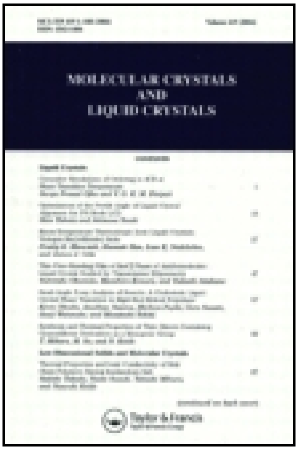

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Miscibility of Liquid Crystalline Polymers; Mixtures of (Hydroxypropyl)cellulose and Ester Derivatives

G. V. Laivins [a] & P. Sixou [a]

[a] Laboratoire de Physique de la Matière Condensée, Parc Valrose Université de Nice, 06034, NICE, France

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Miscibility of Liquid Crystalline Polymers; Mixtures of (Hydroxypropyl)cellulose and Ester Derivatives

G. V. LAIVINS and P. SIXOU

Laboratoire de Physique de la Matière Condensée, Parc Valrose Université de Nice 06034 NICE, France

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Heavily substituted cellulosic polymers including (hydroxypropyl)cellulose (HPC), (acetoxypropyl)cellulose (APC), and the propionate ester of HPC (PPC) form both lyotropic and thermotropic liquid crystalline phases. The miscibility of binary mixtures of these cellulosics in methanol and in film form are examined by polarizing microscopy. In methanol all of the binary polymer systems demix and segregate into distinct regions. Decreasing the molar mass of HPC and APC polymers does not inhibit the demixion in solution, but facilitates the phenomenon. Ester–ether blends once heated above the isotropization temperature, Tñi, exhibit two co-existing phases. The segregated regions do not mix even when reheated to a temperature at which both regions are isotropic. The ester–ester blends are apparently miscible since segregation was not observed. The Tñi of the ester blends (with the esters in a 1:1 ratio) is an average of the Tñi of the two esters.

INTRODUCTION

The physical properties of a polymer or polymer solution can be significantly modified when another polymer with differing properties is added to the system.[1,2] However systems involving several different polymers generally are inhomogeneous as the polymers tend to segregate unless there is some specific interaction such as ionic or hydrogen bonding between the different types of polymeric chains.[3] The size of the homogeneous regions into which the polymers migrate can vary greatly and depends notably on the relative affinity (χ parameters) between the different components in the system. When the size of the locally homogeneous regions is relatively small and the regions are in close proximity, it may appear that the system is macroscopically uniform. However on a more minute scale it is heterogeneous. The long term stability of the physical properties exhibited by the system requires that the system is homogeneous at the molecular level. As a consequence, a large number of experimental techniques[1,2,3] have been used to investigate the miscibility of systems involving several polymers or blends. Recently it was shown in this laboratory that the phase separation of two cellulosic polymers ethyl cellulose and (hydroxypropyl)cellulose either in solution or in film form (cast from a solution) could be investigated using polarizing microscopy.[4] The heterogeneity of a mixture of ethyl cellulose and (hydroxypropyl)cellulose, HPC, was evident as the liquid crystalline phase formed by each of the polymers had a different texture when examined under the polarizing microscope. In addition when the polymers are completely immiscible and segregate into well defined regions, each region may have a distinct isotropization temperature, Tn̊i. The Tn̊i of cellulosic polymers which is conveniently measured by polarizing microscopy is generally within a few degrees of the Tn̊i measured by a thermal analysis technique.[5]

In this study the textures (observed with a polarizing microscope) of mixtures of similar cellulosic polymers are examined. In HPC, hydroxypropyl substituents are attached to the cellulose backbone by ether linkages. To synthesize (acetoxypropyl)cellulose (APC) the reactive hydroxyl groups of the hydroxypropyl substituents are acetylated. When incomplete esterification occurs, products with properties intermediate between those of HPC and of APC are formed. A large number of ester derivatives of HPC have been prepared, including the proprionate ester (PPC). These ester derivatives differ from HPC only in the end group of the substituent. Binary combinations of several cellulosic polymers (all of which form thermotropic and lyotropic cholesteric liquid crystals) were mixed. In this fashion, the degree of chemical modification which the system would tolerate while remaining homogeneous (as evidenced by the textures seen under the polarizing microscope) could be investigated.

EXPERIMENTAL

Polymers

i) HPC The commercially available product supplied by Hercules, labelled Klucel (nominal molar mass of 60000 g/mol) was used as such. The reported Tñi is 195°C.[6] The HPC was subjected to an acid catalyzed methanolysis[7] reaction for nine hours to yield HPC-B. The methanolysis reaction cleaves the interanhydroglucose ether linkages, but does not attack the hydroxypropyl substituents. The procedure used in the methanolysis reaction of HPC has been described.[8] The limiting viscosity number, $[\eta]$, of HPC-B in ethanol at 25°C was determined to be 0.060 ± 0.003, using suspended level KPG-Ubbelohde viscometers. From the published[9] Mark-Houwink-Sakarada relationship, $[\eta] = 2.6 \times 10^{-5}\,\overline{M_w}^{0.915}$, the molar mass of HPC-B is 4800 g/mol.

ii) APC The preparation and characterization of the material used has been previously described.[8] The weight average molar mass of this fully acetylated derivative (unit ester content of three) is $(180 \pm 5) \times 10^3$ g/mol. The Tñi is 175°C.

APC-B An APC sample which previously was subjected to a methanolysis reaction was then acetylated according to the procedure outlined by Malm *et al.*[10] The preparation and characterization of the material has been described.[8] The weight average molar mass of this derivative (USC of three) is 30,000 g/mol^{-1}. The Tñi is 164 ± 3°C.

APC-C The polymer has been extensively characterized previously.[11] The product is 67% acetylated. The reported $\overline{M_w}$ and Tñi values are $(230 \pm 10) \times 10^3$ g/mol and 182°C respectively.

iii) PPC This sample was prepared by reacting Aldrich (100,000) g mol^{-1} HPC and proprionic anhydride. The isotropization temperature, Tñi, measured was 154 ± 2°C. The infra-red spectrum of the polymer had sharp strong peaks at 1735 and 1190 cm^{-1} indicating the presence of ester linkages. A substantial peak centered at 3500 cm^{-1} is attributed to hydroxyl groups, indicating that the esterification reaction was incomplete. Propionyl (CH_3CH_2CO) content of the polymer was determined.[12]

Mixtures

Methanol (Merck) was added to a 1:1 binary composition of polymers. Methanol was chosen as the solvent (in all the systems) since dissolution of the polymers (necessary for mixing) used in this study could be effected. The eventual casting of films required that the solvent be volatile. Unfortunately the rate of evaporation of methanol from these viscous systems is a variable parameter. Thus any effort to standardize the percentage of methanol in the series of systems listed in Table I would be negated by the uncontrolled but desired evaporation of methanol. The systems were stirred manually to distribute the components throughout the system. The weight percentage of the two cellulosic derivatives in methanol is given in Table I.

Investigation of the Texture

A drop of the composition was placed under a cover glass on a microscope slide. The texture was observed under an Olympus BH2 polarizing microscope. The magnification of the objectives ranged from x10 to x40. When photographs were taken (developed from a 35 × 16 mm film), an internal eyepiece magnification of 2.13 occurs. The apparent lack of focus seen in several photographs is attributed to heterogeneity in the composition. The consequence of light passing through several microdomains of textures (on top of each other) is a field which appears out of focus.

Transition Temperatures

To form a film, the solution was cast onto a microscope slide and the solvent evaporated. The slide was heated while under a vacuum during the final stage of evaporation. The film sandwiched between a microscope slide and coverglass was placed on a Mettler FP52 hot stage which was positioned under the objective of the microscope. While the film was heated at 2°/min, the variation in the intensity of light transmitted through the crossed polars was monitored with a photomultiplier tube and registered on a chart recorder. The total light intensity measured is integrated over the field of view. The temperature (upon heating) at which the intensity of light transmitted through the film attains the minimum value, is defined as the isotropization temperature. A uniform dark background is observed at

TABLE I

The weight percentage of the cellulosic derivatives in methanol

Ether/Ester	% Polymer1	% Polymer2
HPC/APC-A	24.6	25.5
HPC/APC-C	23.6	22.7
HPC/PPC	30.4	29.7
HPC-B/APC-B	33.8	33.2
PPC/APC-A	34.2	32.6
PPC/APC-C	33.4	33.0
APC-A/APC-C	24.8	24.8

temperatures which exceed Tñi. At these temperatures, bright areas in the field of observation due to birefringent regions are no longer visible.

RESULTS AND DISCUSSION

Ether-Ester Mixtures

Mesomorphic cellulosic solutions generally are translucent shimmering and slightly turbid. The HPC/APC-A mixture in methanol exhibited these characteristics but was milky-white. The change in the texture of a drop of the mixture (sandwiched between a slide and coverglass was observed through the eyepiece of the microscope) as a function of time is shown in Figure 1. Initially, 1a, small islands of anisotropic material (light areas) are dispersed in an isotropic sea (dark areas).

In 1b (a 1 day old solution) the anisotropic material is coalescing to form circular regions. As the solution ages and methanol evaporates, the quantity of anisotropic material relative to the isotropic material increases. The segregation of the mixture into regions is still clearly evident. After 21 days (texture shown in Figure e) almost all the methanol has evaporated, leaving apparently uniform anisotropic material with little indication of polymer segregation.

The apparent segregation seen in Figures a and b but not clearly evident in Figure e could be caused by the differing affinities of the polymers (APC-A and HPC) for methanol, or a genuine immiscibility between the polymers. The changes in texture of the blend which had been previously melted, upon reheating are shown in Figures 2a to 2d. In 2a, two anisotropic phases with similar textures at ambient temperatures are seen. Upon heating to 165°C, the anisotropic material contained within the circles appears to have melted forming an isotropic phase, while large regions remain anisotropic. The sample is biphasic with an isotropic and anisotropic phase co-existing as shown in 2b. A totally isotropic sample results upon further heating to 210°C as indicated in 2c. However, even when completely isotropic, demixion is evident. Cooling the sample gradually, allows the regions which have higher Tñi to reform an anisotropic texture as shown in 2d. When recooled to ambient temperature, the separation of two anisotropic phases of similar texture is once again apparent as in 2a.

The change in light intensity through the crossed polarizers of a microscope as an APC-A/HPC blend is heated above the isotropi-

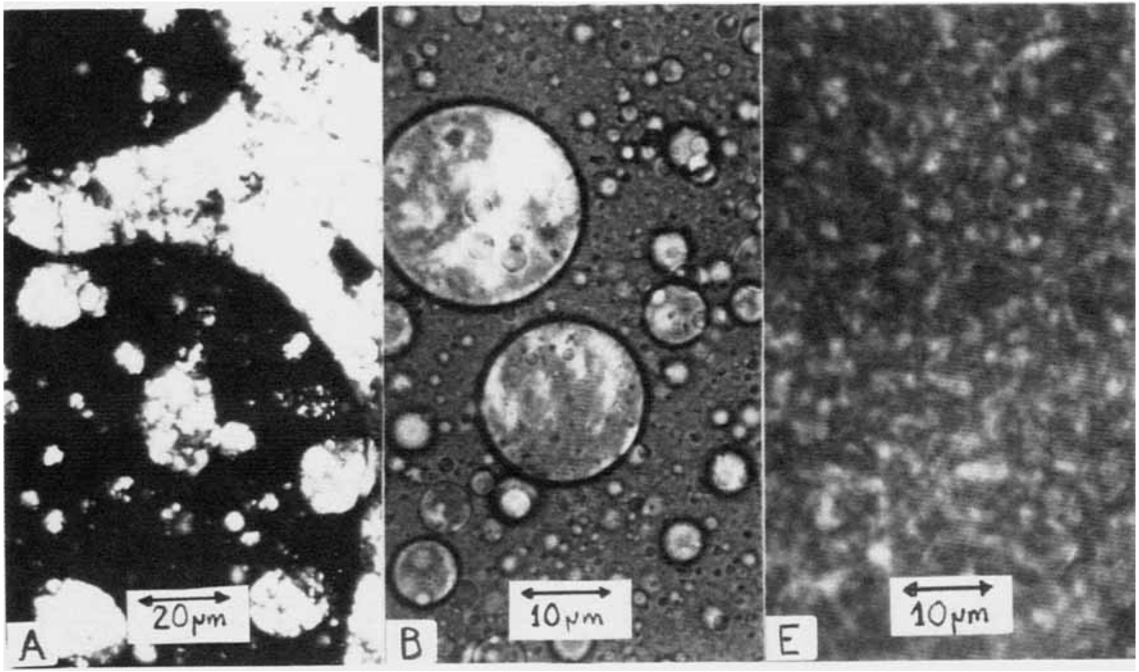

FIGURE 1 The texture (observed with a polarizing microscope) of a 1:1 HPC/APC-A methanol mixture as methanol evaporates, at ambient temperatures.
A day 0—(isotropic/anisotropic)
B day 1—biphasic (isotropic/anisotropic)
E day 21—appears monophasic anisotropic

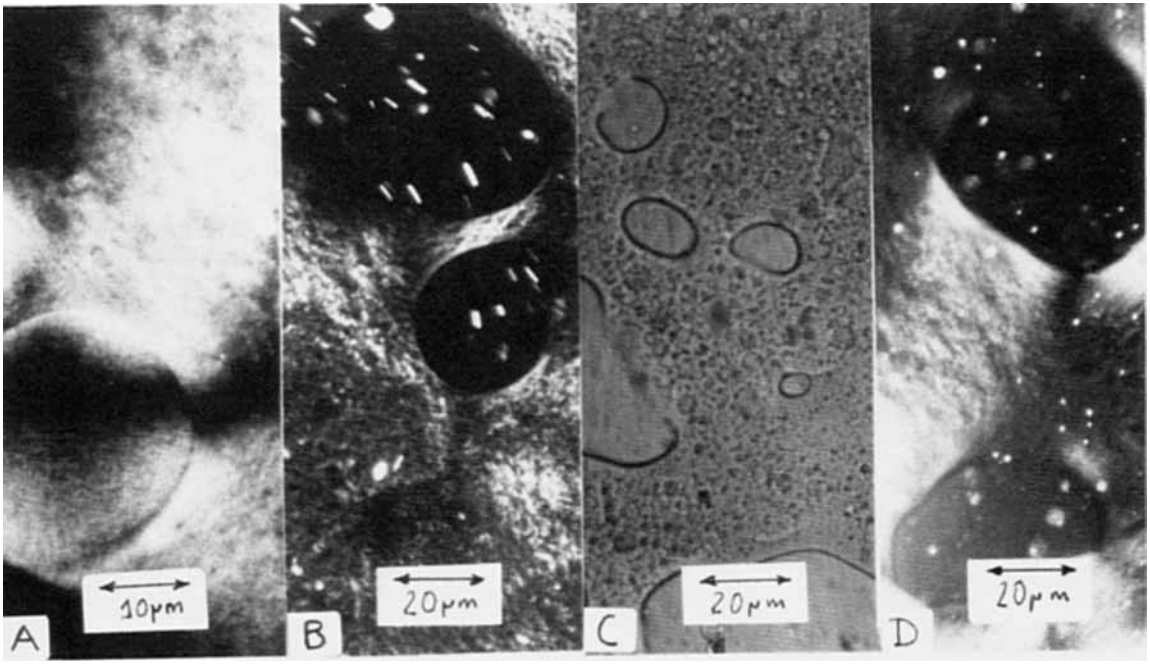

FIGURE 2 The texture (observed with a polarizing microscope) as an HPC/APC-A blend is heated into the isotropic melt and subsequently recooled.
A at 25°C—biphasic (anisotropic/anisotropic)
B at 165°C—biphasic (isotropic/anisotropic)
C at 210°C—biphasic (isotropic/isotropic)
D at 95°C—biphasic (isotropic/anisotropic)

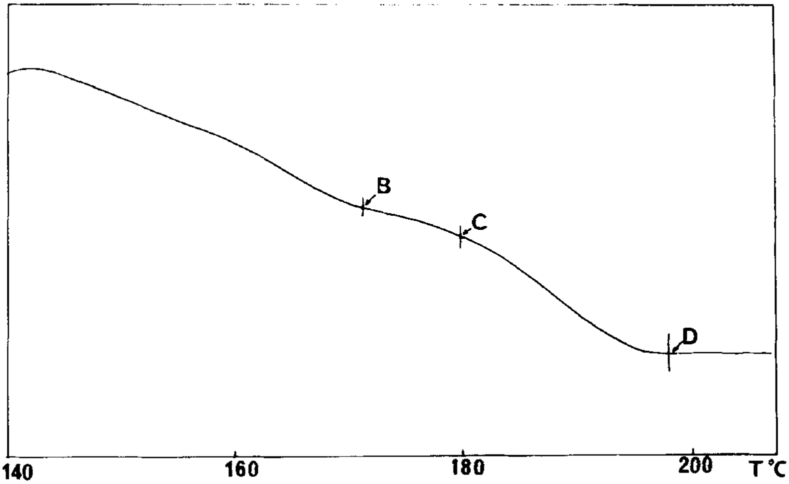

FIGURE 3 The variation in the intensity of light transmitted through the crossed polarizers of a microscope with temperature when a 1:1 APC-A/HPC blend is heated into the isotropic phase.

zation temperature is shown in Figure 3. A rapid decrease in the intensity of the light occurs within the temperature range in which the isotropic material forms. Following this sharp decrease, the light intensity decreases more slowly. This temperature range resembles a plateau on Figure 3 and is delimited by the points B and C. The light intensity once again decreases rapidly for temperatures within the region defined by the points C and D. The Tñi (temperature corresponding to point D) is 198 ± 2°C. The Tñi of Klucel HPC is 195°C. Thus it appears that the anisotropic regions in the APC-A/HPC blend which are converted to the isotropic phase at the elevated temperatures and define Tñi are mainly HPC. The variation in the light intensity upon heating shown in Figure 3 became more pronounced as the blend was reheated. This observation suggests that the segregation of the polymer chains into regions of differing composition is facilitated at higher temperatures where the viscosity of the blend is reduced.

Effect of Molar Mass on the Miscibility of HPC and APC

Flory and co-workers[13-15] have derived expressions for the free energy for mixtures (blends or in solution) of polymers as a function of molar mass. The entropic contribution to the free energy decreases when polymers of higher molar mass are mixed. Therefore the affinity of two different polymers is promoted when the molar mass of the two polymers is decreased.

The differentiation between the HPC-B/APC-B/methanol and the APC/HPC/methanol systems is the molar mass of the polymers. HPC and APC-A are high polymers with molar masses of 60,000 and 180 ± 5 × 10^3 g/mol^{-1} while those of HPC-B and APC-B are 4800 and 30,000 g/mol^{-1} respectively. Therefore the influence of molar mass on the miscibility of the polymers can be analyzed when the two systems are compared. When methanol was added to a 1:1 composition of HPC-B and APC-B only the HPC-B powder dissolved and two distinct layers formed in the vial. The upper layer was a clear free flowing homogeneous isotropic fluid. The bottom layer was a homogeneous mesomorphic fluid exhibiting shimmering colours. When the solution was stirred it appeared turbid but without the whitish allure exhibited by the stirred HPC/APC-A methanol system. When examined (using polarizing microscopy) the stirred solution appears as circular islands of anisotropic material dispersed in an isotropic sea, similar to that in Figure 1b. As the solution ages and the methanol evaporates, the isotropic areas begin to exhibit an anisotropic texture. Finally when most of the methanol has evaporated a system consisting mainly of two anisotropic phases with similar textures formed. The change in texture of HPC-B/APC-B as methanol evaporates greatly resembles the HPC/APC-A system that seen in (Figure 1a–c). Decreasing the molar masses of the polymers apparently did not significantly alter the affinity of the polymers for each other. The decrease in the chain lengths facilitated the demixion phenomenon. This is attributed to the greater mobility of the polymers. Upon long equilibration, the HPC/APC-A and HPC/APC-C methanol systems separated into two layers. The layers were turbid, and slightly shimmering.

As the phenomena for the HPC/APC-C and HPC/PPC/methanol systems are similar to that described for the HPC/APC-A/methanol system, detailed descriptions will not be repeated. The textures of the HPC/APC-C and HPC/PPC-methanol systems also indicated that the polymers in the mixture were immiscible. When the HPC/APC-C and HPC/PPC films (solvent evaporated) which had been previously melted were examined under the polarizing microscope separation of anisotropic regions was evident. The melting behavior of the HPC/APC-C and HPC/PPC blends indicates that an isotropic phase co-exists with an anisotropic phase within the temperature range limited by the Tfi of the two pure polymers. The Tfi of the HPC/APC-C and HPC/PPC blends are 200 ± 2 and 192 ± 3°C respectively. The blends remain biphasic at temperatures exceeding the isotropization temperature. The two co-existing phases are isotropic.

Ester–Ester Mixtures

When in methanol, and when blended the three ester/ester systems (APC-C/PPC, APC-A/PPC and APC-A/APC-C) all basically exhibit the same demixion phenomenon. The APC-A/APC-C/methanol system will be described in detail. This system was chosen as both polymers are acetates of HPC. In APC-A, all the hydroxyl groups of HPC were acetylated whereas APC-C has acetoxypropyl and some hydroxypropyl substituents. Thus the degree of modification which the system would tolerate while remaining homogeneous could be investigated.

The APC-A/APC-C/methanol system visually appeared homogeneous. The textures in the system as methanol evaporates are shown in Figure 4. These were observed under the polarizing microscope. Initially, Figure 4a, anisotropic material is dispersed in an isotropic medium. The anisotropic material organizes to form circular droplets, Figure 4b.[4b] As methanol evaporates the isotropic regions become anisotropic. Two anisotropic phases with similar textures (Figure 4c) are observed when most of the methanol has evaporated.

Compared with the ester/HPC blends, the texture of the APC-A/APC-C system remained homogeneous and appeared monophasic upon heating. The formation of an isotropic phase at temperatures below Tñi was not observed. Furthermore, a single isotropic phase was present at temperatures exceeding Tñi. Despite repeated cycles of heating and cooling, phase segregation was not induced.

The change in the intensity of light transmitted through the crossed polarizers as a function of temperature when the APC-A/APC-C film was heated into the isotropic phase is shown in Figure 5. The decrease in the light intensity as the anisotropic phase becomes isotropic is a continuous curve and occurs within one temperature span. The melting behavior of the APC-A/APC-C film is consistent with the suggestion that the system remains homogeneous and monophasic. An isotropic phase was not evident below the Tñi of 180 ± 2°C. The Tñi of APC-A and APC-C are 182 and 175°C respectively.

Similarly two anisotropic phases co-exist in the APC-A/PPC and APC-C/PPC methanol systems. Blends or films appeared to remain homogeneous and monophasic when heated. The formation of an isotropic phase below Tñi was not observed.

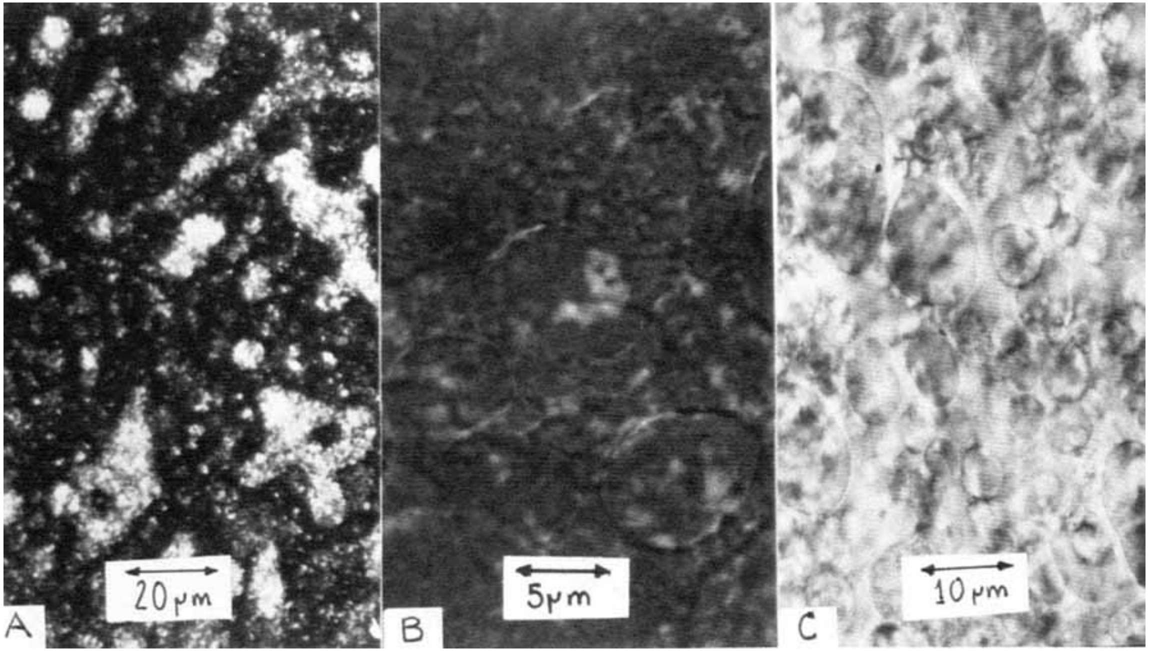

FIGURE 4 The texture (observed with a polarizing microscope) of a 1:1 APC/APC-C methanol mixture as the methanol evaporates, at ambient temperatures.
A 6 hrs—biphasic (isotropic/anisotropic)
B day 1—biphasic (anisotropic/anisotropic)
C day 7—biphasic (anisotropic/anisotropic with the polarizer removed)

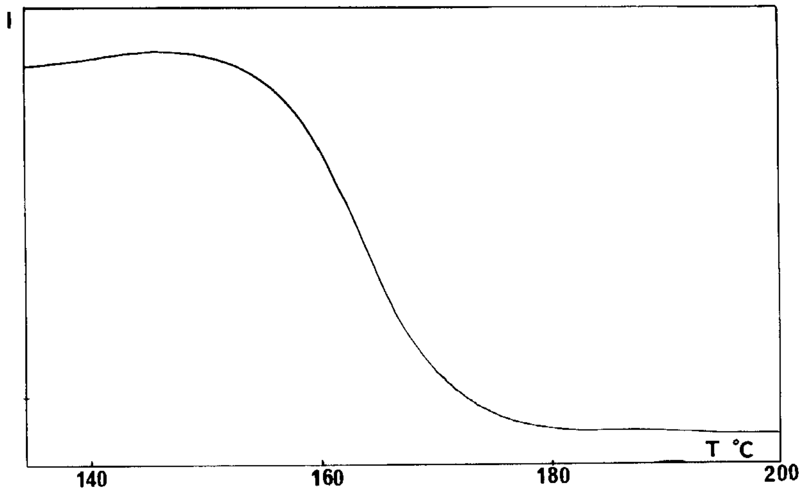

FIGURE 5 The variation in the intensity of light transmitted through the crossed polarizers of a microscope with temperature when a 1:1 APC-A/APC-C blend is heated above Tñi.

In the ester/ester/methanol systems, a segregation of two phases, an isotropic and anisotropic or two anisotropic ones (depending on the concentration), apparently occurs. However, demixion is not evident when methanol is evaporated. Either the demixion occurred on such a localized scale that the blend only appeared uniform or the polymers are miscible. If the two ester polymers are miscible the demixion observed in the presence of methanol is attributed to the greater affinity of one of the polymers for the methanol. The polymer with the lesser affinity for methanol would migrate towards each other and exclude the solvent. When the methanol evaporates the two ester polymers co-exist in the same localized region. The fact that the Tñi of the ester blends is an average of the Tñi of the pure polymers suggests miscibility.

CONCLUSIONS

Polarizing microscopy is a useful technique to investigate the phase demixionof substituted cellulosic polymers (exhibiting liquid crystalline properties) in methanol or as films. In methanol, all the binary polymer mixtures (ester/ether and ester/ester) exhibit demixion. The segregation of the polymers in ester/ester mixtures is attributed to the greater affinity of the polymer with the most hydroxyl groups for methanol. Despite decreasing the molar mass of immiscible polymers, demixion still occurs.

Only the blends or films involving polymers with dissimilar chemical structure (ethers and esters) exhibit segregation after several heatings into the isotropic phase. At ambient temperatures, the texture of the film indicates that two anisotropic phases are present. Upon heating one anisotropic phase "melted" leaving an isotropic/anisotropic biphasic system. Above Tfli, two separate isotropic phases are present. When two esterified polymers (even when one was only 2/3 esterified) are blended, segregation into enriched polymer regions is not observed. The dissimilarity of the polymers is not significant enough to induce segregation of the polymers.

This preliminary investigation involving the miscibility of liquid crystalline cellulosic polymers suggests further investigations. The kinetics and mechanism in which the demixion occurs merits attention. The extent to which a polymer poor in abundance is excluded from regions rich in the other polymer is of interest. The apparent immiscibility of HPC with an esterified HPC polymer suggests that partially or incompletely esterified HPC polymers which possess both ester and hydroxyl end-groups may exhibit interesting properties, notably the optical properties associated with the cholesteric phase formed by these polymers.[8]

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