# Preparation and Structures of Ethyl–Cyanoethyl Cellulose/Cross-Linked Polystyrene Composites

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SYNOPSIS

Ethyl–cyanoethyl cellulose [(E–CE)C]/cross-linked polystyrene (PS) composites were prepared via polymerization of styrene in (E–CE)C/styrene solutions with glycol diacrylate as a cross-linking reagent. The polymerization of the solution, morphology, and miscibility of (E–CE)C/PS composites were studied with polarizing microscopy, small-angle light scattering (SALS), differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). It was found that the mixing state of the (E–CE)C/PS system and the thermal stability of composites were modified by cross-linking of PS. In the intensively cross-linked composite prepared from the anisotropic solution, there existed cylindrical domains in which (E–CE)C spherulites were dispersed in PS. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The liquid crystalline organization of rigid or semirigid polymer can be retained during the polymerization of the olefinic solvent in mesomorphic polymer/olefin solutions under certain conditions.[1-4] The characteristic features of the polymer cholesteric mesophase can be studied by observing the morphology and structure of composites with electron microscopy. Also, a new kind of material with liquid crystalline organization and some specific properties can be achieved by polymerizing vinylic monomer incorporated in the system. Flory[5] showed that the phase separation of a ternary solution of rigid rod and random coil polymer may appear when the concentration of the random coil polymer increases above a negligible amount. The phase separation exists during the polymerization of vinyl monomer in the polymer/vinyl monomer liquid crystalline system. This will lead to the destruction of the ordered polymer organization during polymerization. Consequently, composites with perfect liquid crystalline organization can be prepared only when the polymerization is carried out at a signifi-

cantly faster rate than the phase separation or when the cross-linking polymer network has enough density, which will limit the phase separation, is formed during polymerization.

The ethyl–cyanoethyl cellulose [(E–CE)C]/acrylic acid (AA) mesomorphic solution[6] and the polymerization of AA in the (E–CE)C/AA system[4] have been studied. With photoinitiation, the (E–CE)C/AA solution could be polymerized completely in 0.5 min; it was so fast that the homogeneous (E–CE)C/PAA composite formed with full retention of the mesomorphic structure. The investigation of the (E–CE)C/styrene mesomorphic solution and the polymerization of (E–CE)C/styrene with AIBN heat-initiation have also been reported.[7] The styrene was polymerized in the (E–CE)C/styrene solution quite slowly, for about 5 h, phase separation occurred, and the (E–CE)C/polystyrene (PS) composites had multiphase features. However, the (E–CE)C in the (E–CE)C/PS composites showed a rodlike form, which was related to the cholesteric features of the solution.

In an attempt to control the phase separation during the AIBN heat-initiated polymerization, (E–CE)C/cross-linked PS composites were prepared by free-radical-initiated polymerization of the (E–CE)C/styrene solution with a cross-linking reagent. In this article, the preparation, morphology, and

structure of the (E–CE)C/styrene solution and the composites were studied with polarizing microscopy, small-angle light scattering, differential scanning calorimetry, and electron microscopy.

## EXPERIMENTAL

The (E–CE)C was prepared by reaction of ethyl cellulose and acrylonitrile. The (E–CE)C molecular formula is as follows:



R = H, CH$_2$CH$_3$, CH$_2$CH$_2$CN
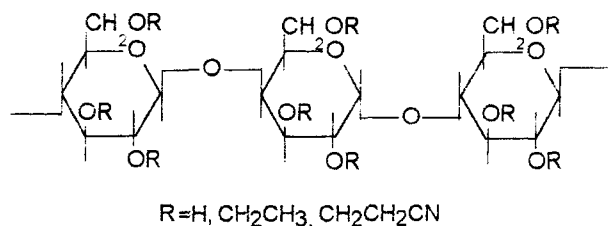
The degree of substitution for ethyl was about 2.1, and for cyanoethyl, about 0.43. The molecular weight, $M_n$, measured by gel permeation chromatography (GPC) (HPLC, Waters-209), was $7 \times 10^4$. Azobisisobutyronitrile (AIBN) and styrene were chemically pure reagents. The styrene was distilled before use. The cross-linking reagent glycol diacrylate (GDA) was prepared in our laboratory by reaction of glycol and AA.

The (E–CE)C was added to the styrene with 0.005 g/mL AIBN and the desired amount of the GDA. After being mixed thoroughly, the solution was laid aside for more than 2 days at about 5°C to form a homogeneous solution. Then, the solution was sealed in the glass cell ($25 \times 15 \times 0.9$ mm) by solid wax and kept at 50°C for 48 h, so that the styrene in the solution was completely polymerized to obtain white and opaque or partly transparent (E–CE)C/PS composites.

A polarizing microscope (ORTHOPLAN-POL, Leitz) and a small-angle laser light-scattering instrument (LS-1, Yingkou Measuring and Testing Instrument Factory, Liaoning, China) were used to observe the polarized light textures and the SALS $H_V$ patterns, respectively. For this purpose, slide polymerization was done. A drop of the solution was placed on a glass slide and depressed into a thin-solution film with another slide; then, the solution film forming between the two slides was transferred onto a hot stage (Leitz, Microscope Heating Stage 350) to polymerize at 50°C.

The temperature of the glass transition ($T_g$) of (E–CE)C, PS, and the composites was measured by differential scanning calormetry (DSC) (DSC-2C,

Perkin-Elmer). The morphology and structure of the composites was studied by observing their ultrathin sections with a transmission electron microscope (JEOL-100CX/II, Japan).

## RESULTS AND DISCUSSION

(E–CE)C can be dissolved in styrene and forms a cholesteric mesophase when the concentration is high enough.[7] When observed under a polarizing microscope, the (E–CE)C/styrene solution is isotropic and shows no birefringence when the concentration is less than 47 wt %. As the concentration increases above 47 wt %, the solution becomes turbid and anisotropic. Consequently, the critical concentration is about 47 wt %, at which the solution transforms from an isotropic solution to an anisotropic one. Figure 1 shows the texture of the mesomorphic (E–CE)C/styrene solution at a concentration of 55 wt %. The (E–CE)C/styrene mesophase in Figure 1 shows a polygonal texture, which means that the mesophase is a cholesteric one.

Figure 2 shows the polarized light photograph of the 55% mesomorphic (E–CE)C/styrene solution with a 10 wt % (6.4 mol %, with respect to styrene) cross-linking reagent GDA. It also shows the polygonal texture similar to that of mesomorphic (E–CE)/styrene solutions without GDA. Therefore, the addition of GDA does not change the characteristic features of (E–CE)C/styrene liquid crystalline solutions provided that the GDA content is smaller than 10 wt %. To determine a suitable polymerizing temperature for both isotropic and anisotropic solutions, the effect of temperature on liquid crystallinity had to be investigated. Liquid crystalline solutions change to an isotropic state when the tem-
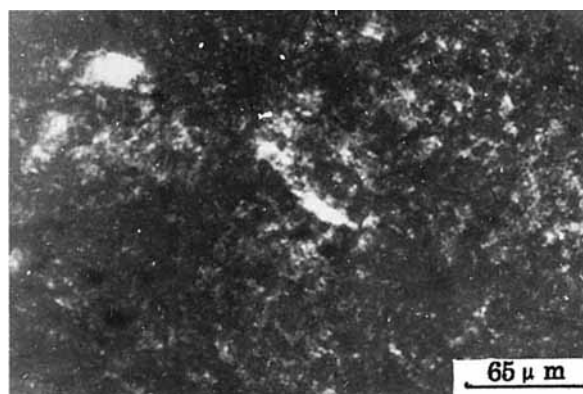


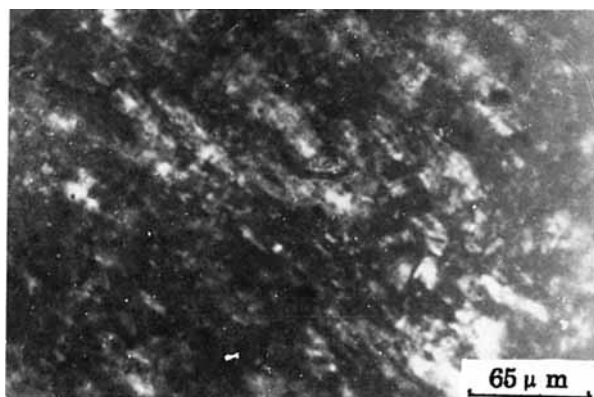**Figure 1**   The texture of the mesomorphic (E–CE)C/styrene solution without GDA; $C = 55$ wt %.

**Figure 2** The texture of the mesomorphic (E–CE)C/ styrene solution with 10 wt % GDA; $C = 55$ wt %.

**Table I** $T_g$'s of PS, (E–CE)C, and Composites from the 55 wt % (E–CE)C Sytrene Solution With and Without GDA

| Sample | PS | (E–CE)C | Composite I | Composite II |
|---|---|---|---|---|
| $T_g$ (K) | 368.9 | 410 | 369 and 408 | 399 |

I: Prepared from the solution without GDA. II: Prepared from the solution with 10 wt % GDA.

perature rises above the critical point. With heating and observing the mesophase by using a polarizing microscope equipped with a hot stage, it can be found that the 50 and 55 wt % solutions become isotropic completely at 55 and 120°C, respectively. With polymerization at 50°C, therefore, the (E–CE)C/styrene system is anisotropic when the concentration is over 50 wt %.

Both (E–CE)C/PS composites prepared from the solution with GDA and without GDA are heated and observed using a polarizing microscope equipped with a hot stage. The composites from the solution without GDA begin to flow just at about 150°C, but the composites from the solution with GDA do not

change until 260°C. At 260°C, which is the melting point of (E–CE)C, they begin to melt and are gradually oxidized to dark brown when the temperature increases continuously. Obviously, this is because the effective styrene cross-linking network has been formed in the composites from the solution containing GDA and no cross-linking network forms in cellulose or between it and PS.

The composites prepared from the solution without GDA are white and opaque. But if the cross-linking reagent GDA is added before polymerization, the transparency of composites increases significantly. The temperature of the glass transition ($T_g$) measured by DSC shows that (E–CE)C and PS are completely incompatible in uncross-linked composites prepared from the solution without GDA, and two $T_g$'s appear close to the ones of pure (E–CE)C and PS, respectively. But in the cross-linked composites prepared from the solution with 10 wt % GDA, only one $T_g$ located between those of pure (E–
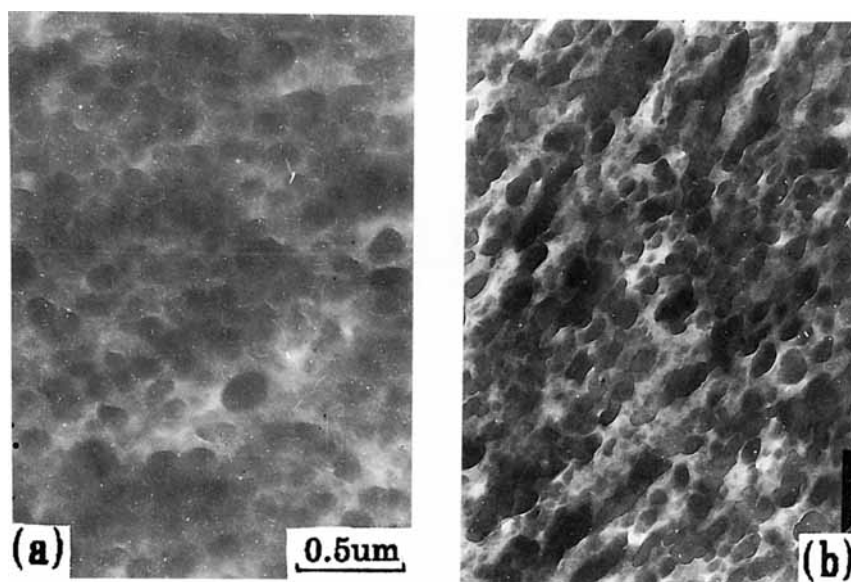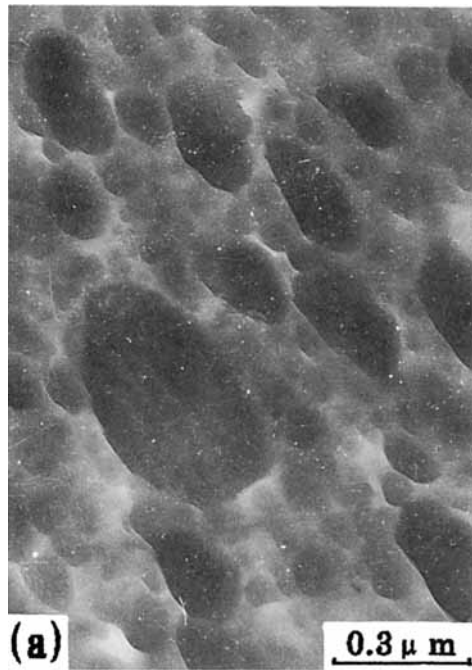


**Figure 3** Transmission electron micrographs of (E–CE)C/PS composites prepared from anisotropic solutions; the section is (a) perpendicular and (b) parallel to the composite plane. $C = 55$ wt %.
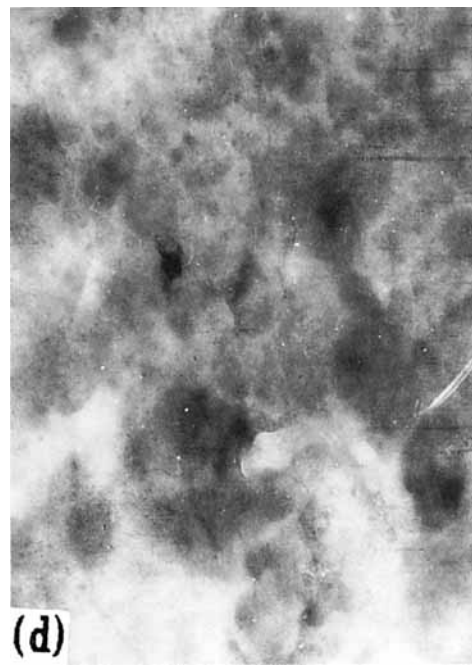
**(a)**    $0.3 \mu m$

0% GDA

2% GDA

5% GDA

10% GDA

**Figure 4**   TEM micrographs of (E–CE)C/PS composites prepared from isotropic solutions.
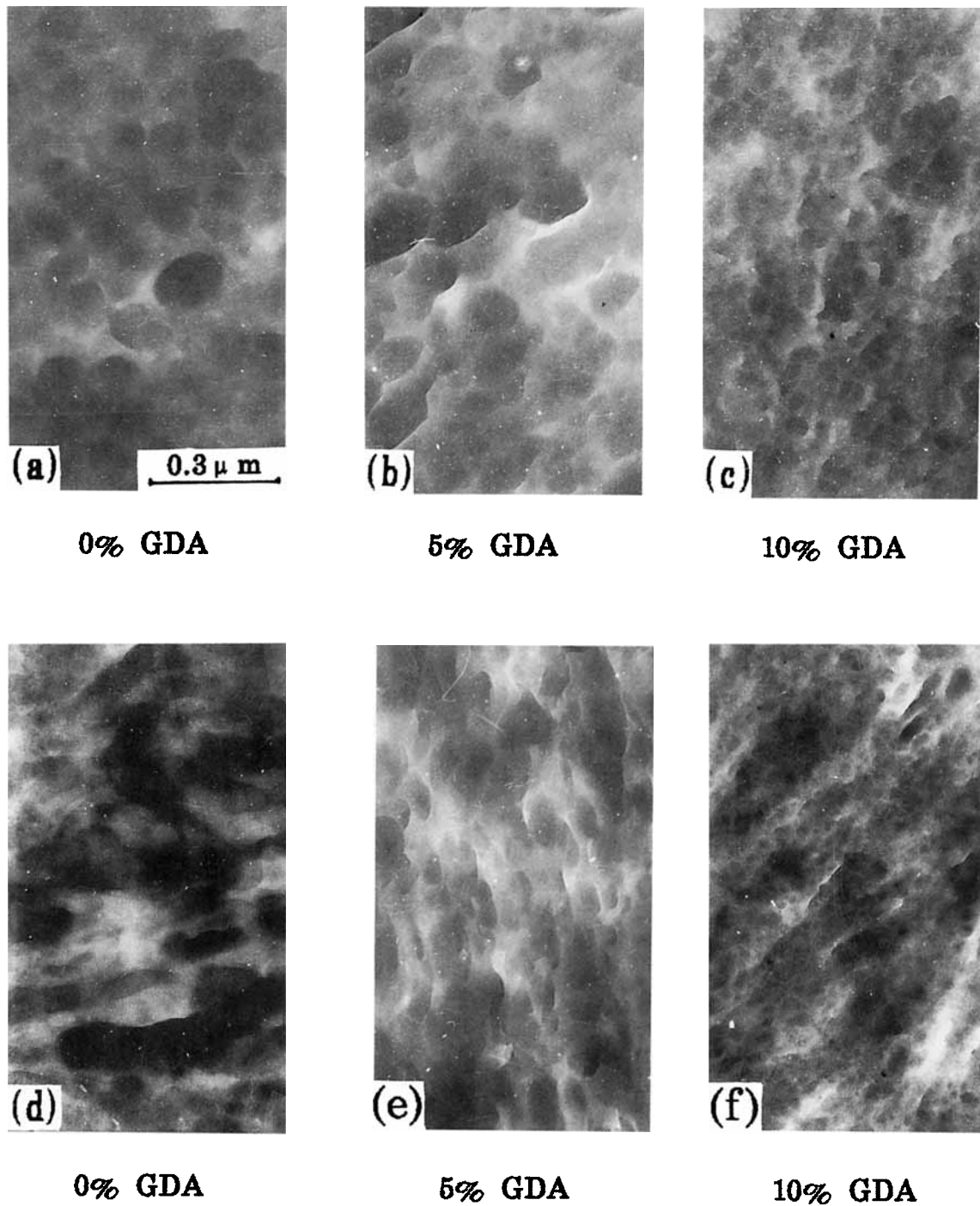
**Figure 5**   TEM micrographs of (E–CE)C/PS composites prepared from anisotropic solutions, $C = 55$ wt %; the sections are (a)–(c) perpendicular and (d)–(f) parallel to the composite plane.

CE)C and pure PS appears in the DSC curves. Obviously, during the polymerization, the cross-linking has suppressed the phase separation, and the mixing state of (E–CE)C and PS in the composites is improved (Table I).

The morphology and structure of (E–CE)C/PS composites are related to the solution state before polymerization.[7] (E–CE)C forms the dispersive phase and PS forms the continuous phase. In the (E–CE)C/PS composite prepared from the aniso-

tropic solution, the (E–CE)C phases shows rodlike aggregates that are about 0.1–0.2 μm in diameter and 0.2–2 μm in length. Figure 3 shows the transmission electron micrographs of the (E–CE)C/PS composites prepared from anisotropic solutions. The (E–CE)C phase shows circular domains when the specimen is sectioned along the direction perpendicular to the composite plane and shows rodlike domains when the specimen is sectioned along the direction parallel to the composite plane. This means that the (E–CE)C rodlike domains lie in the composite plane.

Figure 4 shows the transmission electron micrographs of the (E–CE)C/PS composites prepared from the 47 wt % isotropic (E–CE)C/styrene solution with different contents of GDA. The morphology and structure changes gradually with increasing GDA content. In these composites, (E–CE)C exists as spherulites and their diameter is about 0.1–0.5 μm and decreases with increasing GDA content. When the GDA content is high, about 10

wt %, the spherulites become much smaller and the phase boundaries become vague.

Figure 5 shows the transmission electron micrographs of the (E–CE)C/PS composites prepared from the 55 wt % anisotropic (E–CE)C/styrene solution with different contents of GDA. When GDA content is low, the (E–CE)C morphology and structure is almost the same as that of composites without GDA. But when GDA content is high enough, about 10 wt %, a complex morphology and structure appears. The (E–CE)C exists as spherulites whose diameter is about 0.015–0.04 μm, and these spherulites aggregate in rodlike domains, whose size is as large as that of the (E–CE)C rodlike domains in the composites prepared from the anisotropic solutions without GDA. To explain how such a complex structure forms, let us turn to polarizing microscopy and SALS.

Figure 6 shows the polarized micrographs of the (E–CE)C/styrene mesomorphic solutions and the composites prepared from them. The texture does
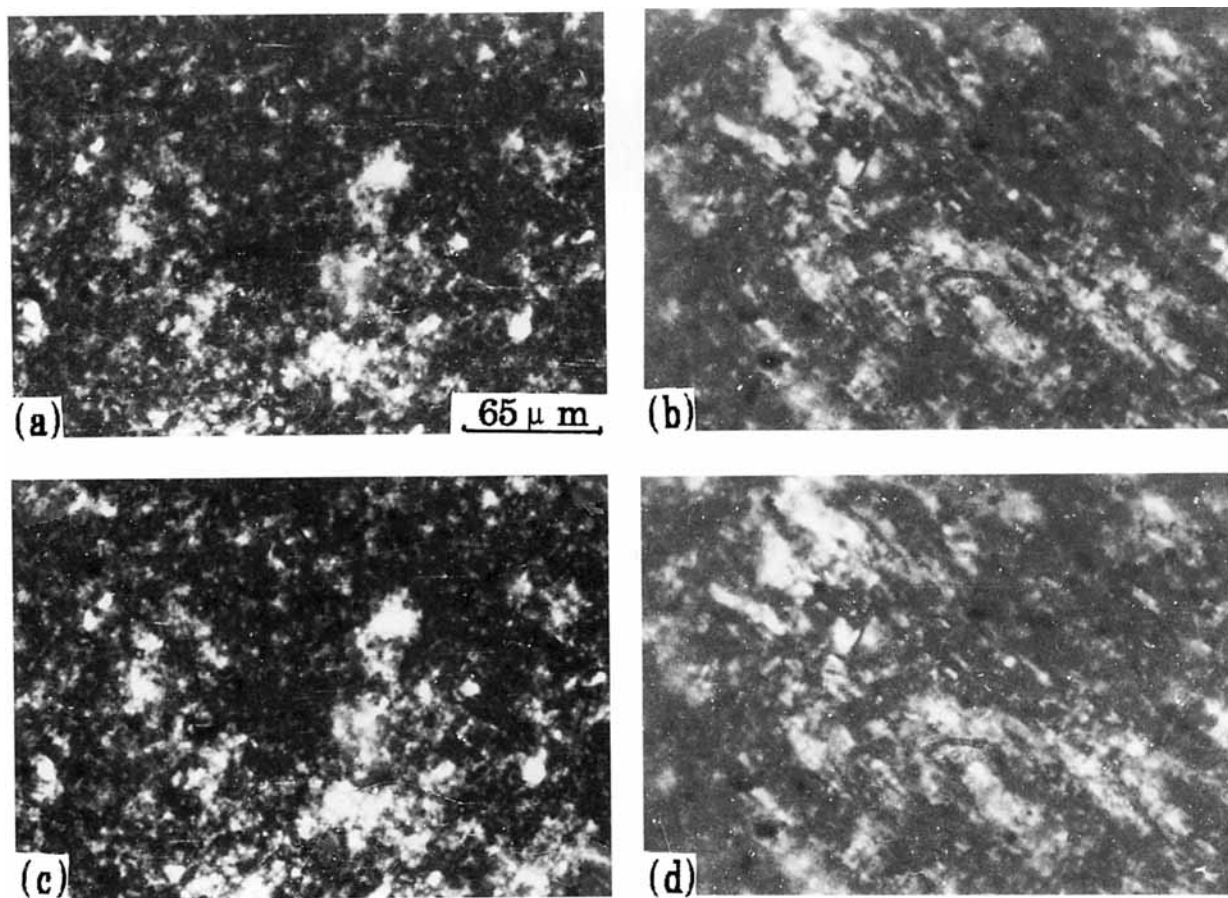


**Figure 6** Polarized micrographs: (a) 55 wt % (E–CE)C/styrene solution; (b) 55 wt % (E–CE)C/styrene solution containing 10 wt % GDA; (c) the composite prepared from (a); (d) the composite prepared from (b).

not change during the polymerization of the solution with and without GDA. This means that the large size (E–CE)C morphology of the system and the (E–CE)C molecular orientation do not change during the polymerization, although phase separation occurs. Figure 7 gives the SALS $H_V$ patterns of the (E–CE)C/styrene mesomorphic solutions with and without GDA and the composites prepared from them. The solutions give an X-type SALS $H_V$ pattern whose scattering intensity increases with increasing scattering angle. This is a typical scattering

pattern of a rodlike particle in which the molecular orientation direction is parallel or perpendicular to its axial direction. The X-type SALS $H_V$ patterns do not change either during the polymerization in both of the solutions with and without GDA. Although from the polarized micrographs we cannot determine the domain shape, SALS tells us that the mesomorphic domains are rodlike. Since the domain morphology does not change during the polymerization, the rodlike (E–CE)C phases with a diameter of about 0.1–0.2 $\mu$m and length of about 0.2–2.0 $\mu$m
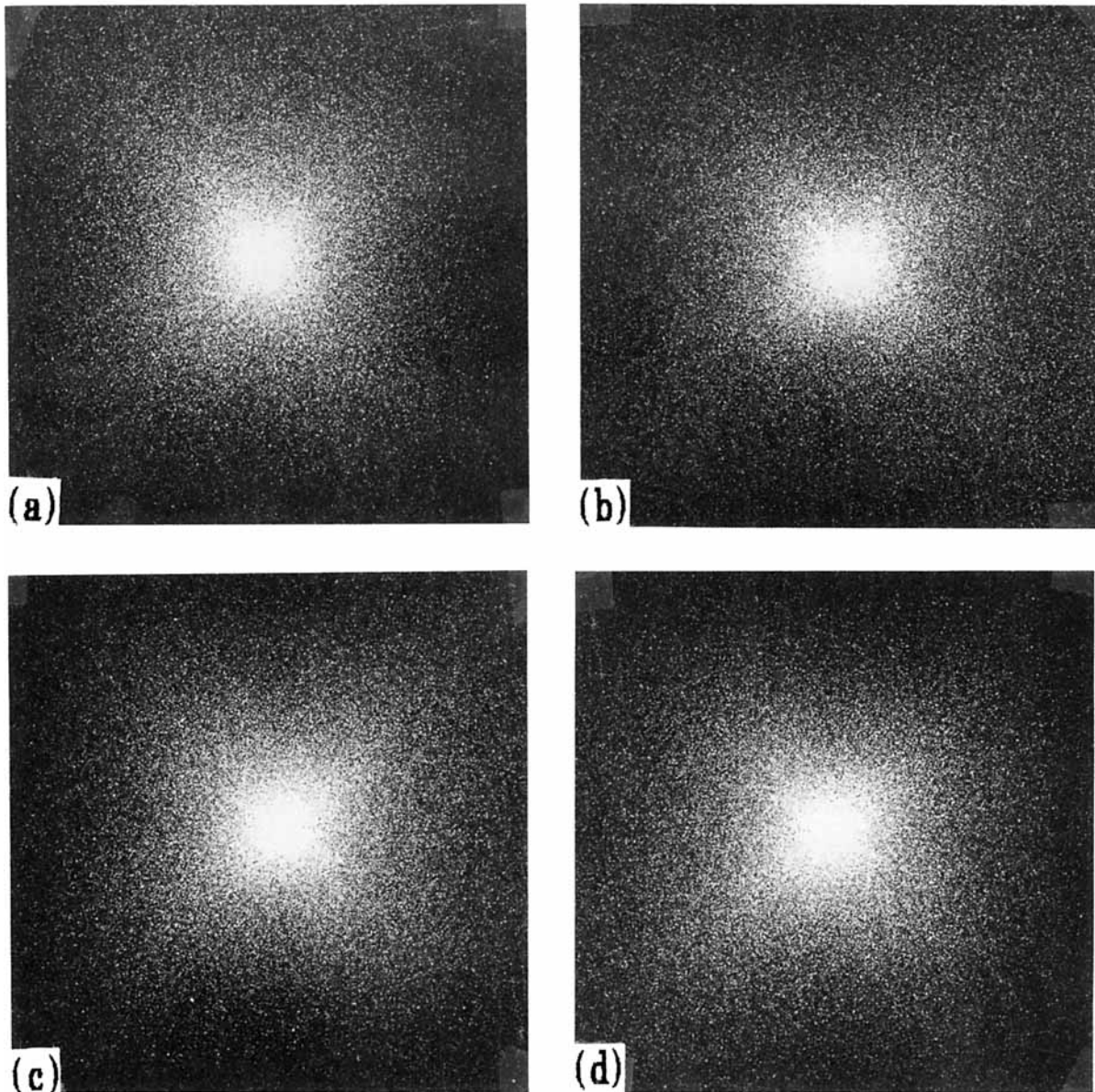


**Figure 7**   SALS $H_V$ patterns: (a) 55 wt % (E–CE)C/styrene solution: (a) 55 wt % (E–CE)C/styrene solution; (b) 55 wt % (E–CE)C/styrene solution containing 10 wt % GDA; (c) the composite prepared from (a); (d) the composite prepared from (b).

in the composites should originate from the rodlike mesomorphic domains. In our previous studies on the (E–CE)C/AA system,[4] the retention of the morphology of the liquid crystalline domains has also been observed during the AIBN-initiated polymerization. From the above, we can see that (E–CE)C has the tendency to keep its morphology and orientation during the polymerization of the mesomorphic (E–CE)C/olefinic solution; this may be because the semirigid (E–CE)C molecules are correlatively oriented in one liquid crystalline domain. When the styrene is polymerized to PS, phase separation occurs between (E–CE)C and PS because of their inherent incompatibility. Then, the PS moves out from the rodlike liquid crystalline domains, and the rodlike (E–CE)C phase maintaining the original morphology and orientation is formed. In the case of the system containing GDA, phase separation occurs and the PS moves out from the liquid crystalline domains at the beginning of polymerization, similar to the case without GDA. But after the polymerization has proceeded to a certain extent, the system is viscous enough and the degree of cross-linking is high enough to prohibit PS from moving out. At this time, the cross-linking network is formed in liquid crystalline domains and the (E–CE)C aggregate to the spherular microphase in rodlike domains. In this way, the mixing state of (E–CE)C and PS in the composite prepared from the solution with GDA is improved. Specifically, the (E–CE)C spherulites with a diameter of about 15–40 nm that appear in rodlike domains in the cross-linked composite from the mesomorphic solution do not lead to light scattering because the size of the spherulites is much smaller than is the wavelength of the laser.

## CONCLUSIONS

Multiphase (E–CE)C/cross-linked PS composites were prepared via in situ polymerization of styrene in (E–CE)C/styrene solutions. The (E–CE)C in the composites prepared from liquid crystalline solutions showed the rodlike morphology, which is originated from the rodlike mesomorphic domain. When the degree of cross-linking is high enough, a complex morphology and structure, i.e., rodlike domains containing the (E–CE)C spherular microphase, appeared. Cross-linking significantly improved the thermal stability of composites and the miscibility of the (E–CE)C and PS in the composite.

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