Characterization and Radical Polymerization of (E–CE)C/AA Mesomorphic Solutions

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SYNOPSIS

Ethyl–cyanoethyl cellulose (E–CE)C/poly(acrylic acid) (PAA) composites were prepared by polymerizing acrylic acid (AA) in (E–CE)C/AA cholesteric liquid crystalline solutions. The morphology and structure and the compatibility of composites prepared in different conditions were studied by small-angle light scattering (SALS), differential scanning calorimetry (DSC), X-ray spectrometry, polarizing microscopy, and electron microscopy. Homogeneous composites with the cholesteric structure could be obtained by photopolymerization. During the photopolymerization, however, the morphology of the liquid crystalline domains became cylindric and the axial direction of the cylindric domain was at an angle of about 45° to the layers of the ordered molecular chains. The polymerization initiated by azobisisobutyronitrile (AIBN) resulted in the phase separation. The morphology of the liquid crystalline domains was maintained although the cholesteric structure of the composite was partly destroyed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, the interest in preparing molecular composites with both rigid-rod and random-coil polymers has escalated because these unique polymer blends exhibit some desirable features such as high strength, high toughness, and good processibility.[1–5] In general, it is difficult to prepare homogeneous blends of polymers with significantly different conformations. Flory[6] has shown that in ternary solutions of rigid-rod and random-coil polymers the phase separation will appear when the concentration of the random-coil polymer increases to above a negligible amount. Consequently, to "lock in" the orientation of rigid-rod polymer by *in situ* polymerization of monomer solvent, it is necessary for the polymerization to occur at a significantly faster rate than the phase separation of the inherently incompatible polymers.

Ethyl–cyanoethyl cellulose (E–CE)C, a cellulose derivative with two different ether groups, can form cholesteric mesophase in many organic solvents.[7]

The (E–CE)C/polystyrene (PS) composites can be obtained by free radical polymerization of the styrene in (E–CE)C/styrene solution.[8] The composites have different morphologies, which are related to the solution state before polymerization.

In this paper, the polymerization of the acrylic acid (AA) in the (E–CE)C/AA mesomorphic solution is studied. Both the azobisisobutyronitrile (AIBN) initiating polymerization and photopolymerization are conducted. The morphology and structure of the (E–CE)C/PAA composites is also discussed.

EXPERIMENTAL

The (E–CE)C was obtained by reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.43. The M_n of the (E–CE)C measured by gel permeation chromatograph (GPC) (HPLC, Waters Mode-209) was 70,000. The AA was distilled before use.

(E–CE)C/AA solutions for polymerization were prepared in glass vials by weighing the desired amount of (E–CE)C, AA, and initiator into a vial

and mechanically mixing with a spatula for several minutes. The mixtures were allowed to sit for one more week and the resulting homogeneous and transparent solutions were then stored in the dark until used.

The solutions for photopolymerization contained 2 wt % benzophenone as photoinitiator (with respect to the solvent AA) and 0.5 wt % N,N-methyl aniline as promoter. The photopolymerization was conducted by sealing the solution with solid wax in the glass cell (25 × 15 × 0.2 mm) and then inserting it into the ultraviolet chamber with a 250 W high-intensity mercury arc lamp until complete polymerization. The solutions for AIBN initiating polymerization, which contained 0.5 wt % AIBN as initiator, were sealed in a glass cell (25 × 15 × 0.9 mm) by solid wax and kept at 50°C for polymerization.

Microscope slide polymerizations were also conducted for the purpose of polarizing microscope (Leitz, Orthoplan-POL) observation and small-angle light scattering (SALS) (LS-1, Yingkou Measuring and Testing Instrument Factory) study. The samples for slide polymerization were prepared by sandwiching a drop of solution between a microscope slide and a cover glass and a solution thin film was formed. A quartz coverslip was used when in photopolymerization.

The (E–CE)C/AA solution, the (E–CE)C/PAA composites that were produced via the photopolymerization and via the AIBN initiating polymerization were abbreviated to S, P, and A, respectively. The weight percentage of (E–CE)C was indicated by numbers. For example, the 45 wt % (E–CE)C/AA solution will be abbreviated to S45.

The structure characteristics of the solutions and the composites were studied by using an X-ray spectrometer (TUR-M62). To study the morphology and structure, the (E–CE)C/PAA composites were sectioned to super-thin films about 500 Å in thickness, and a transmission electron microscope (TEM) (JEOL-100CX/II) was used to examine the specimens. The T_g of (E–CE)C, PAA, and the composites were determined by differential scanning calorimeter (DSC) (Perkin–Elmer DSC-2C) at the heating rate of 10 K/min.

RESULTS AND DISCUSSION

(E–CE)C can be dissolved in AA and forms cholesteric mesophase when the concentration is high enough.[9] The critical concentration C_1, at which the mesophase begins to appear, is 33.8 wt %, and C_2, at which the isotropic phase disappears completely,
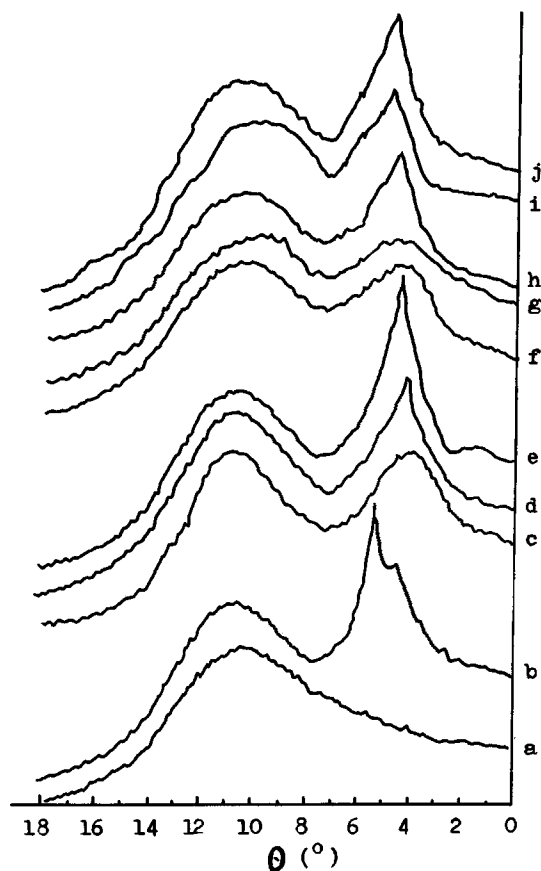

Figure 1   X-ray diffraction spectra of (a) PAA; (b) (E–CE)C; (c) S33; (d) S45; (e) S55; (f) A33; (g) P33; (h) A47.5; (i) P45; and (j) P55.

is 43 wt %. When the concentration is between 42–52 wt % at room temperature, the (E–CE)C/AA mesomorphic solution exhibits brilliant color because of selectively reflecting visible light at a certain wavelength.

Figure 1 shows the X-ray diffraction spectra of the (E–CE)C, PAA, the (E–CE)C/AA solutions, and the composites that are produced in different conditions. When the concentration is below 33.8 wt %, the (E–CE)C/AA solution is isotropic, and its X-ray diffraction spectrum has at the angle, two amorphous peaks, about 4.0° and 10.7°. But when the concentration is above 33.8 wt %, the peak at about 4.0° becomes sharp and can be considered as a characteristic diffraction of the (E–CE)C cholesteric mesophase. The (E–CE)C is a semicrystalline polymer, which has two crystalline peaks at the angle $\theta = 4.5°$ and $\theta = 5.5°$ and an amorphous peak at $\theta = 10.5°$ in its X-ray spectrum. The PAA is amorphous and in its X-ray spectrum, there is only one amorphous peak at $\theta = 10.5°$. The characteristics
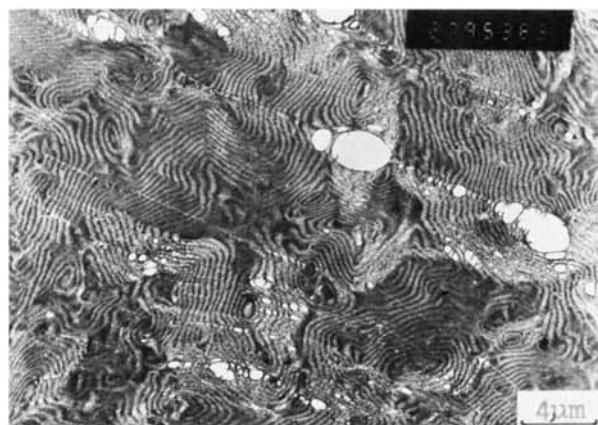
(a)
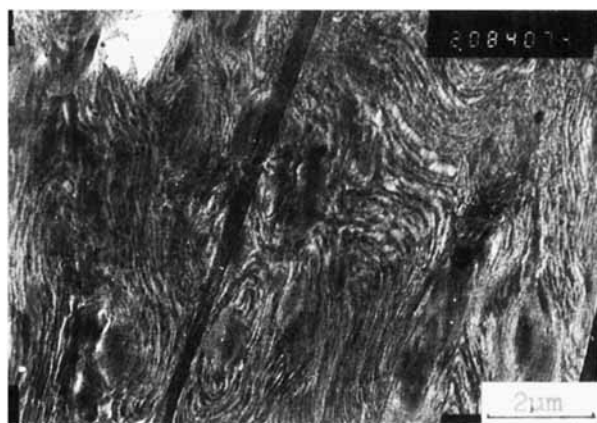
(b)

Figure 2   Transmission electron micrographs of (a) P45 and (b) A47.5.

in the X-ray spectra of the solution are kept during the polymerization. The composites produced from the isotropic solution (P33 and A33) have two amorphous peaks whose angles are the same as those of the solution (S33). Those produced from the mesomorphic solution (A47.5, P45, and P55) have a cholesteric diffraction peak, which is at a higher diffraction angle than that of the mesomorphic solution. Therefore, the interplanar spacing of the cholesteric structure is shortened during the polymerization. This is because of the volume contraction of the AA during polymerization. The spectra in Figure 1 demonstrate that the composites with cholesteric structure can be prepared by polymerizing the AA in the (E–CE)C/AA mesomorphic solution with both photoinitiation and AIBN initiation.

Cholesteric structure can be observed directly

with the TEM (Fig. 2). When produced from the mesomorphic solutions, both the photopolymerized composites and AIBN initiating polymerized composites show the striated structure extending over the whole specimen. The regular striation may be similar to the retardation lines (so-called fingerprint texture) that are frequently found in the cholesteric liquid crystals with the polarizing microscope. Although the latter arises from a periodicity of molecular orientation and not from the difference of the density, they may have a relationship.

The (E–CE)C/AA mesomorphic solution can reflect visible light selectively when the concentration is at the 42–52 wt % region. The wavelength of the light selectively reflected λ and the cholesteric pitch of the (E–CE)C/AA mesophase P satisfy the De Vries equation[10]:

$$\lambda = nP$$

where n is the mean refractive index, about 1.4 at room temperature. λ can be recorded with a UV–VIS spectrophotometer and then P can be calculated from the De Vries equation. The periodicity of the striation of the composites when observed with the TEM decreases with the increasing (E–CE)C. Table I gives the half of the cholesteric pitch calculated from the wavelength of the strongest selective reflection caused by the mesomorphic solutions and the periodicity of the striation. It can be seen that they coincide very well.

The striation has also been observed in the triacetyl cellulose film cast from the triacetyl cellulose/trifluoroacetyl acid cholesteric mesomorphic solution with the electron microscope by Giasson et al.[11] It is thought that the triacetyl cellulose film has a periodicity of mechanical strength arising from a periodicity of molecular orientation. During sectioning, therefore, the periodical variation in thickness of the ultrathin section prepared for TEM observation appears. This may work also for the (E–CE)C/PAA composites with cholesteric structure. Since the periodical striation arises from the helically twisted structure of the cholesteric mesophase

Table I   Half of Cholesteric Pitch Calculated From Wavelength of Strongest Selective Reflection and Periodicity of Striation

C (wt %)	44	50
P/2 (nm)	232	157
P.S. (nm)[a]	240	150

[a] P.S. is the abbreviated form of the periodicity of the striation.

Table II T_g **of the Composites, PAA and (E-CE)C**

Sample	PAA	(E-CE)C	P50	A50
T_g (°K)	364	400	395	380 and 398

and the periodicity of the striation coincides with the half of the cholesteric pitch, it is believed that the periodical direction of the striation, similar to the band-like texture, is parallel to the axial direction of the cholesteric helicoid and the striation is parallel to the layers of the ordered molecular chains.

The cholesteric structure can be observed in both the photopolymerized composites and the AIBN initiating polymerized composites. From Figure 2, however, it can be seen that the striation in pho-

topolymerized composite is very clear while that in AIBN initiating polymerized composite is indistinct. The striation in AIBN initiating polymerized composite is not continuous and its boundaries are obscure. It is obvious that the cholesteric structure is partly destroyed during the AIBN initiating polymerization.

The glass-transition temperature (T_g) of the composites, PAA and (E-CE)C are given in Table II. The photopolymerized composite with 55 wt %

(a)

(b)

(c)

Figure 3 Polarized micrographs of (a) S45; (b) P45; and (c) the rotation of (b) with an angle of 45°.
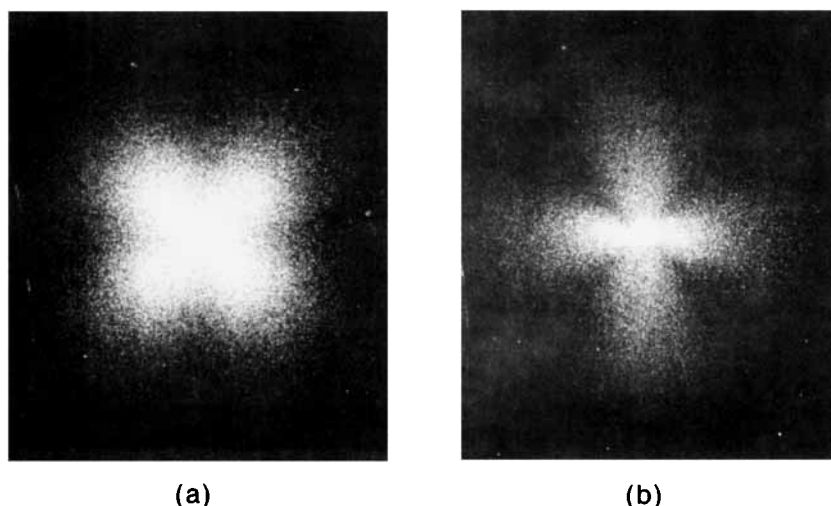
(a)   (b)

Figure 4   SALS Hv patterns of (a) S45 and (b) P45.

(E–CE)C (P55) shows a single T_g, which means that the photopolymerized composite is homogeneous within the DSC resolution. The composite prepared by polymerization with AIBN initiation, however, gives two glass-transition points, which implies the phase separation during the polymerization. Flory[6] has shown that in the ternary solution of rigid-rod and random-coil polymers, the phase separation will appear when the concentration of the random-coil polymer increases to above a negligible value. Consequently, to lock in the cholesteric structure of the (E–CE)C in the mesomorphic solution by *in situ* polymerization of AA, it is necessary for the polymerization to occur at a significantly fast rate that is higher than that of the phase separation of the (E–CE)C and PAA. Photopolymerization takes only about 20 s, so fast that the phase separation in the system cannot occur and the homogeneous transparent composite film can be formed. When the concentration is in the 42–52 wt % region, the film can exhibit vivid color because the composite maintains the cholesteric structure that can selectively reflect the visible light at a certain wavelength. AIBN initiating polymerization takes quite a long time, about 5 h, which is long enough for phase separation. Hence, the opaque composite with partly destroyed cholesteric structure is formed through the AIBN initiating polymerization of the mesomorphic solution.

Figure 3 shows the polarized micrographs of the 45 wt % (E–CE)C/AA mesomorphic solution (S45) and the correspondent photopolymerized composite (P45). It can be observed that the texture of the system is changed during the photopolymerization. S45 is at a unitary anisotropic state and gives the polygonal and planar texture. But after the photopolymerization, the rod-like texture appears, in which the rods mainly lie in the polarizing directions of the polarizers [Fig. 3(b)]. When the sample is rotated, the rods become gradually dark and finally disappear when the angle between the rods and the polarizing directions of the polarizers is about 45°. At the same time, some new rods that now lie on the polarizing direction of the polarizers appear [Fig. 3(c)]. It is known that under the crossed polarizing light, the birefringence is the strongest when the orientation direction of molecular chains is at an angle of 45° to the polarizing direction. Hence, from the texture of the photopolymerized composite, it is implied that in the rod-like domains, the oriented molecular chains have an angle of about 45° with the axial direction of the domains. This is also confirmed by the SALS study. Figure 4 shows the SALS Hv patterns of the solution (S45) and the composite (P45). S45 gives an X-type four-leaf Hv pattern, and P45 shows a +-type four-leaf pattern. The scattering intensity of the +-type four-leaf pattern given by P45 decrease simply with the increasing scattering angle. This is a typical rod-like scattering pattern of anisotropic rods in which the optical axes of the scattering elements lie at an angle of about 45° to the axial direction of the rods.[12]

From the transmission electron micrograph of the photopolymerized composite [Fig. 2(a)], the cholesteric domains can be seen clearly. Figure 5 is the partly enlarged micrograph of Figure 2(a): it shows a rectangular domain in which the direction of the striation is at an angle of about 45° to the axial direction. This implies that the domain may take the shape of a cylinder of which the axial direction
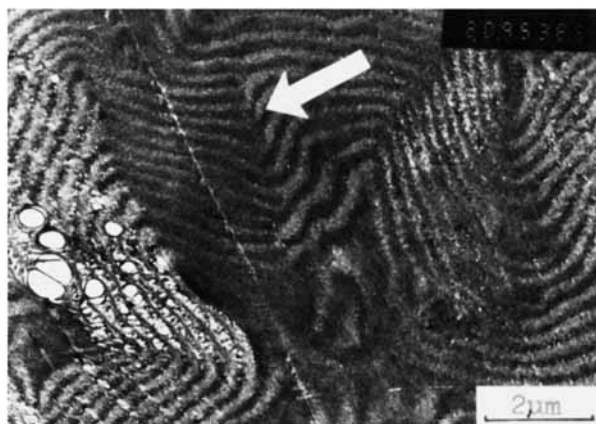
**Figure 5**   Transmission electron micrograph of P45. The rectangular domain is indicated by an arrow.

is at an angle of about 45° to the layers of ordered molecular chains. The electron microscope observation has revealed the details in structure of the rod-like domains observed with polarizing microscope and SALS.

Figure 6 shows the polarized micrographs of the 55 wt % (E–CE)C/AA mesomorphic solution (S55) and the correspondent photopolymerized composite (P55). It can be seen that the polygonal texture is partly maintained in the composite. Figure 7 gives the SALS Hv patterns of S55 and P55. The composite gives a complex SALS Hv pattern composed of a +-type four-leaf pattern and an X-type four-leaf pattern. The +-type four-leaf pattern is similar to the SALS Hv pattern of P45 and can be attributed to the scattering of the rod-like domains of which the axial direction is at an angle of about 45° to the

layers of the ordered molecular chains. The X-type four-leaf pattern is similar to that of the solution, which indicates that the morphology of the liquid crystalline domain in the solution at higher concentration is maintained partly. At such a high concentration, the viscosity of the solution is very high and the deformation of the domain becomes more difficult. In addition, the deformation is weakened with the increasing concentration because of the decrease in the content of AA. Therefore, the morphology can be partly maintained after the photopolymerization when at the high concentration.

Figure 8 shows the polarized micrographs of the system with 47.5 wt % (E–CE)C before and after AIBN initiating polymerization at 50°C (S47.5 and A47.5). The polymerization is essentially complete after 5 h. When the polymerization occurs, the texture is nearly unchanged, which means that the morphology of the system is maintained during the polymerization. This is also confirmed by their SALS Hv patterns (Fig. 9). That is, the SALS Hv pattern of the system is not changed after the AIBN initiating polymerization.

The polymerization of the AA in the (E–CE)C/AA solution leads to volume contraction. If the contraction of the (E–CE)C/AA system is isotropic during polymerization, the retention of the original morphology is reasonable. Maybe this is the case of the AIBN initiating polymerization. A possible alternative assumption is that the volume contraction takes place only in the directions perpendicular to the orientation direction of the ordered molecular chains under the influence of anisotropic nature of the semirigid (E–CE)C moleculars. In case of an-
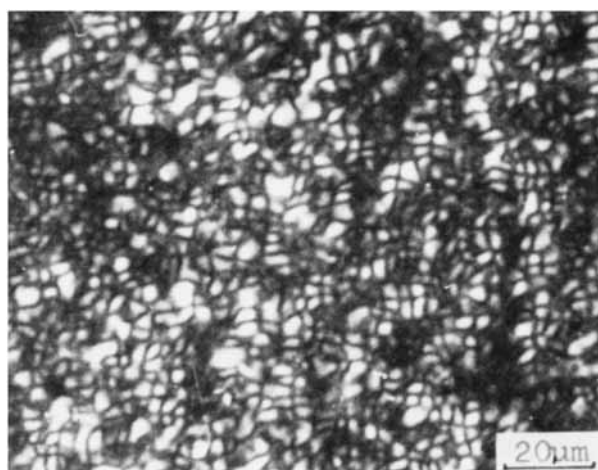
(a)
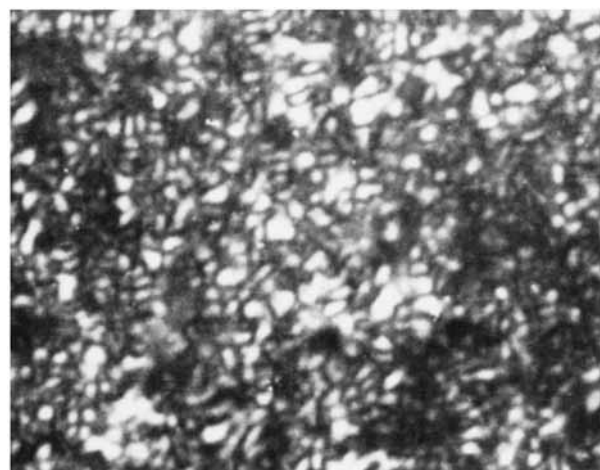
(b)

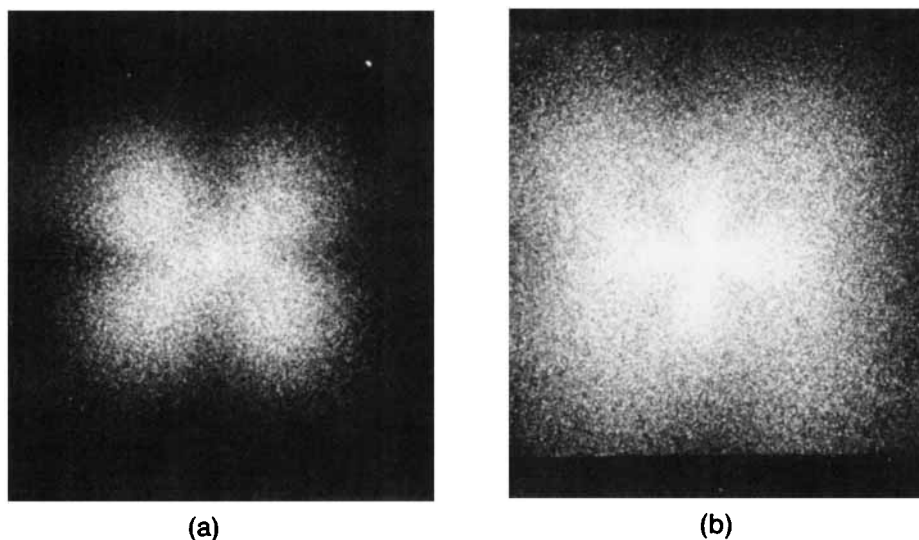**Figure 6**   Polarized micrographs of (a) S55 and (b) P55.

Figure 7 SALS Hv patterns of (a) S55 and (b) P55.

isotropic contraction, the morphology varies during the polymerization.

The speed of the photopolymerization is so high that the phase separation cannot occur and the cholesteric structure is maintained completely. In this time, however, the orientation of the semirigid (E–CE)C molecular chains can greatly affect the line contractive ratio in different directions. That is to say, the volume contraction in photopolymerization is anisotropic. In the condition of anisotropic contraction, there are two kinds of stresses acting on the mesomorphic domains. One is the anisotropic contracting stress of the domain itself; the other is the squeezing stress caused by the deformation of

the other domains. Under the action of these stresses, therefore, the layers of ordered molecular chains may move to each other and the domains may be distorted and twisted to become a kind of cylindric domain of which the axial direction is at an angle of about 45° to the layers of the ordered molecular chains.

CONCLUSIONS

(E–CE)C/PAA composites with cholesteric structure can be prepared by polymerizing the AA in the (E–CE)C/AA mesomorphic solutions with both
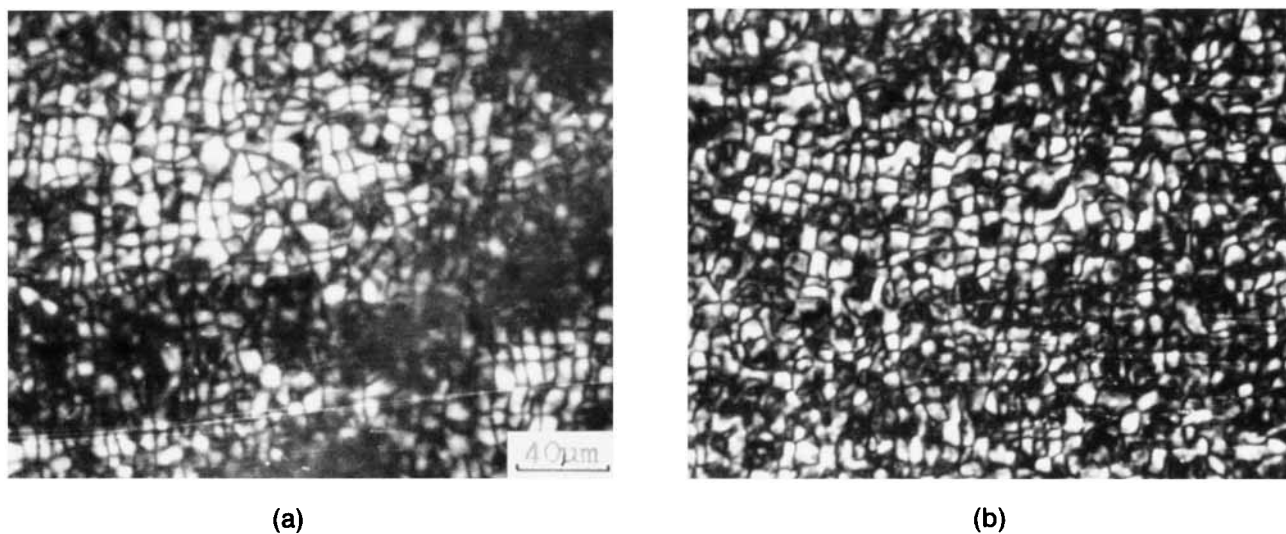

Figure 8 Polarized micrographs of (a) S47.5 and (b) A47.5 at 50°C.
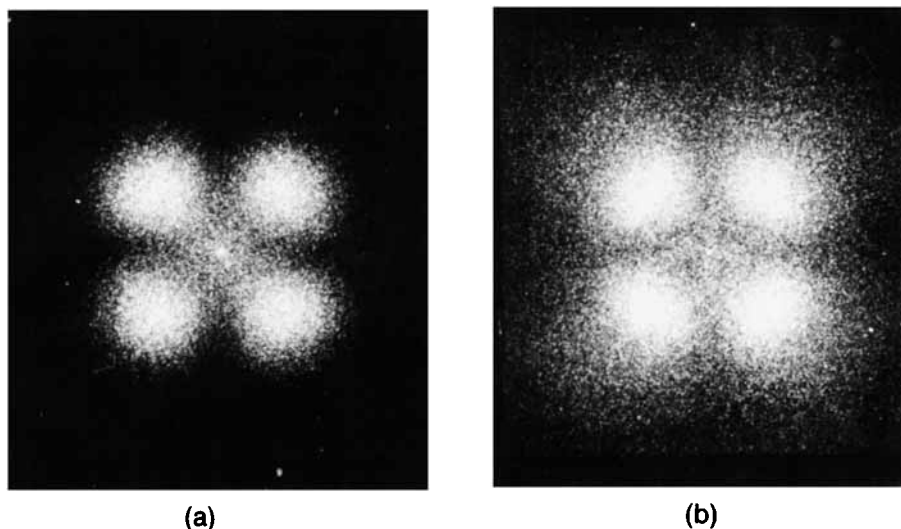
Figure 9   SALS Hv patterns of (a) S47.5 and (b) A47.5 at 50°C.

photoinitiation and AIBN initiation. But during the AIBN initiating polymerization of which the speed is fairly low, the phase separation occurs and the cholesteric structure is partially destroyed. Very high speed photopolymerization yields a homogeneous blend with a single T_g. The photopolymerized composite with 42–52 wt % (E–CE)C exhibits vivid color because of selectively reflecting visible light. To obtain the molecular composite, a high speed of polymerization is very important.

In the photopolymerization, the volume contraction is anisotropic because of the anisotropic orientation of the molecular chains, and the liquid crystalline domains are deformed into cylindrical ones of which the axial direction is at an angle of about 45° to the layers of the ordered molecular chains. But when the polymerizing speed is low, i.e., in the AIBN initiating polymerization, the volume contraction is perhaps isotropic, and the morphology of the liquid crystalline domains is almost unchanged.

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