Mesophase formation of hydroxypropyl cellulose as affected by miscibility with a flexible polymer

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The concentration for mesophase formation of hydroxypropyl cellulose (HPC) in water or acetic acid was affected by the addition of a flexible polymer such as poly(*N*,*N*-dimethyl acrylamide) (PDMA) and poly(vinylpyridine), which were proton acceptors with preferential affinity for the solvent. The critical concentration decreased when the amount of flexible counterpart increased. HPC and PDMA produced a two-phase blend by solvent casting but a single-phase blend was obtained by *in situ* polymerization. Solution blending of HPC with poly(acrylic acid) resulted in precipitation. The precipitates and the films cast from supernatant solutions each showed a single glass transition. The *in situ* polymerization of acrylic acid with HPC also resulted in a single-T_g material.

(Keywords: liquid crystalline structure; hydroxypropyl cellulose; polymer blends)

INTRODUCTION

Occurrence of a cholesteric liquid-crystalline phase in concentrated aqueous solutions of hydroxypropyl cellulose (HPC) was first reported by Werbowyj and Gray in 1976[1] and interest in this system has continued to grow since then[2–23]. The mesophase formation occurred at a volume fraction of polymer (v^{**}) higher than that predicted by the Flory theory[24] and v^{**} is often highly solvent-dependent[3]. These effects might be attributed to solvent interaction strongly affecting polymer chain flexibility or side-group interactions. Aharoni[25] also found that, for solutions of cellulose acetate, v^{**} is dependent on solvent acidity and varies linearly with the pK values of the solvents.

In the literature of HPC studies, systems of increasing complexity have been investigated: pure thermotropic HPC[8,15,18,26–28], HPC in a simple solvent[1–17] or in mixtures of solvents[16,20], and HPC blended with a second polymer with[29] or without[19,30] a solvent. In this study, we investigated the properties of several mixtures of HPC and a flexible polymer. The miscibility of HPC with the flexible polymers were studied both in the isotropic and anisotropic states. As a prelude to the study of these blends in the solid state, the phase behaviour of HPC solutions in the presence of a flexible polymer was also examined.

Our primary aim is to find a coil-like polymer that will form a miscible blend with HPC through hydrogen-bonding interactions. The miscibility of HPC with its flexible counterparts such as poly(acrylic acid), poly(vinylpyrrolidone) or poly(*N*,*N*-dimethyl acrylamide) was studied by using solvent-cast blend films. However, solvents are known to cause, in some cases, heterogeneity in miscible polymer systems during solvent evaporation[31,32]. In order to overcome phase separation via this $\Delta\chi$ effect, the miscibility of complexes and semi-IPNs (interpenetrating networks) prepared by *in situ* polymerization of an antecedent monomer containing dissolved HPC, either in the liquid-crystalline state or the isotropic state, was also conducted. Secondarily, with the evidence of specific interactions between the HPC and its flexible counterparts, it was of interest to replace a portion of an isotropic solvent with a non-mesomorphic polymer, such as poly(*N*,*N*-dimethyl acrylamide) and poly(vinylpyridine) in the HPC solutions, so that the morphology and the phase behaviour of a mixture might be altered by the interplay of interactions among the HPC polymer, the solvent molecules and the non-mesomorphic polymers.

EXPERIMENTAL

Materials

Monomers and polymers. Hydroxypropyl cellulose (HPC) was obtained from Aldrich, with a nominal M_w value of 100 000 and a degree of substitution $DS = 3$ (i.e. the average number of oxygens of the original cellulose repeat unit bearing a substituent); vinylpyrrolidone (VPo) and poly(vinylpyrrolidone) (PVPo) were likewise obtained from Aldrich, with a reported M_w of 360 000 for PVPo. *N*,*N*-Dimethyl acrylamide (DMA) and acrylic acid (AA) were purchased from Aldrich and distilled under vacuum. The purified monomers were polymerized in 1,4-dioxane solutions (20% by weight) at 70°C for 3 h, using azobisisobutyronitrile (AIBN) as initiator. Poly(*N*,*N*-dimethyl acrylamide) (PDMA) and poly(acrylic acid) (PAA) were purified by filtration of solutions, which were dialysed against a large amount of water for 7 days prior to freeze-drying. Poly(4-vinylpyridine) (PVPy) was a gift from Dr Y. Okamoto's group at Polytechnic University and was used without further purification. The molecular weights of these polymers were measured either by intrinsic viscosity or by gel permeation chromatography (g.p.c.) using a Waters model 590,

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Table 1 Molecular weight determined by g.p.c. or viscometry

Polymer	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	$[\eta]$ (dl g^{-1})	M_v ($\times 10^{-4}$)[33]
HPC	9.77	15.6		
PDMA			0.61	16[a]
PVPy			0.17	1.3[b]
PAA			1.42	350[c]
PVPo			1.38	104[d]

Mark–Houwink constants used:
[a]At 25°C in methanol, $K = 17.5 \times 10^{-3}$ ml g^{-1}, $a = 0.68$[34]
[b]At 25°C in ethanol, $K = 25 \times 10^{-3}$ ml g^{-1}, $a = 0.68$[35]
[c]At 30°C in 1,4-dioxane, $K = 76 \times 10^{-3}$ ml g^{-1}, $a = 0.5$[36]
[d]At 25°C in chloroform, $K = 19.4 \times 10^{-3}$ ml g^{-1}, $a = 0.64$[37]

which contains three μ-Styragel columns with the pore sizes of 500, 10^3 and 10^4 Å. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml min^{-1}. The column setting was calibrated by using ten monodisperse polystyrene (PS) standards. The molecular-weight data are given in *Table 1*.

Reagents. All reagents were purchased from Aldrich Chemical Co. without further purification: *N,N*-dimethyl formamide (DMF), dimethylsulphone (DMSO), trifluoroacetic acid (TFA) and acetic acid (HAc).

Preparation of HPC solutions containing a flexible polymer

Distilled water and reagent-grade acetic acid were used to prepare specimens. The concentration of HPC required to form the ordered phase was found by preparing a series of solutions of known compositions in a parallel-sided glass tube (0.6 × 6 mm, Vitrodynamics Inc.) and by centrifugation after maturing a thin layer in the glass tube to remove bubbles. A period of several weeks was required between sample preparation and examination to obtain a uniform specimen and to generate a characteristic mesophase of HPC.

Preparation of blend films

Films of polymer blends were prepared by dissolving the component polymers in water (2 wt%). After most of the solvent had evaporated at room temperature, the blend films were dried in a vacuum oven at 95°C for 7 days. In the case of HPC/PAA solution blending, precipitation occurred. The supernatant and precipitated portions were separated by centrifugation. Each part was collected and dried under vacuum at 95°C or room temperature for 7 days. The dried films were ground into small pieces for calorimetric measurements.

Blend films were also prepared by another method. After dissolution of HPC in acrylic acid, vinylpyrrolidone or *N,N*-dimethyl acrylamide (about 3 weeks), benzoin methyl ether. 0.5 wt% with respect to the monomers, was added to the solution. The solution was cast onto a Teflon plate and covered with a thin polyethylene film which served to minimize the evaporation of monomers and to reduce the inhibitory effect of oxygen during photopolymerization. For microscopy studies, the solution was cast onto glass slides with thin covers. The cast solution was exposed to a long-wavelength u.v. lamp, Black-Ray model B-100A, for 10 min during which the monomer polymerized to high conversions. The films were dried under vacuum at 80°C for 7 days and then at 95°C for 2 days to remove any unreacted monomer that might be present. In another experiment, a set of HPC/PAA films were prepared by polymerizing for intervals of 1, 2, 4, 6 and 10 min. These films were not dried and the solubilities were tested. The semi-IPN was prepared by the same method except that diethylene glycol diacrylate (DEGDA) or 1,1,1-trimethylolpropane triacrylate (TMPTA), obtained from Polyscience Inc., was added as the crosslinking agent. The PDMA content of the complexes and semi-IPNs of HPC/PDMA was determined by elemental analysis of nitrogen.

Solubility and extraction experiments

Solubility test was carried out by putting 10 mg of each sample into 10 ml of water, 0.1 M NaOH, DMF, DMSO and TFA. The photopolymerized blends after drying were also immersed in water and DMF at concentrations of 100 mg per 20 ml solvent for 7 days. The hazy solutions were centrifuged and separated into clear supernatant liquids and white solids. Proper material balance was obtained in each experiment after separately drying each phase at 95°C for 7 days under vacuum.

Optical microscopy

A cross-polarized light microscope (Nikon Optiphot) equipped with a hot stage (Mettler FP82) was used to determine mesophase transition temperatures. The maximum experimental temperature excursions were limited by the boiling points of the solvents. The heating rate was 1°C min^{-1} and the transmitted light intensity was recorded to detect phase transitions.

Determination of glass transition temperatures

The glass transition temperatures of the complexes and semi-IPNs were determined by the use of Perkin–Elmer differential scanning calorimeter (DSC-7) controlled by a 7500 serial computer. The midpoint of the abrupt heat-capacity jump during the second run was taken as T_g and reported in this paper.

RESULTS AND DISCUSSION

Physical properties of hydroxypropyl cellulose

Hydroxypropyl cellulose is both a lyotropic and a thermotropic liquid-crystalline polymer. The majority of the studies reported in the literature are concerned with its lyotropic behaviours[1–24], and only a few[8,26–28] described its thermotropic properties. In the course of determining the glass transition temperature of HPC, it came upon us that the thermogram was sensitive to moisture absorption by the specimen. The standard procedure adopted in our T_g determination for a fresh sample consisted of heating the specimen in the d.s.c. cell to 210°C followed by quenching. The thermogram of the second scan was reproducible and was used to identify T_g. A typical set of curves is shown in *Figure 1*. Curve C represents the cooling curve after the first scan while curve A is the second scan. In the latter curve, a broad and weak transition occurs between 0 and 50°C, which is to be identified as the glass transition. When the specimen was exposed to moisture (80% r.h., 15°C) for 12 h, the increase in specific heat in the first scan became prominent and the T_g value increased from about 25°C in curve A to about 115°C in curve B. The intensities of the X-ray diffraction peaks at 2θ of 8.5° and 20° also

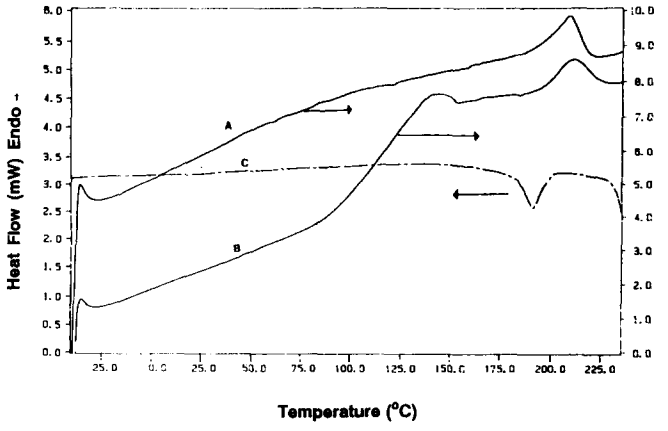

Figure 1 D.s.c. thermograms of HPC: (A) second scan of a fresh sample; (B) run after moisture exposure; and (C) cooling scan after the first heating run

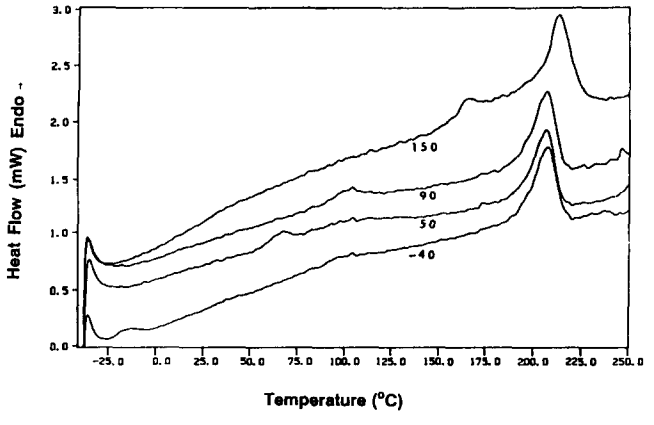

Figure 2 The effect of thermal treatments on HPC transitions. The annealing temperature is indicated on each curve for 1 h

increased after moisture exposure. It appears that moisture enables HPC molecules to align in a more ordered manner both in the amorphous and the crystalline regions. Solvent-induced crystallization of polymers is, of course, a well known phenomenon[38–40], but we are unaware of any published report on the glass transition temperatures of polymers after solvent-induced crystallization.

Common to curves A and B is the transition to the isotropic state occurring between 180 and 220°C. The temperature range of the transition agrees with that reported by Suto *et al.*[28]. According to these authors, this endotherm encompasses two events, which are distinguishable after cooling, and such a material is called monotropic liquid crystal. However, our material did not show resolvable endotherms, perhaps due to the high molecular weight of the specimen.

The thermal response of HPC is also sensitive to the thermal history of the material. In *Figure 2*, representative thermograms are shown for specimens that have undergone thermal treatments at different temperatures. In each case, the identification of T_g becomes uncertain but an endothermic event occurs near the annealing temperature. The observation is similar to that found in segmented polyurethanes[38]. In the latter polymers, the organization of the hard-segment domain is strongly influenced by the annealing temperature; the thermogram for the annealed sample shows an endotherm representing the 'disordering' of the hard-segment domain and the inception of each endotherm corresponds closely to the annealing temperature. Although there is no evidence of domain formation in the HPC films studied, the explanation used for polyurethanes can nevertheless be adapted to interpret our results. It is postulated that the packing of anhydroglucose units and hydroxypropyl groups, the latter being able to form inter- and intramolecular hydrogen bonds, is temperature-dependent. Thermal treatment of a fresh sample permits the reorientation of segments to arrive at a more preferred state of chain packing. Annealing at successively higher temperatures results in higher degrees of perfection of packing, which are unattainable at lower temperatures. The reduced chain mobility attendant with improved chain packing then manifests itself in the endothermic event occurring at the respective annealing temperature. In this sense, the observed endotherms bear comparison with the 'disordering' phenomena in segmented polyurethanes. In view of these complications, we used quenched samples that did not show such endothermic peaks in order to facilitate the interpretation of experimental results.

Effect of a flexible polymer on the mesophase of HPC in a solvent

The mesomorphic character of a mixture can be observed in several ways, the simplest being cross-polarized light microscopy. If the solution is anisotropic, a characteristic texture appears. In our experiments, the cloud points of aqueous solutions at low concentrations were determined to be about 45°C, in agreement with literature values. The results in 5.16 wt% PDMA/H_2O solutions are analogous to those observed for pure aqueous solutions of HPC. Whether the solutions were initially isotropic or anisotropic at room temperature, all turned turbid upon heating. The cloud points had the same value of 50°C up to a HPC concentration of 50%. For the 60% solution, the cloud temperature increased to 60°C. The critical concentration necessary for the observation of birefringence under crossed polarizers was between 27.7 and 32.7 wt%. A different phase diagram of aqueous HPC was illustrated by Fortin and Charlet[41], who used carefully fractionated HPC samples. In their studies, isotropic solutions give almost identical turbidity curves, characterized by an abrupt increase of turbidity at a well defined onset temperature between 40 and 45°C. In contrast, cholesteric liquid crystals show a variation of turbidity with temperature that depends on the polymer weight fraction. Systems that are already biphasic at room temperature exhibit a fair amount of turbidity and seemingly experience two turbidimetric transitions upon heating. In the solutions used in this study, the turbidity of HPC in PDMA/H_2O solutions increased abruptly between 35 and 40°C (onset), similar to the isotropic aqueous solutions found by Fortin *et al.* A biphasic region was not observed. The discrepancy probably originates from the high-molecular-weight, unfractionated HPC used in this study. No characteristic texture appeared except iridescence in all specimens at room temperature (*Figure 3*).

The phase transition temperatures of mixtures of HPC in PDMA/HAc solutions are represented in *Figure 4*. The critical concentrations are between 24.4 and 28.2% for 4.25 wt% PDMA/HAc solutions and between 19.4 and 22.4% for 9.34 wt% PDMA/HAc solutions, respectively. Both ranges are smaller than the value of HPC in pure HAc, which is 30.8%. At the same HPC content

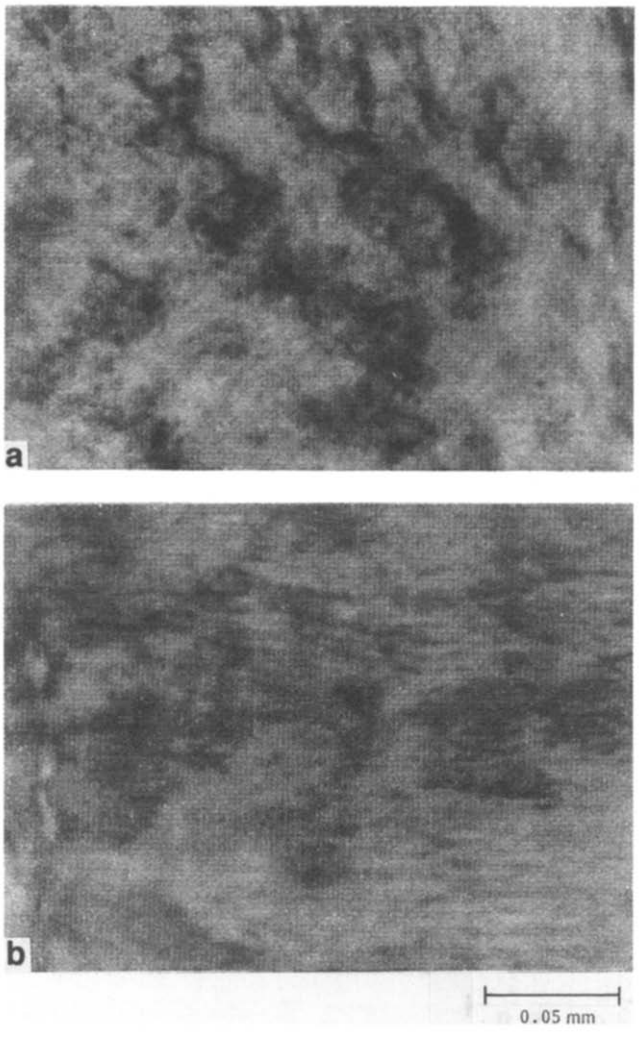

Figure 3 Polarized-light micrographs of birefringent polymer solutions of HPC in 5.16 wt% PDMA/H_2O: (a) 39.9%, (b) 61.4% by weight

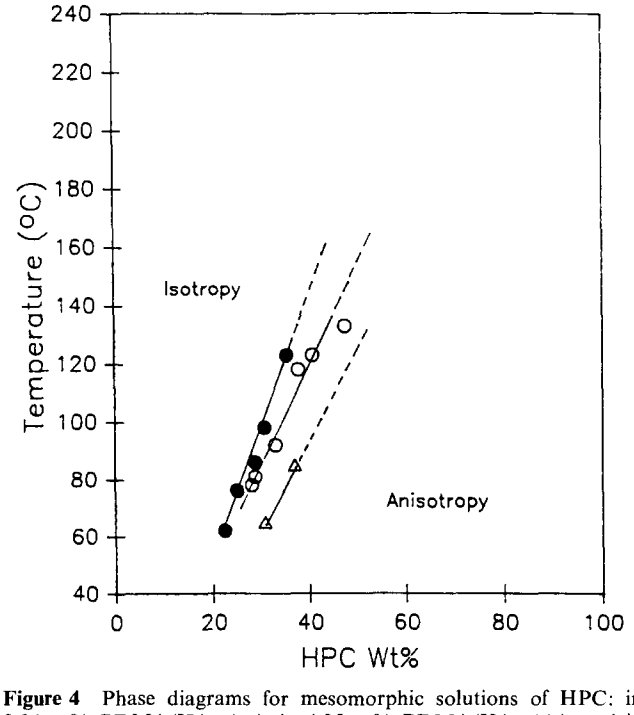

Figure 4 Phase diagrams for mesomorphic solutions of HPC: in 9.34 wt% PDMA/HAc (●); in 4.25 wt% PDMA/HAc (○); and in pure HAc (△)

in the solutions, the phase transition temperature increased when the concentration of PDMA increased. Coincident results were found by Seurin *et al.*[29] in HPC/poly(acrylonitrile)/TFA systems. The authors concluded that the flexible polymer with preferential affinity for the solvent segregated the enclosures of concentrated semi-rigid polymers. Therefore, the transition temperature became higher. The interpretation by Seurin is applicable to HPC/PDMA/HAc solutions since PDMA is an effective proton acceptor. Furthermore, the pitch distances in HPC/PDMA/HAc mixtures decreased with increasing concentrations of PDMA (*Figures 5* and *6*). Analogous phase diagrams shown in *Figure 7* were obtained for HPC in PVPy/HAc solutions. The phase transition temperatures were even higher in these solutions. Two possible explanations could be considered.

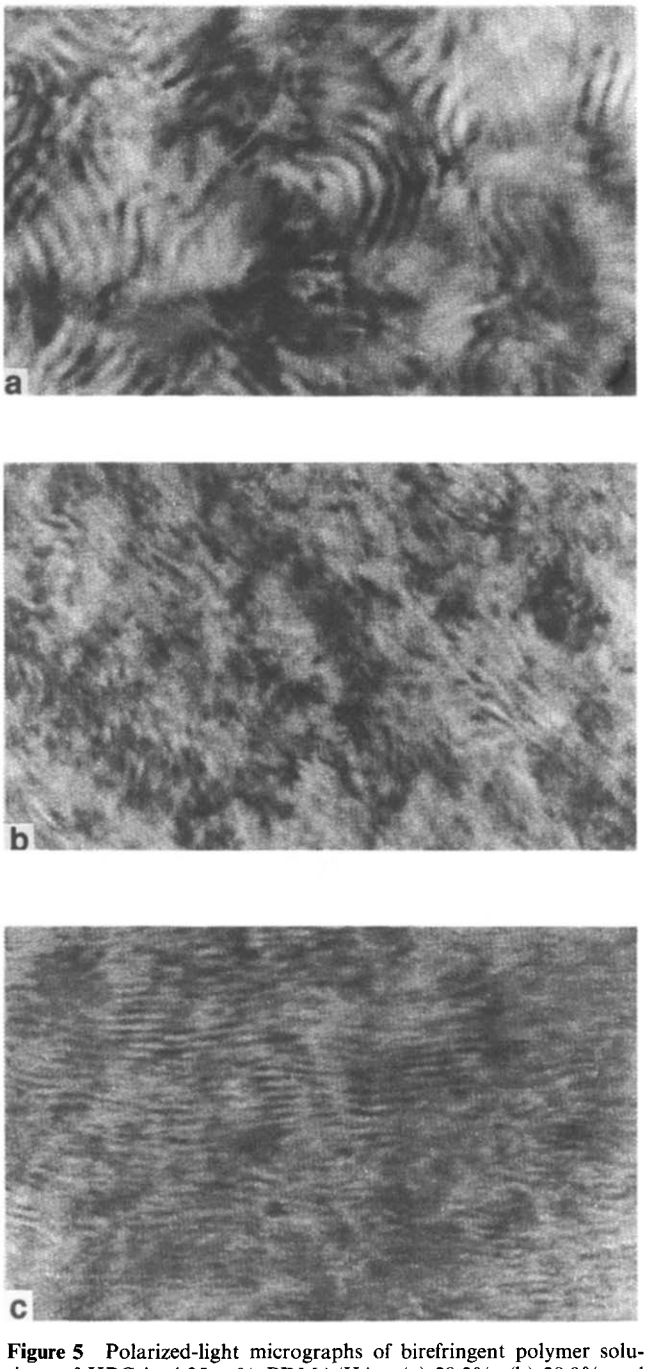

Figure 5 Polarized-light micrographs of birefringent polymer solutions of HPC in 4.25 wt% PDMA/HAc: (a) 28.2%, (b) 28.9% and (c) 40.8% by weight

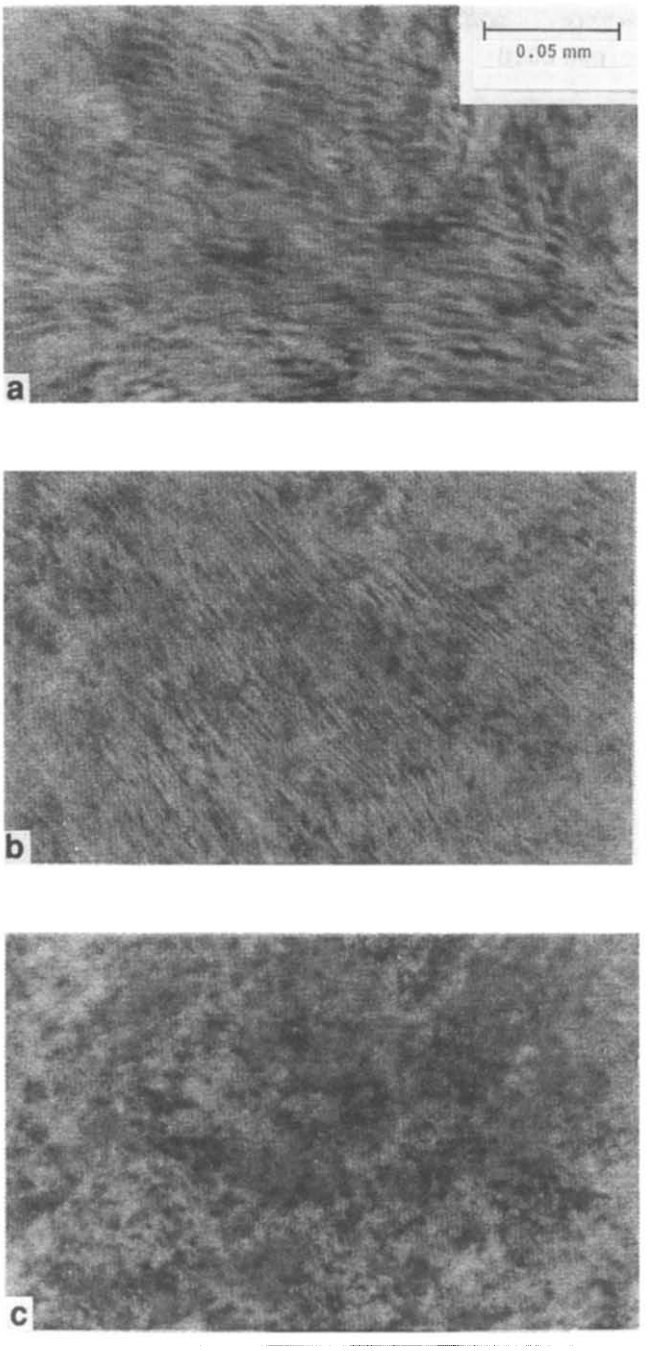

Figure 6 Polarized-light micrographs of birefringent polymer solutions of HPC in 9.34 wt% PDMA/HAc: (a) 32.0%, (b) 35.5% and (c) 42.6% by weight

First, since pyridine is a stronger base than dimethyl acetamide, hydrogen-bonding interactions between HAc and PVPy are stronger than between HAc and PDMA, so that PVPy segregates the enclosure of HAc to HPC more severely. The second interpretation is that PVPy molecules cause the cholesteric mesophase to tend more likely to nematic formation. The morphological features in the series of HPC/PVPy/HAc mixtures are elucidated in *Figure 8*, where the retardation lines become ill defined.

Morphology of HPC in solutions of N,N-dimethyl acrylamide and acrylic acid

As will be described later, we have explored the method of photopolymerizing a solution of HPC in a monomer as a route to obtain single-phase blends. Therefore we have carried out preliminary experiments to study the morphology of HPC dissolved in *N,N*-dimethyl acrylamide and in acrylic acid. Acrylic acid is of particular interest because its acidity is comparable to that of acetic acid in which the mesophase formation of HPC has been documented[3,6].

After a 50% HPC solution in DMA was allowed to stand for a month, a four-brushed pattern developed, which was characteristic of nematic liquid crystals (*Figure 9A*). However, alternately dark and bright retardation lines were seen in the solution of 40% HPC in acrylic acid (*Figure 9B*). The fingerprint patterns are connected to the pitch distance in cholesteric liquid crystals. We believe that the different morphologies observed here are caused by the different degrees of hydrogen-bonding interaction between HPC and the two monomers.

Aharoni[25] has found that the critical concentration for mesophase formation in cellulose acetate is dependent on solvent acidity and varies linearly with the pK values of the solvents. In our study, the critical concentrations in acrylic acid, water and *N,N*-dimethyl acrylamide are 32.5, 40 and 50%, respectively. The increase in critical concentration goes hand in hand with decreasing power of the three solvents to break hydrogen bonds in HPC, thereby influencing the transformation from the crystalline states to the liquid-crystalline states. The high concentration of HPC required for mesophase formation in DMA monomer restricts chain mobility due to the high viscosity of the medium. It is possible that, in the duration of our experiments, the solution has not had sufficient time to achieve its equilibrium cholesteric structure.

In a separate experiment, birefringence appeared when some of the acrylic acid monomer evaporated from a 27.5% HPC solution which was initially isotropic. After the amount of monomer loss was determined, the critical concentration was calculated to be 30.1%, in agreement

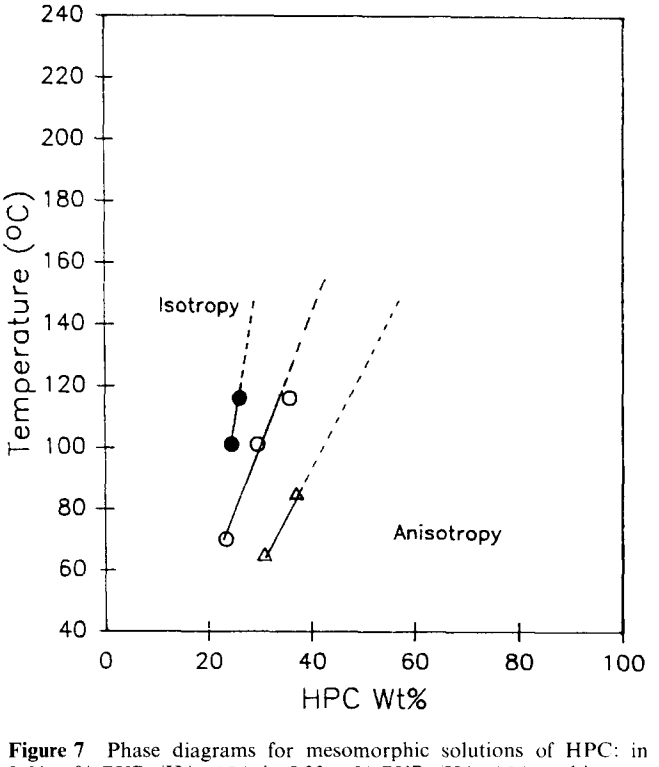

Figure 7 Phase diagrams for mesomorphic solutions of HPC: in 9.66 wt% PVPy/HAc (●); in 5.33 wt% PVPy/HAc (○); and in pure HAc (△)

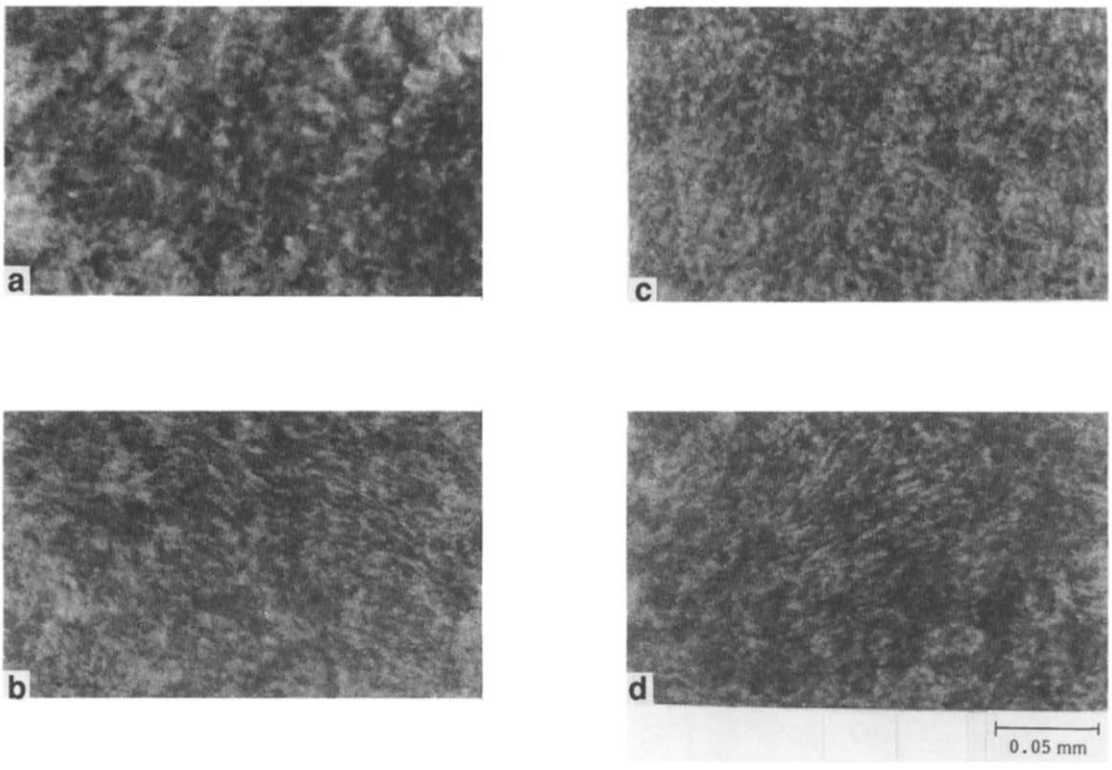

Figure 8 Polarized-light micrographs of birefringent polymer solutions of HPC in 5.33 wt% PVPy/HAc: (a) 23.4%, (b) 54.6%; in 9.66 wt% PVPy/HAc: (c) 26.2%, (d) 52.3% by weight

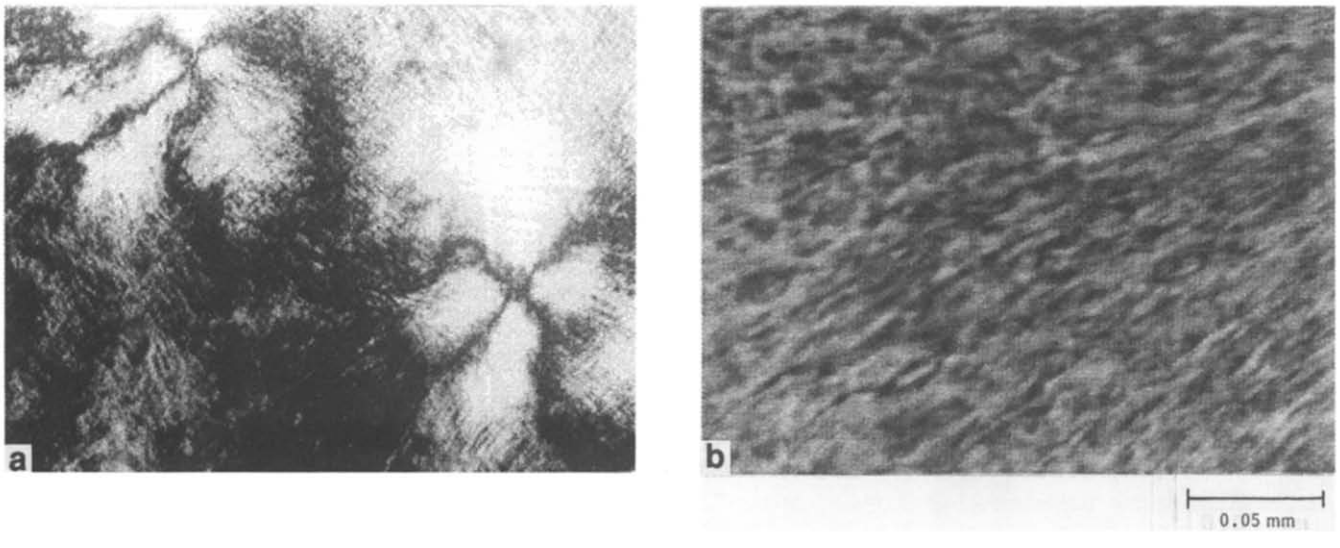

Figure 9 Polarized-light micrographs of birefringent polymer solutions of (a) 50 wt% HPC in DMA monomer and (b) 40 wt% HPC in AA monomer

with the range of 27.2–32.5% determined in parallel-sided glass tube experiments.

Miscibility of HPC with a flexible polymer in the solid state

In the second phase of this work we attempted to study the miscibility between HPC and a flexible polymer in the solid state. The d.s.c. thermograms of blend films of HPC and PDMA cast from water solutions showed for each film two glass transition temperatures intermediate between the T_g values of the component polymers, 25 and 124°C, respectively. According to the commonly used criterion of miscibility based on T_g measurements, the blends can be considered to be partially miscible. The lower T_g values (*Figure 10*) corresponding to HPC-rich phases changed only slightly as the HPC contents of the films increased. In contrast, the upper T_g values, corresponding to PDMA-rich phases, decreased steadily as HPC contents increased. The partial miscibility in the heterogeneous films, however, did not inhibit the crystallization of HPC. Characteristic X-ray diffraction peaks were seen in films containing 50% or higher weight percentage of HPC. In HPC/PVPo films cast from solutions, two-phase behaviours were also observed.

Since solution casting resulted in heterogeneous blends of HPC with PDMA or PVPo, an alternative method of preparation was attempted. The hydroxypropyl cellulose

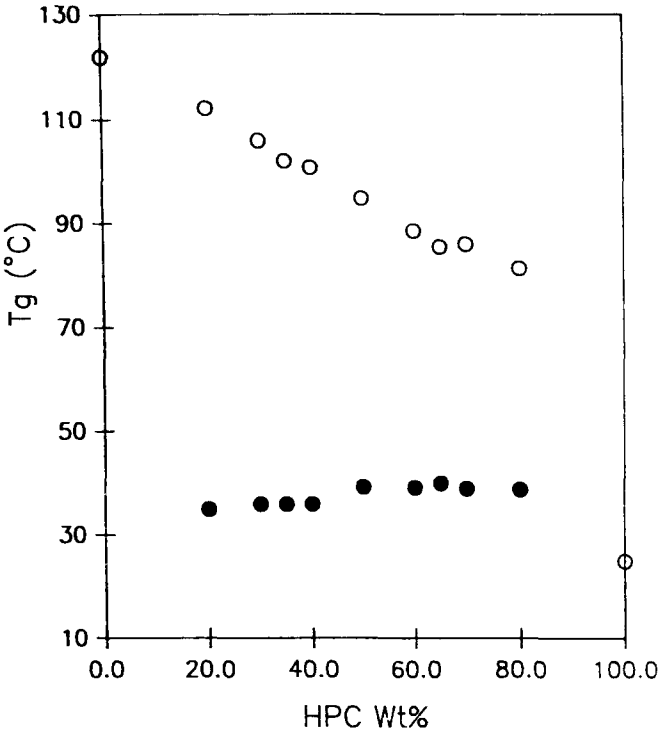

Figure 10 Plot of T_g *versus* HPC wt% for HPC/PDMA blend films cast from water

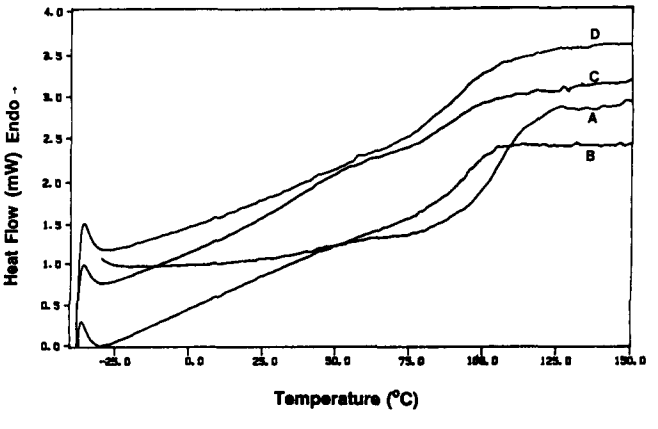

Figure 11 D.s.c. thermograms of HPC/VPo *in situ* polymerized films: (A) 30 wt% HPC; (B) 40 wt% HPC; (C) 40 wt% HPC + 4 wt% DEGDA; and (D) 40 wt% HPC + 4 wt% TMPTA

polymer was dissolved in DMA or VPo monomer and polymerization of the monomer was carried out via the use of a photoinitiator. PVPo still produced two-phase blends with HPC by the *in situ* polymerization method (*Figure 11*). However, each of the three complexes and two semi-IPNs prepared by *in situ* polymerization of DMA showed a single glass transition (*Figure 12*). The results are listed in *Table 2*. In each case, the PDMA content of the film was lower than that of the original solution, due to the inevitable loss of monomer through evaporation and incomplete conversion.

In a previous study of poly(acrylic acid)–poly(ethyl oxazoline) complexes prepared by *in situ* polymerization[42], the complexes were found to be insoluble in certain solvents that dissolved the component polymers. Strong intermolecular association between the two polymers was responsible for insolubilization. In the HPC/PDMA system, hydrogen-bonding interaction is weaker and solubility change is expected to be less pronounced. Indeed, we found that the three as-polymerized films (samples 1–3 in *Table 2*) contained large soluble fractions when extracted by water or DMF. The small amounts of insoluble materials can be attributed to inadvertently crosslinked chains through grafting or to a small number of HPC and PDMA chains that have established among them a large number of hydrogen bonds and therefore resist dissolution. The remainder of the HPC and PDMA chains probably do not have a sufficient number of hydrogen bonds to produce a cooperative effect to resist dissolution in water. When a strong proton acceptor, DMF, is used, its effective competition for hydrogen bonds results in nearly complete dissolution. The semi-IPNs had only small amounts of extractables, as expected, because the diffusion of HPC was restricted by network formation.

The glass transition temperatures of the as-polymerized HPC/PDMA films and the extracted materials are listed in *Table 3*. It is noteworthy that the two semi-IPNs (samples 4 and 5), after water or DMF extraction to remove the soluble fractions, had T_g values higher than those of the as-polymerized films by 10°C or more. Since the results for samples 1–3 do not indicate low T_g values for the soluble fractions, it appears that the process of network swelling and subsequent solvent removal permit the rearrangement of chains to arrive at an improved state of chain packing, leading to higher T_g values.

When aqueous solutions (2%) of HPC and poly(acrylic acid) were mixed, precipitation occurred. Mutual precipitation of acid–base polymer pairs is a common phenomenon where extensive interaction between the functional groups exists. In this regard, we note that precipitation occurred in HPC/PAA but not in HPC/PDMA. The composition of the supernatant solutions were determined by titration of PAA with a standard

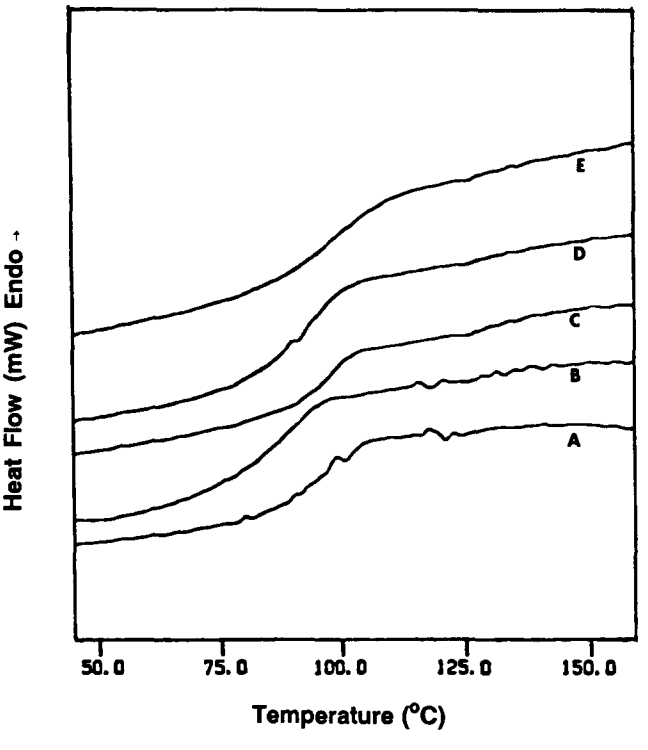

Figure 12 Calorimetric curves in the T_g region of HPC/DMA *in situ* polymerized films: (A) 30 wt% HPC; (B) 50 wt% HPC; (C) 40 wt% HPC; (D) 40 wt% HPC + 4 wt% DEGDA; and (E) 40 wt% HPC + 4 wt% TMPTA

Table 2 Compositions and solubilities of HPC/PDMA blends and semi-IPNs by *in situ* polymerization

	Sample No.				
	1	2	3	4	5
Feed					
DMA (wt%)	70	50	60	60	60
Crosslinking[a]				DEGDA	TMPTA
Agent (wt%)	0	0	0	4	4
Solution[b]	iso	bir	iso	iso	iso
Polymerized film after drying					
PDMA (wt%)	61.52	49.50	55.30	55.92	51.97
Wt% loss[c]	7.39	5.18	6.09	5.06	5.29
Film[b]	iso	bir	iso	iso	iso
Extraction in water					
PDMA (wt%)	63.50	49.15	55.86	54.17[e]	53.88[e]
Wt% diss.[d]	82.21	88.50	86.10	4.10	4.12
Solution	Clear	Clear	Clear	Hazy	Hazy
Solid	Particle	Particle	Particle	Pieces	Powder
Extraction in DMF					
PDMA (wt%)	62.37	49.71	55.79	57.42[e]	52.68[e]
Wt% diss.[d]	94.57	96.54	93.50	5.63	8.54
Solution	Clear	Clear	Clear	Clear	Clear
Solid				Small pieces	Powder

[a]The weight percentage is based on the total weight of mixture
[b]Determined by cross-polarized light microscopy: iso, isotropic; bir, birefringent
[c]The weight percentage is based on the weight before drying
[d]The weight percentage is based on the weight before extraction: diss, dissolution
[e]The weight percentage of PDMA in insoluble fraction

Table 3 T_g and width of T_g of *in situ* polymerized HPC/PDMA films after drying at 95°C

	Sample No.				
	1	2	3	4	5
Polymerized complexes after drying					
T_g (°C)	95	85	95	92	96
Width (°C)	10	14	7	13	12
After water extraction					
T_g (°C)	100[a]	88[a]	91[a]	101[b]	110[b]
Width (°C)	8	15	8	11	14
After DMF extraction					
T_g (°C)	97[a]	92[a]	94[a]	103[b]	107[b]
Width (°C)	8	9	8	5	10

[a]Soluble fraction
[b]Insoluble fraction

Table 4 Solution blending of HPC/PAA in water

	Composition in feed: PAA (wt%)			
	80	70	60	50
Precipitate[a]				
Composition	64.0	61.5	48.7	43.9
Wt% ppt	38.7	47.2	51.9	61.5
T_g (°C)	105	104	100	101
Width (°C)	10	11	11	11
Film cast from supernatant[a]				
Composition	90.1	77.6	72.2	59.7
T_g (°C)	125	126	119	110
Width (°C)	8	7	9	13

[a]Dried at 95°C for 7 days

alkali solution[43]. The compositions of the precipitates were then calculated by material balance. The results are given in *Table 4*. Representative photomicrographs of the wet and dried precipitates are shown in *Figure 13*. Since retardation lines can be seen in these micrographs, the precipitates are thought to contain substantial amounts of HPC to form mesophases. This is verified by the composition data in *Table 4*. It is significant and unexpected that HPC molecules, originally in a 2% water solution, can organize themselves into cholesteric structure during the process of mutual precipitation with poly(acrylic acid). Also of interest is the fact that each of the precipitates shows a single glass transition temperature in the range of 100 to 105°C. The T_g values are higher than expected when compared with the T_g of 106°C for PAA and 25°C for HPC. Films cast from the supernatant solutions also have high glass transition temperatures between 110 and 125°C. The high T_g values in both cases have precedents in many other hydrogen-bonded blends[42,44,45].

The solubilities of HPC/PAA precipitates dried at room temperature increase in the order water < DMF < DMSO < TFA < 0.1 N NaOH, as shown in *Table 5*. The results are readily understood by assuming that strong proton accepting solvents (DMSO and TFA) or alkali solution (NaOH) dissolved the precipitates. However, after being dried at 95°C for 7 days, the precipitates became insoluble and swelled only in the stronger solvating media like DMSO, TFA and 0.1 N NaOH. At first, it was thought that anhydride formation of PAA or esterification between hydroxyl groups of HPC and carboxyl groups of PAA had occurred during the process of drying[46]. The infra-red spectra in the regions of hydroxyl vibrations (4000–2500 cm^{-1}) and carbonyl

vibrations (1850–1550 cm^{-1}) were therefore examined. *Figure 14* shows the spectra for the 43.9% PAA precipitated film and the 59.7% PAA film cast from the supernatant solution. The broad band at 3400 cm^{-1} corresponding to hydroxyl stretching frequencies was intact, and no absorption at 1806 cm^{-1} due to the anhydride formation was seen. Since the broad hydroxyl stretching absorption is unsuitable for quantitative analysis, the results are inconclusive about the esterification reaction. Thus, the cause for insolubilization is unresolved and additional chemical and physical characterization is needed to clarify this phenomenon.

Each of the photopolymerized HPC/AA films showed a single glass transition (*Figure 15*), indicative of miscibility, as was found for the corresponding HPC/

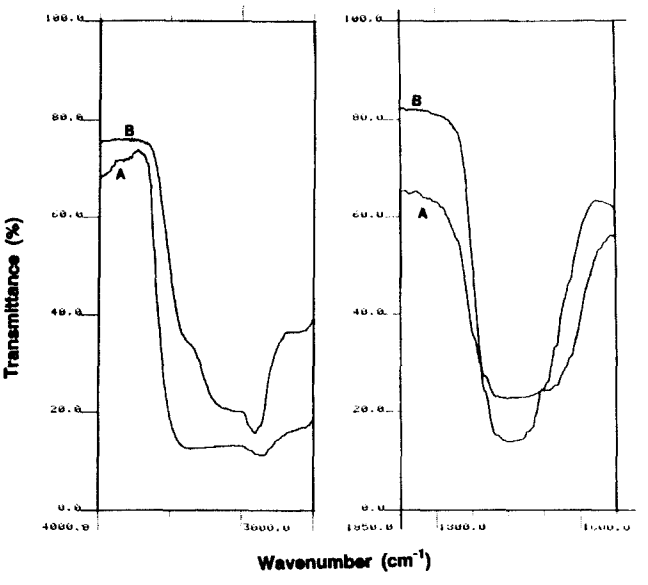

Figure 14 I.r. spectra in the regions of 4000–2500 cm^{-1} and 1850–1550 cm^{-1} of (A) a 43.9% PAA precipitated film and (B) a 59.7% PAA film cast from supernatant water solution with HPC

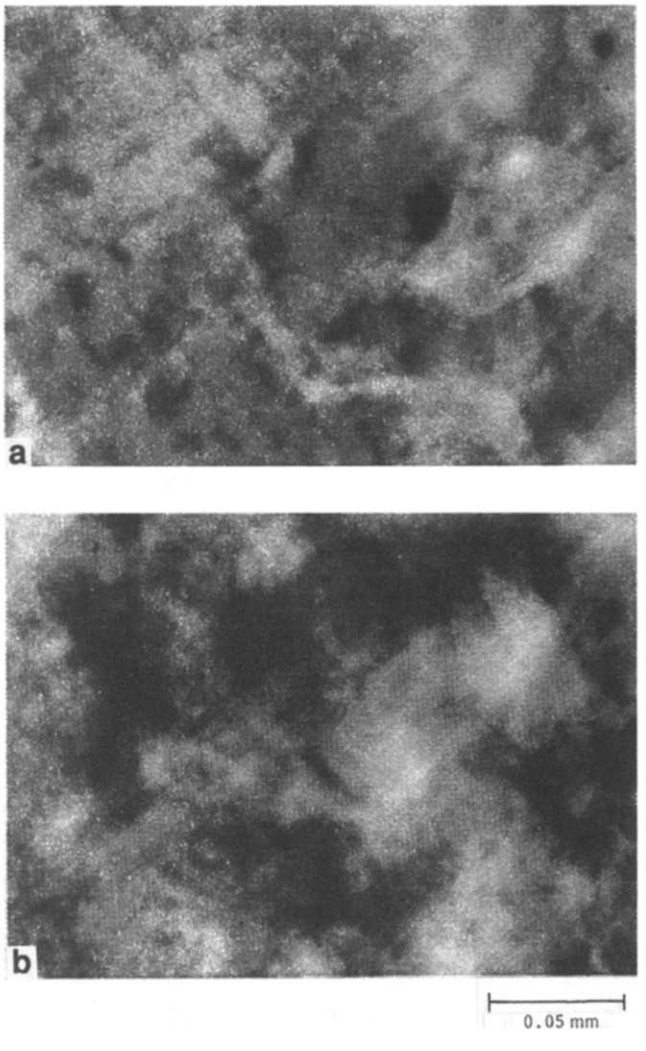

Figure 13 Polarized-light micrographs of an HPC/PAA precipitate from water containing 48.7 wt% PAA: (a) before drying; (b) after drying (~1.8 wt% loss) at 95°C

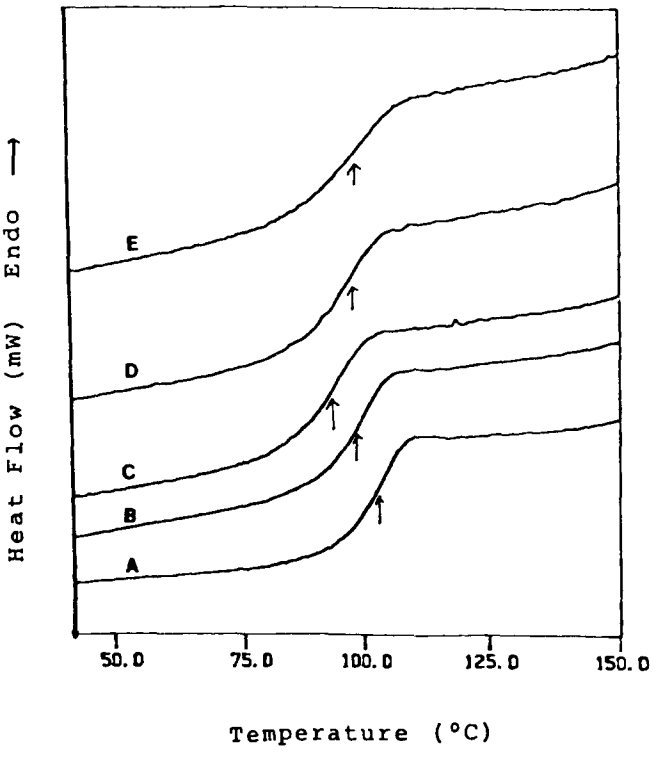

Figure 15 Calorimetric curves in the T_g region of HPC/AA *in situ* polymerized films: (A) 20 wt% HPC; (B) 27.5 wt% HPC; (C) 40 wt% HPC; (D) 40 wt% HPC + 3 wt% DEGDA; and (E) 40 wt% HPC + 3 wt% TMPTA

Table 5 Solubilities of HPC/PAA blends

Prepared method	H_2O	0.1 N NaOH	DMF	DMSO	TFA
HPC/PAA precipitates dried at 95°C	No visible change	Swollen	No visible change	Slightly swollen	Swollen
HPC/PAA precipitates dried at room temperature	No visible change	Dissolved	Swollen particles	Dissolved	Dissolved
HPC/PAA *in situ* polymerized films	No visible change	Swollen	Break into particles	Break into particles	Slightly swollen

Table 6 HPC/PAA blends and semi-IPNs by *in situ* polymerization

	Sample No.				
	1	2	3	4	5
Feed					
PAA (wt%)	80	72.5	60	60	60
Crosslinking[a] agent				DEGDA	TMPTA
(wt%)	0	0	0	3	3
Solution[b]	iso	iso	bir	bir	bir
Polymerized film after drying					
Wt% loss[c]	2.44	2.64	2.90	3.15	2.93
Film[b]	iso	bir	bir	bir	bir
T_g (°C)	102	98	93	95	97
Extraction by water					
Wt% diss.[d]	1.35	2.46	0.4	0.9	1.5
Solution	Clear	Clear	Clear	Clear	Clear
Solid	Hazy film	Hazy film	Hazy film	Clear film	Clear film
T_g (°C)	$2 \times T_g$	$2 \times T_g$	$2 \times T_g$	95	95
Extraction by DMF					
Wt% diss.[d]	6.83	3.10	3.04	1.65	1.07
Solution	Clear	Clear	Clear	Clear	Clear
Solid	Powder	Powder	Powder	Powder	Fleck
T_g (°C)	$2 \times T_g$	$2 \times T_g$	$2 \times T_g$	97	95

[a]The weight percentage is based on the total weight of mixture
[b]Determined by cross-polarized light microscopy: iso, isotropic; bir, birefringent
[c]The weight percentage is based on the weight before drying
[d]The weight percentage is based on the weight before extraction: diss, dissolution

DMA films. In striking contrast with the latter, however, are the insolubilities of the polymerized HPC/AA films. The water-soluble fractions amounted to only 0.4 to 2.4% (*Table 6*). The films broke into small particles in DMF and DMSO and swelled in TFA and 0.1 N NaOH. The solubility characteristics of these films are similar to those of the mutual precipitates that had been dried at 95°C.

In order to acquire a better understanding of the process leading to insolubilization, a set of 34.3% HPC in AA solutions was polymerized for different time periods: 1, 2, 4, 6 and 10 min. We found that after 1 min irradiation under a u.v. lamp, the HPC/PAA film was already insoluble in all solvents. Clearly in this case, insolubility was not caused by the drying process. The texture of the HPC mesophase was not changed by the matrix polymerization of the AA monomer. Another point of interest is the birefringence of the polymerized films when HPC content is 27.5% or higher. In this connection, HPC/hydroxyethyl methacrylate system has also been reported to have a cholesteric structure[30].

Since each of the photopolymerized HPC/AA films showed a single transition, but blending of aqueous solutions of HPC and PAA resulted in two phases, we conducted the following experiments to see whether the single-T_g state of the polymerized film would be altered by exposure to water. After swelling by water, samples 1–3 in *Table 6* exhibited two T_g-values for each specimen, as though the original glass transition had split into two, one occurring at a higher and the other at a lower temperature (*Figure 16*). Although water was unable to break the association between HPC and PAA to a sufficient extent to solubilize these films, it nevertheless induced the swollen film to separate into two phases. It was also possible that phase separation occurred during the drying process, as in the case of poly(vinyl chloride) blended with poly(ethyl acrylate)[31].

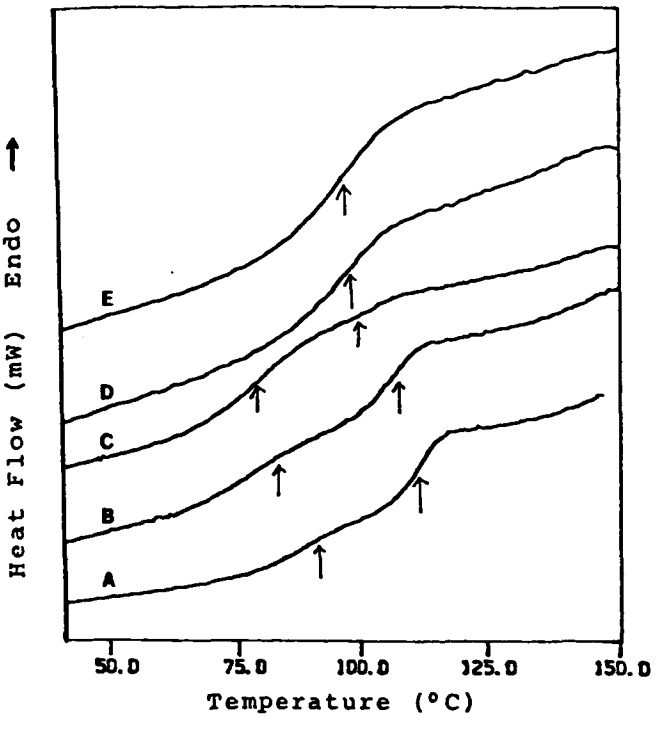

Figure 16 Calorimetric curves in the T_g region of HPC/AA *in situ* polymerized films after extraction by water: (A) 20 wt% HPC; (B) 27.5 wt% HPC; (C) 40 wt% HPC; (D) 40 wt% HPC + 3 wt% DEGDA; and (E) 40 wt% HPC + 3 wt% TMPTA

Dimethyl formamide likewise did not solubilize the polymerized HPC/AA films to a significant extent.

However, its stronger solvating power caused the properties of the swollen films to change in a different way. Two glass transition temperatures were found for each swollen film of samples 1–3; but in contrast with water-swollen films, both T_g values were lower than the original values. The lower values were not caused by residual DMF in the specimens, because the T_g values of the two semi-IPNs (samples 4 and 5) did not decrease. Rather, we believe that DMF disrupts the association between HPC and PAA to a greater degree than water and the disrupted interchain hydrogen bonds are not completely recovered during drying.

CONCLUSIONS

The critical concentration for mesophase formation of HPC in water or acetic acid was decreased by the presence of a flexible polymer such as poly(*N*,*N*-dimethyl acrylamide) and poly(vinylpyridine), both polymers being effective proton acceptors with preferential affinity for the solvent. Solution blending of HPC with PDMA or PVPo or PAA resulted in phase separated film in the former two cases and mutual precipitation in the latter. However, single-T_g blends were obtained by dissolving HPC in DMA or AA, followed by photopolymerization of the respective monomer. The *in situ* polymerization films of HPC/AA retained birefringence.

A major point of interest is the fingerprint pattern seen in the polymerized HPC/AA films (*Figure 9b*). While it is difficult to ascertain from the photomicrographs whether the pitch distance has changed during polymerization, there is no question that the cholesteric structure of HPC is preserved. Additional work is planned to characterize more fully the properties of these liquid-crystalline polymer blends.

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