferroelectric mesogen. These two materials are found to be completely miscible in all proportions. Spontaneous polarization values and electro-optical response times are found to be monotonic functions of the weight percentage of the mesogen in the mixture, while optical tilt angles do not exhibit such a monotonic dependence.

1. Introduction

The combination of different liquid crystalline materials in a mixture to produce mesophases with wide temperature ranges, enhanced birefringence, and low viscosity is an important practice in the development of materials for device applications [1]. Recently, many ferroelectric liquid crystalline side-chain polymers (FLCPs) have been synthesized and their properties investigated [2–10]. Some of these polymers exhibit the smectic C* (S_C^*) phase over a wide range of temperature and possess large values of spontaneous polarization, as well as sub-millisecond electro-optical response times [6, 11]. The question naturally arose as to how the properties of these interesting compounds would be affected and possibly enhanced by mixing with a low molecular weight (LMW), ferroelectric liquid crystalline (FLC) material.

Recent papers [12, 13] have reported on the properties of mixtures of FLCPs and FLCs. We were interested in expanding on this work in order to study in detail the concentration dependence of the ferroelectric properties of a high polarization polymer–mesogen mixture. We chose to mix a FLC side-chain copolymer with its side-group antecedent, an unattached LMW FLC material, because we wanted to maintain the high spontaneous polarization of the pure systems, while attempting to tune other properties. In addition, the near perfect structural equivalence of the side-group of the copolymer and the free mesogen was expected to ensure thorough mixing of the two components.

We have studied the phase diagrams of the mixtures, as well as three important parameters associated with the S_C^* phase: the optical tilt angle (θ), the spontaneous polarization (P_s), and the optical response time (τ). The nature of the coupling of P_s to θ has also been examined qualitatively.

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2. Experimental

The mesogen studied is 10PPB2 ((*R*)-4'-(1-ethoxycarbonyl-1-ethoxy)phenyl-4-[4-(9-decenyloxy)-phenyl]benzoate) [6]. The polymer is 10PPB2-CO [6], a side-chain copolymer obtained through the classical hydrosilylation reaction [14] between the 10PPB2 mesogen and poly[dimethylsiloxane-co-methylhydrosiloxane] in the presence of a platinum catalyst. The covalently bonded 10PPB2 or side-group is located on an average of 30 per cent of the silicon atoms of the backbone siloxane, while the remaining 70 per cent are occupied by methyl groups (see figure 1). The side-group and the mesogen can be treated as structurally identical, differing only at the two terminal carbons in the spacer chain (see figure 1). ^1H NMR spectroscopy indicated that virtually all of the Si-H bonds were converted by Si-(mesogen bonds. Gel permeation chromatography and light scattering measurements determined the degree of polymerization (~ 30) and the polydispersity (~ 1.2). Additional details of the syntheses and analyses are reported elsewhere [6].

Sample mixtures were produced by weighing out appropriate masses of copolymer and mesogen into microcentrifuge tubes and then dissolving them completely in a small amount of HPLC-grade chloroform. The tubes were closed and the solution vigorously mixed on a vortex shaker to ensure complete mixing. The samples were then dried by evaporation of the solvent and stored under dry argon. The mixtures are identified according to the weight percentage of the mesogen in the mixture (0 per cent = copolymer and 100 per cent = mesogen). The mixtures were stable since the purified mesogen does not dimerize nor does it react with the purified copolymer.

For our electro-optical measurements, we used commercially prepared sample cells from E.H.C. Company, Ltd., Japan. They were $10\ \mu\text{m}$ thick, with ITO electrodes forming a $4\ \text{mm} \times 4\ \text{mm}$ square active area, and their polymer coated surfaces were rubbed to obtain planar alignment of the FLC materials. The cells were filled *in vacuo* at a temperature close to the isotropic-smectic A ($I-S_A$) transition. By heating the sample just enough to permit capillary action to fill the cell, the viscosity remained sufficiently high for filling to proceed slowly and this process could be stopped when the electrodes were covered. This technique helped to prevent thermal degradation and conserved the FLC materials.

The rubbed polymer coatings and the application of a square-wave electric field (E_{app}), as the sample was cooled from the S_A to the S_C^* phase, combined to produce well aligned samples which displayed nearly uniform planar textures. Although the $10\ \mu\text{m}$ samples were too thick to permit suppression of the helical structure of the samples by

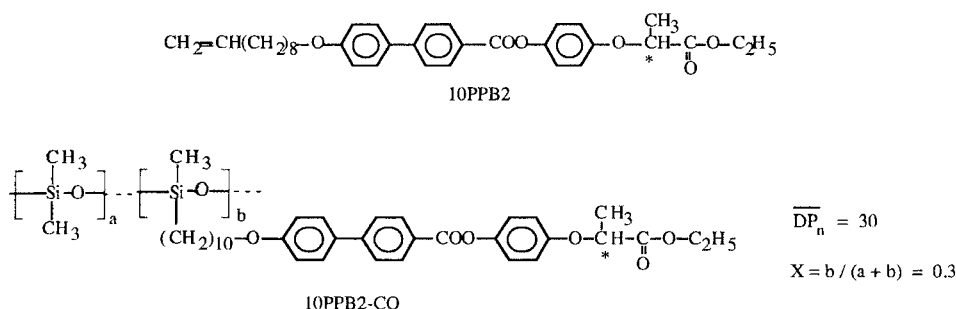


Figure 1. Structures of the mesogen and copolymer. The mean degree of polymerization of the copolymer is 30, and the side-groups are covalently bonded to an average of 30 per cent of the silicon atoms in its backbone.

surface interactions alone, it was possible to unwind the helices completely by applying a sufficiently large electric field (typically $E_{\text{app}} > 1 \text{ V } \mu\text{m}^{-1}$). All measurements used an applied field greater than this ‘threshold’ value.

The temperature of the cells was controlled to $\pm 0.05^\circ\text{C}$ in a microscope hot stage (Mettler FP 80 HT). The spontaneous polarization (P_s) measurements were made using the triangular wave technique [15]. The output of a function generator (Wavetek 271) was fed to a high-output amplifier (Trek 601B-2) which excited an RC circuit consisting of the liquid crystal cell and a high-precision series load resistance. The voltage drop across this resistance was recorded on a digital storage scope (Hitachi VC-6165), and the waveforms were retrieved, stored, and analysed on a 386-based computer. The frequencies of the applied triangular wave, with an amplitude of 10 V, varied from 500 Hz to 0.5 Hz. The samples became more viscous at lower temperatures and the frequency had to be decreased to ensure that each waveform contained a sufficiently long baseline. This adjustment permitted a reliable determination of the area under the spontaneous polarization peak.

All measurements were made as the samples were cooled. P_s was measured first, then the sample was reheated and the optical tilt angle (θ) determinations were made. Optical response time measurements (τ) then followed. Since a slight sample degradation could occur as the measurements progressed, T_{AC^*} for each P_s and θ run was estimated by fitting data close to the S_A – S_C^* transition to a simple power law, and the data were displayed and compared as a function of the relative temperature $T - T_{\text{AC}^*}$. The accuracy of this approach was checked by comparing T_{AC^*} determined from the P_s fits to T_{AC^*} determined from microscopic observations of the textures. The agreement was good—within $\pm 0.5^\circ\text{C}$. The T_{AC^*} determined from the θ fits was between 0.5 and 2.0 $^\circ\text{C}$ lower than the T_{AC^*} determined from the P_s fits, the variation depending on the length of time between the measurements.

These determinations of T_{AC^*} also permitted construction of P_s versus θ plots. The θ versus $T - T_{\text{AC}^*}$ data were interpolated so that each experimentally measured value of P_s could be assigned a value of θ . Due to the increase in the error of data so constructed, the P_s versus θ plots are useful only in establishing general trends and for comparing gross features of the behaviour of the different samples. No precise determination of exponents or coupling constants was possible.

The optical tilt angle determinations were performed using a polarizing light microscope (Nikon Optiphot) with a standard halogen lamp light source. Early microscopic observations and measurements were hampered by sample degradation. Inclusion of a GG-400 edge filter in the illumination path of the microscope blocked UV light and eliminated the degradation. To minimize electrochemical degradation of the samples due to prolonged exposure to a DC electric field, a low frequency (~ 0.1 Hz) square wave voltage was applied to the cell. The intensity of the transmitted light was measured with a photodiode coupled to an amplifier (UMT 101C), and the output was read on a digital multimeter (Keithley 197). The angle of rotation of the microscope stage from extinction in one switched state (E_{app} in one direction) to extinction in the other switched state (E_{app} in the opposite direction) was determined. This angle is equal to the cone angle of the director and one half of this value gives the optical tilt angle θ .

Optical response time measurements (switching times) were determined by connecting the photodiode amplifier to the oscilloscope and recording the transmitted intensity as a square wave electric field was applied to a sample.

Both the mesogen and the copolymer have large optical tilt angles, and θ exceeds the ‘optimum’ 22.5 $^\circ$ value for most of the S_C^* phase in all of our samples. In a tridirectional

determination of the optical response time for small tilt angle materials ($\theta \leq 22.5^\circ$), one orients a switched liquid crystal cell between a crossed polarizer and analyser (their optic axes crossing at 90°) to achieve maximum extinction of the transmitted light. The cell is then said to be in the 'off' state, and the other switched state of the cell, which transmits the maximum amount of light that the cell can transmit, becomes the 'on' stage. Denoting the increase in intensity from 'off' to 'on' by ΔI , one then measures the time it takes for the transmitted intensity to increase by 90 per cent of ΔI after \mathbf{E}_{app} changes sign. This time is called the 0–90 per cent switching time or τ_{90} . When θ exceeds 22.5° , however, the transmitted intensity reaches a maximum before switching to the 'on' state is complete. This maximum occurs when the director crosses the bisector of the axes of the polarizer and analyser. Since the 'on' state occurs at a different director orientation, the transmitted intensity of the 'on' state is less than the maximum, and a peak appears in the oscilloscope trace.

We used this traditional determination of the response time as long as the temperature of a sample was sufficiently high such that no peak appeared in the oscilloscope trace of the transmitted intensity. Once a peak appeared, we employed a 'balance' technique in which the microscope stage was rotated until the intensities transmitted by the 'off' and 'on' states were equal, thereby establishing a baseline intensity I_{base} . The transmitted intensity in this 'balanced' configuration varied from the baseline to the maximum (I_{max}) and back to the baseline as the cell switched. $I_{\text{bal}}(\tau_{90})$, the intensity on a 'balanced' trace corresponding to the traditional τ_{90} value, was estimated by first recording a 0–90 per cent trace at a temperature at which no peak appeared. The cell was then rotated into the 'balanced' configuration and a second trace was recorded. $I_{\text{bal}}(\tau_{90})$ was then determined by graphical comparison of these two traces. The ratio $(I_{\text{bal}}(\tau_{90}) - I_{\text{base}})/(I_{\text{max}} - I_{\text{base}})$ was then used to determine $I_{\text{bal}}(\tau_{90})$ and τ_{90} for all lower temperatures.

All measured values for the S_C^* phase were finite field values. No extrapolation to zero field was performed. This presents no problem far from the S_A – S_C^* transition where an electric field has little effect on the data, and it should not alter the fundamental interpretation of our data close to this transition.

3. Results and discussion

An important feature of these mixtures is that the components are completely miscible in all proportions in all phases. This miscibility is not surprising since the mesogen and the copolymer side-group are nearly identical in structure. Optical microscopic observations could discern no macroscopic phase separation from the isotropic phase down to an unidentified phase below the S_C^* phase. This unknown phase could be a higher order smectic or crystalline phase and is referred to as the X phase.

The differential scanning calorimetry (DSC) data exhibited single peaks at the phase transitions, also indicating completely mixed samples. The DSC data also indicate that the S_A – S_C^* transition is second order for the pure materials, a conclusion supported by high-resolution AC calorimetry measurements [16]. The DSC scans established all the phase transition temperatures except the S_A – S_C^* for the 50 per cent and 70 per cent mixtures (see figure 2 and the table). No features could be discerned to indicate these transitions and the reported temperatures were determined from the onset of spontaneous polarization as each sample was cooled from the S_A phase.

The phase diagram (see figure 2) shows the I – S_A transition temperature decreasing as the mesogen percentage increases. The S_A – S_C^* transition temperature decreases from a high value of 405.3 K for the pure copolymer, reaches a minimum of 354.6 K for the 70

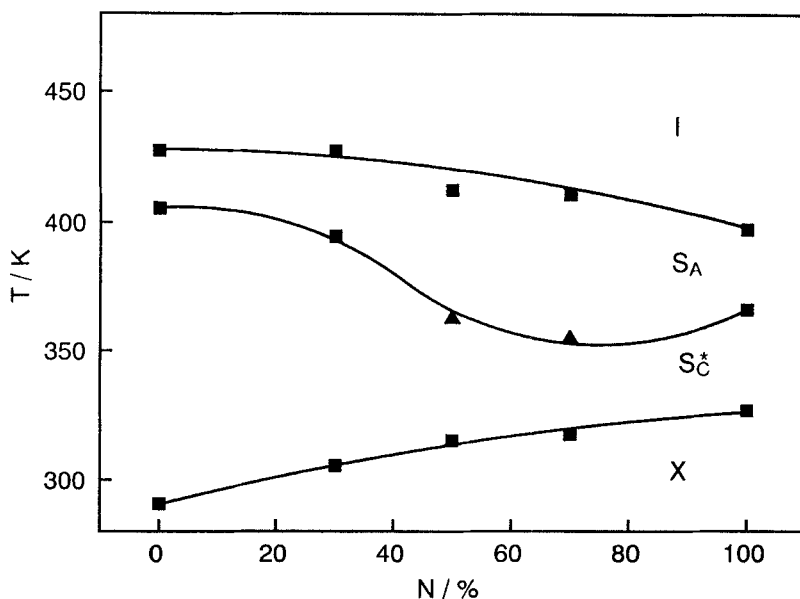


Figure 2. Phase diagram for binary mixtures of the ferroelectric copolymer 10PPB2-CO and its side-group antecedent, the ferroelectric mesogen 10PPB2. N is the mesogen weight percentage in a mixture. All data were collected while cooling the samples. The squares denote data determined by differential scanning calorimetry. The triangles denote data determined by the onset of spontaneous polarization. The solid lines are only guides to the eye.

Phase transition temperatures for the pure materials and the mixtures†.

Mesogen weight percentage	Phase transition temperatures/K		
	S_C^* to X	S_A to S_C^*	I to S_A
0	290.7	405.3	427.4
30	305.5	394.7	427.3
50	315.2	362.5‡	412.4
70	317.6	354.6‡	410.8
100	326.9	366.3	397.4

† These values were obtained from differential scanning calorimetry performed in the cooling mode except for those denoted by ‡, which were obtained from the onset of spontaneous polarization observed while cooling the samples. These values are plotted in figure 2. (0 per cent = copolymer, 100 per cent = mesogen.)

per cent mixture, and rises to 366.3 K for the pure mesogen. The S_C^* -X transition temperature increases as the mesogen percentage increases. The result is a widely varying temperature range of the S_C^* phase, widest for the copolymer and narrowest for the 70 per cent mixture.

The spontaneous polarization P_s (see figure 3) is an increasing monotonic function of the mesogen weight percentage. Over a large range of temperatures (~ 30 K below T_{AC^*}), the mesogen exhibits the largest values, the copolymer the smallest, and P_s for the mixtures increases with increasing mesogen weight percentage. This increase appears

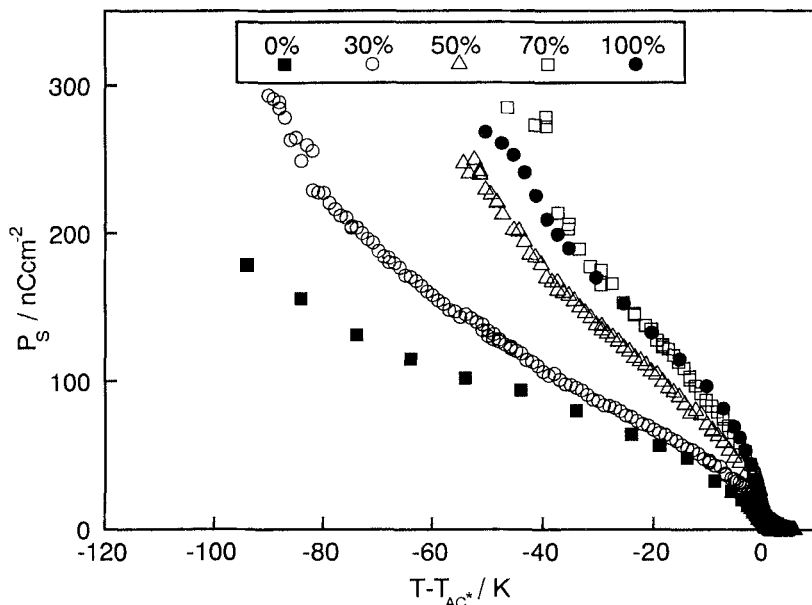


Figure 3. Spontaneous polarization P_s as a function of relative temperature $T - T_{AC^*}$ for mixtures containing different mesogen weight percentages. (0 per cent = copolymer, 100 per cent = mesogen.)

to saturate at mesogen concentrations between 100 per cent and 70 per cent as the P_s values of the 70 per cent mixture are almost the same as those of the pure mesogen. As reported previously [17], this variation is likely to be due to the differences in the density of mesogenic dipolar groups of the mesogen in each sample, highest for the pure mesogen and lowest for the copolymer.

The P_s data are rounded near T_{AC^*} due to the electric field that was used to perform the measurements: the measured optical tilt angle has a field induced component which, in turn, increases P_s . Close to T_{AC^*} , the value of P_s increases with decreasing temperature according to a power law. Far from T_{AC^*} , the value of P_s shows an anomalous increase with decreasing temperature. This trend is likely to be due to the influence of the X phase at these lower temperatures. In fact, the 30 per cent and 70 per cent mixtures display a jump in the data at temperatures associated with the S_C^* -X transition.

The ferroelectric response times (switching times) τ for our samples are presented in figure 4. At nearly 40 K below T_{AC^*} the switching times of each sample are in the sub-millisecond regime. Another significant feature of these data is that τ is a decreasing monotonic function of the mesogen weight percentage, probably due to the decrease in viscosity with the addition of mesogen.

In figure 5 we see that the optical tilt angle θ in the S_C^* phase, unlike the spontaneous polarization P_s , is not a monotonic function of the mesogen weight percentage. It does decrease as this percentage increases, with a large jump between 0 per cent and 30 per cent, but for the pure mesogen, θ jumps back to near the values for the copolymer. In all cases, θ is large and greater than 30° for the lowest temperatures. The mixtures show a small variation in θ as the amount of mesogen increases, reaching a minimum for 50 per cent, and the θ values for mesogen and copolymer are similar over nearly 40 K.

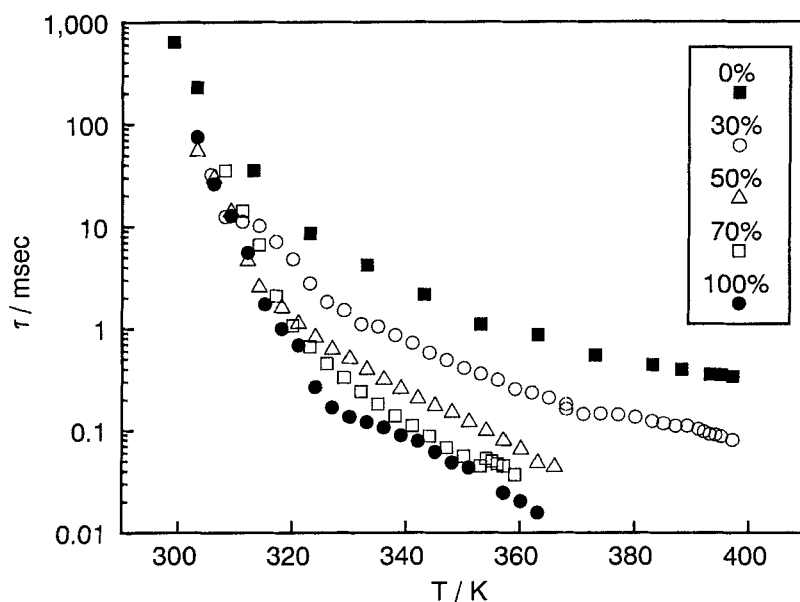


Figure 4. Electro-optical response time τ as a function of absolute temperature T for mixtures containing different mesogen weight percentages. (0 per cent = copolymer, 100 per cent = mesogen.)

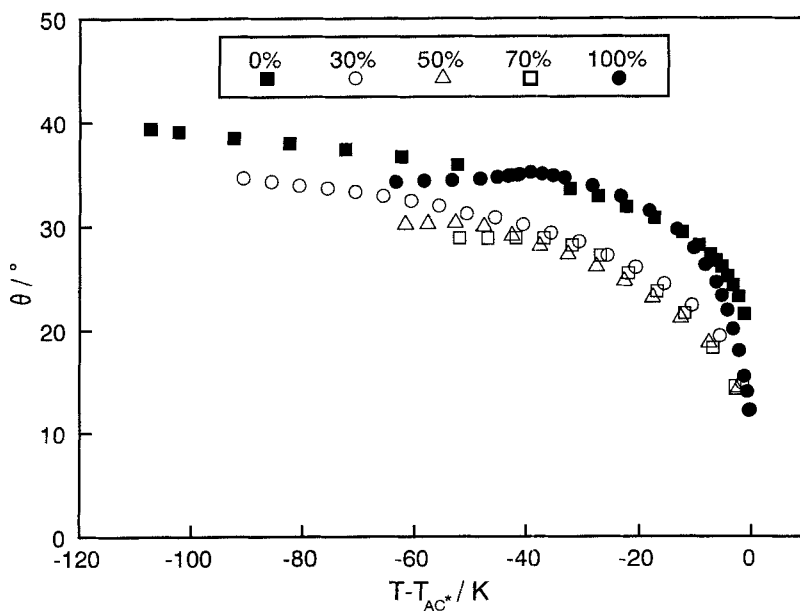


Figure 5. Optical tilt angle θ as a function of relative temperature $T - T_{AC}^*$ for mixtures containing different mesogen weight percentages. (0 per cent = copolymer, 100 per cent = mesogen.)

The similarity of the optical tilt angles for the pure systems implies that the rigid cores of the free 10PPB2 mesogen molecules and the 10PPB2-derived side-chains of the copolymer are similarly tilted with respect to the smectic layer normal. X-ray diffraction measurements have also been performed on the pure systems [18] and they show that the molecular tilts of the mesogen and the copolymer, as determined from the ratio of the layer spacing in the S_C^* and S_A phases, are different and that the mesogen has the higher molecular tilt. This result, taken with the optical tilt angle values, suggests that the two mesogenic entities have different conformations, with the free mesogen (free 10PPB2) being straighter than the side-group (attached 10PPB2). Therefore, although a side-group is essentially decoupled from the backbone, its attachment to the backbone does affect mesogen–mesogen interactions and leads to a different molecular conformation.

The lower optical tilt angles of the mixtures are probably the result of a competition between the two mesogenic entities. Assuming that each mesogen prefers to take on the conformation it would have in a pure sample, we expect a mixture to ‘select’ a compromise conformation for the free and side-group mesogenic units. This conformation reduces the tilt of the rigid cores and is expected to produce an intermediate value of the molecular tilt. It will be interesting to perform X-ray measurements on the mixtures to see how the molecular tilt varies with the mesogen weight percentage.

For ferroelectric liquid crystals, the tilt angle θ is the primary order parameter, while the spontaneous polarization P_s is the secondary order parameter. The ratio P_s/θ is therefore important in the phenomenological description of the ferroelectric properties. To compare the nature of the P_s – θ coupling of the mixtures with that of the mesogen and the copolymer, we have plotted P_s versus θ in figure 6. Since, as stated earlier, P_s and θ were not determined simultaneously, and due to the strong influence of

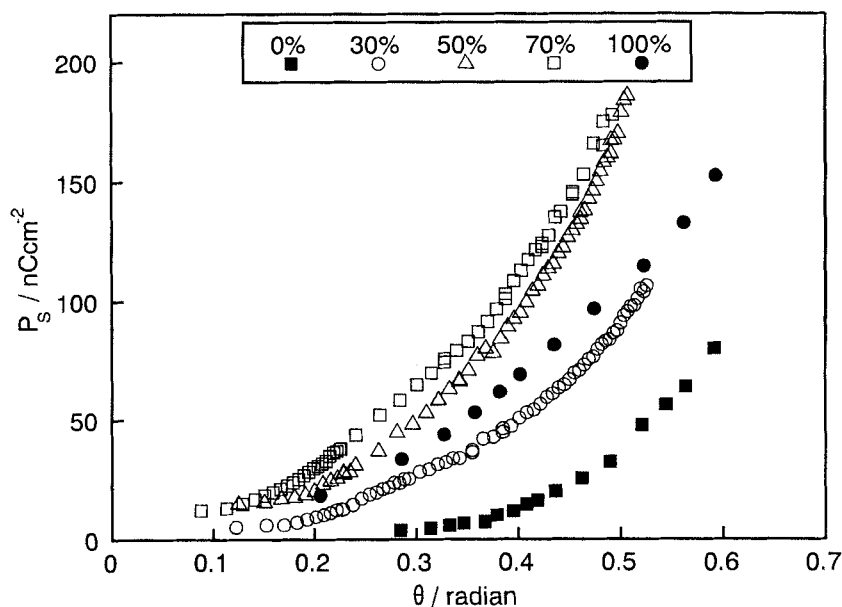


Figure 6. Spontaneous polarization versus optical tilt angle (P_s versus θ) for mixtures containing different mesogen weight percentages. The origin corresponds to the S_A – S_C transition. (0 per cent = copolymer, 100 per cent = mesogen.)

the electric field on both P_s and θ near T_{AC} , the comparisons are only qualitative. We can, however, make meaningful comparisons at a common value of θ , because the magnitude of P_s is generally dictated by three factors—the magnitude of the transverse dipole moment, the proximity of the transverse dipole moment to the chiral centre, and the translational order which affects the free rotation of the molecule. Two of these factors, the transverse dipole moment and the proximity of the dipole to the chiral centre, should be the same for the pure systems and the mixtures. A comparison of the P_s data at a common θ value therefore enables us to examine how the translational order affects P_s .

At $\theta = 0.35$ rad, P_s is seen to increase with increasing mesogen concentration up to 70 per cent. The pure mesogen, on the other hand, has a P_s lower than the 50 per cent value. The initial increase in P_s can be ascribed to an increase in the dipole density caused by the packing of free mesogen into the layers formed by the copolymer side-groups [17]. The fact that P_s for the 50 per cent and 70 per cent mixtures is greater than P_s for the mesogen implies that the translational order of these two mixtures is higher than that of the mesogen. High resolution X-ray studies to determine the extent of the in-plane positional order in these samples would be of considerable interest. It would also be interesting to investigate the effects of mixing larger amounts of the mesogen with the copolymer and to determine at what concentration P_s is maximized for a given θ .

4. Conclusions

Our studies have shown that the high polarization side-chain FLC 10PPB2-CO is completely miscible with its side-group antecedent, the high polarization, low molecular weight, FLC mesogen 10PPB2, in all phases at all concentrations. By varying the concentration of the mesogen in a mixture, it is possible to manipulate the temperature range and properties of the ferroelectric phase. These results suggest that it might be possible to develop ferroelectric polymer–mesogen mixtures suitable for displays, spatial light modulators, and pyroelectric detectors. In addition, the results from our optical tilt angle and P_s – θ coupling investigations give promise of interesting results from detailed studies of the molecular conformations and the in-plane structure of the mixtures.

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References

- [1] See, for example, COATES, D., 1990, *Liquid Crystals: Applications and Uses*, edited by B. Bahadur (World Scientific), Chap. 3.
- [2] SHIBAEV, V. P., KOZLOVSKY, M., BERESNEV, L. A., BLINOV, L. M., and PLATÉ, N. A., 1984, *Polym. Bull.*, **12**, 299.
- [3] DECOBERT, G., SOYER, F., and DUBOIS, J. C., 1985, *Polym. Bull.*, **14**, 179.
- [4] UCHIDA, S., MORITA, K., MIYOSHI, K., HASHIMOTO, K., and KAWASAKI, K., 1988, *Molec. Crystals liq. Crystals*, **155**, 93.
- [5] WALBA, D. M., KELLER, P., PARMAR, D. S., CLARK, N. A., and WAND, M. D., 1989, *J. Am. chem. Soc.*, **111**, 8273.
- [6] NACIRI, J., PFEIFFER, S., and SHASHIDHAR, R., 1991, *Liq. Crystals*, **10**, 585.

- [7] SCHEROWSKY, G., SCHLIWA, A., SPRINGER, J., KÜHNAST, K., and TRAPP, W., 1989, *Liq. Crystals*, **5**, 1281.
- [8] KAPITZA, H., ZENTEL, R., TWIEG, R. J., NGUYEN, H. T., VALLERIEU, S. U., KREMER, F., and WILSON, C. G., 1990, *Adv. Mater.*, **2**, 539.
- [9] COLES, H. J., GLEESON, H. F., SCHEROWSKY, G., and SCHLIWA, A., 1990, *Molec. Crystals liq. Crystals Lett*, **7**, 117.
- [10] FLATISCHLER, K., KOMITOV, L., SKARP, K., and KELLER, P., 1991, *Molec. Crystals liq. Crystals*, **209**, 109.
- [11] PFEIFFER, S., NACIRI, J., and SHASHIDHAR, R., 1992, *SPIE Proc.*, **1665**, 166.
- [12] PARMAR, D. S., CLARK, N. A., KELLER, P., WALBA, D. M., and WAND, M. D., 1990, *J. Phys., France*, **51**, 355.
- [13] DUMON, D., and NGUYEN, H. T., 1992, *Polym. Adv. Tech.*, **3**, 197.
- [14] APFEL, M. A., FINKELMANN, H., JANINI, G. M., LAUB, R. J., LUHMANN, B. H., PRICE, A., ROBERTS, W. L., SHAW, T. J., and SMITH, C. A., 1985, *Analyt. Chem.*, **57**, 651.
- [15] MIYASATO, K., ABE, S., TAKEZOE, H., FUKADA, A., and KUZE, E., 1983, *Jap. J. appl. Phys.*, **22**, L661.
- [16] WU, C., and GARLAND, C. W. (private communication).
- [17] RATNA, B. R., NAMBOODRI, K., NACIRI, J., and SHASHIDHAR, R., 1992, *Presented at the 14th International Liquid Crystal Conference, Pisa, Italy.*
- [18] PRASAD, S. K. (private communication).