

# Characterization and Free Radical Polymerization of Liquid Crystalline Acrylic Acid / Cellulose Diacetate and *N*-Vinyl-2-Pyrrolidinone / Cellulose Diacetate Solutions

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## Synopsis

Polymerizations of liquid crystalline solutions of cellulose diacetate (CDA) in acrylic acid (AA) and *N*-vinyl-2-pyrrolidinone (NVP) were conducted in an attempt to prepare molecular composites (polymer blends) possessing a rigid rod polymer with liquid crystalline orientation. CDA was found to form liquid crystalline solutions in both AA and NVP at concentrations above 40 wt% CDA. Polymerization of anisotropic 50 wt% CDA-AA and CDA-NVP solutions occurred with considerable retention of the starting solution anisotropy and yielded homogeneous blends (1  $T_g$ ) when the rate of polymerization was fast relative to the phase separation of the free radically polymerizing AA or NVP with CDA. Slow polymerizations lead to phase separated blends (2  $T_g$ ).

## INTRODUCTION

In the first paper in this series, it was shown that small-scale preparation of molecular composites via polymerization of liquid crystalline solutions of poly(hexyl isocyanate) (PHIC)-styrene occurred with retention of the cross polarized light texture of the starting solution.<sup>1</sup> Larger scale polymerizations occurred with obvious phase separation. The features controlling the morphology of the final interpenetrating network appeared to be the solution viscosity, polymerization time, temperature, and the compatibility of the polymerizing polymer chains (styrene) with the dissolved polymer (PHIC). Flory has shown that ternary solutions of rigid rod and random coil polymers will phase separate when the concentration of the random coil polymer increases above a negligible amount.<sup>2</sup> Consequently, to "lock in" the orientation of a rigid rod polymer by in situ polymerization of a monomer solvent, it is necessary for the polymerization to occur at a significantly faster rate than phase separation of the inherently incompatible polymers. On anything but a very small scale, phase separation of PHIC and PS proceeded quickly relative to styrene polymerization owing to the low initial solution viscosities, high polymerization temperature, and long polymerization times required.

In an attempt to overcome these difficulties and prepare larger scale, oriented molecular composites composed of a liquid crystalline and a random coil polymer, our studies turned to cellulose polymers. It has been shown that a broad range of cellulose derivatives spontaneously form lyotropic liquid crystalline solutions when dissolved in a solvent at a concentration above

some critical concentration  $c$ .<sup>3-5</sup> Additionally, some cellulose derivatives are known to exhibit thermotropic mesophases.<sup>6,7</sup> Cellulose diacetate (CDA) is soluble in a variety of common solvents and produces anisotropic solutions with relatively high viscosities and therefore is an ideal candidate to utilize as the liquid crystalline polymer in the desired molecular composites. A similar study employing hydroxypropyl cellulose and hydroxyethyl methacrylate was recently published.<sup>8</sup>

The solubility of various molecular weight cellulose diacetate polymers was determined in a number of commercially available monomers and the potential for formation of liquid crystalline solutions examined. Polymerization of CDA in both *N*-vinyl pyrrolidinone (NVP) and acrylic acid (AA) is described along with the  $T_g$  of the respective molecular composites and the final composite morphologies. Both microscope-scale polymerizations and larger scale polymerizations were attempted.

### EXPERIMENTAL

The following cellulose samples were used as received from Eastman: CDA MW 30,300, DP = 115, DS = 2.45; and CDA MW 56,000, DP = 213, DS = 2.41. Monomer solvents were reagent grade and used without further purification.

Initial solubility studies were performed by mixing 200 mg CDA with 2 mL monomer solvent and allowing them to mature for 1 month. The good solvents identified from this study were then used to prepare solutions ranging in concentration from 15 to 50 wt% by mixing the appropriate weight of solvent and CDA in a vial. These mixtures were allowed to mature for 2 months and then observed at 100 $\times$  magnification with an optical microscope.

The optical microscope utilized was a Leitz polarizing microscope equipped with a Mettler hot stage accurate to  $\pm 0.2^\circ\text{C}$ . The sample solutions were prepared for observation by placing a drop of solution on a glass slide, pressing the drop to a thin film under a coverslip, and sealing the edges with 5-min epoxy. Samples were allowed to relax for 1 h before observation.

Heating studies were performed on the samples by heating the solutions rapidly to the desired temperature and allowing the samples to relax 20 min before observation. The samples were typically observed at room temperature, 30, 40, 50, 60, and 70 $^\circ\text{C}$ .

Solutions for polymerization were prepared in glass vials by weighing the desired amount of CDA, monomer, and initiator into a vial and mechanically mixing with a spatula for several minutes. The mixtures were allowed to sit overnight, mixed thoroughly in a Brabender at low speeds for 30 min, allowed to sit for 7 days more, and then centrifuged for 1 h at 12,000 rpm to eliminate air bubbles. The resulting homogeneous, transparent solutions were then stored in the dark until utilized.

Microscope slide polymerizations were performed by placing a drop of CDA-monomer solution on a glass microscope slide and depressing the solution to a thin film with a quartz coverslip. The coverslip edges were sealed with silicon grease and the slide placed in a Rayonet ultraviolet (UV) chamber equipped with high-intensity, narrow-spectrum mercury arc lamps with  $\lambda_{\text{max}} = 300$ . The solutions were removed periodically to determine the degree of

polymerization. The solutions and the composites were characterized optically.

Larger scale polymerizations were conducted by pressing approximately 20 g CDA-monomer solution between Pyrex plates lined with a Teflon mold ( $3 \times 4 \times \frac{1}{16}$  inch) and then inserting into the UV chamber until completely polymerized. Trichlorooctadecylsilane releasing agents were applied to the Pyrex plates to facilitate the removal of the polymerized composite. The CDA-AA solutions were polymerized 10 min and CDA-NVP solutions 6 min to achieve virtually total monomer utilization.

Homopolymers of AA and NVP were prepared by placing the respective monomers between the Pyrex plates lined with rubber gaskets and then polymerizing in the UV chamber. The Vicor rubber was sealed with 5-min epoxy to eliminate loss of monomer.

Thermal stability of composite liquid crystallinity was measured by placing a piece of composite on the Mettler hot stage and raising the temperature while following the relative degree of anisotropy optically with crossed polarized light. The samples were heated at a rate of  $10^{\circ}\text{C}/\text{min}$ .

Glass transition temperatures were determined with a Perkin-Elmer DSC2 or a DuPont 982 DMA with a 990 thermal analyzer. Heating rates of  $10^{\circ}\text{C}/\text{min}$  were utilized.

## RESULTS AND DISCUSSION

### Solubility of Cellulose Diacetate (CDA) in Vinyl Monomers

The solubility of 10 wt% solutions of CDA with molecular weights of 30,300 and 56,000 was studied in 15 common vinyl monomers (Table I). CDA was found to be soluble in acrylic acid (AA), *N,N*-dimethylacrylamide, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, and *N*-vinyl-2-pyrrolidinone

TABLE I  
Solubility of CDA in Vinyl Monomers (10 wt%)

Solvent	Cellulose diacetate <sup>a</sup>	
	30,000	56,000
Acrylic acid	+	+
Acrylonitrile	-	-
Butyl acrylate	-	-
<i>N,N</i> -dimethylacrylamide	+	+
Ethyl acrylate	-	-
2-Hydroxyethyl acrylate	+	+
2-Hydroxyethyl methacrylate	+	+
Methyl acrylate	-	-
Methyl vinyl ketone	-	-
Styrene	-	-
Vinyl acetate	-	-
Vinylidene chloride	-	-
4-Vinyl pyridine	-	-
<i>N</i> -vinyl-2-pyrrolidinone	+	+

<sup>a</sup> + = solubility at 10 wt%; - = incomplete solubility at 10 wt%.

TABLE II  
Solubility of CDA in Vinyl Monomers (50 wt%)

Solvent	Cellulose diacetate <sup>a</sup>	
	30,000	56,000
Acrylic acid	+	+
<i>N,N</i> -dimethylacrylamide	+	-
2-Hydroxyethyl acrylate	+	+
<i>N</i> -vinyl-2-pyrrolidinone	+	+

<sup>a</sup> + = solubility at 50 wt%; - = incomplete solubility at 50 wt%.

(NVP). At 50 wt%, the 56,000 molecular weight sample was completely soluble in AA, 2-hydroxyethyl acrylate, and NVP. The 30,300 molecular weight sample was soluble in these three monomers as well as in *N,N*-dimethylacrylamide (Table II). Both 30,300 and 56,000 molecular weight samples were chosen for further study of potential liquid crystallinity in AA and NVP.

### Liquid Crystallinity of CDA-VP and CDA-AA Solutions

In an effort to determine the concentrations and temperatures needed to achieve liquid crystallinity for subsequent polymerization studies, 40, 45, and 50 wt% CDA-NVP and CDA-AA solutions of 30,300 and 56,000 molecular weight CDA were prepared and examined via crossed polarized light microscopy. The molecular weight, solvent, and temperature were all found to affect liquid crystallinity (Tables III and IV). In both solvents, the higher molecular weight CDA exhibited the transition from isotropic-anisotropic (biphasic) to an anisotropic texture at a lower concentration than the 30,300 molecular weight CDA. In AA, 30,300 CDA exhibited small anisotropic inclusions in a continuous isotropic phase at 40 wt%, small isotropic inclusions in a continuous anisotropic phase at 45 wt%, and a completely anisotropic phase at 50 wt%. The 56,000 CDA passed from a continuous anisotropic phase with small isotropic inclusions at 40 wt% CDA to a completely anisotropic phase at 45 wt%. The same molecular weight effect was observed in NVP, although the concentrations for similar morphologies were shifted to a higher weight percentage CDA. A similar shift in concentration with solvents has been observed before.<sup>3-10</sup> The shift has been attributed to changes in polymer-solvent interactions, which cause changes in the equilibrium rigidity or effective axial ratio of the cellulose polymer.

TABLE III  
Effect of Concentration on Liquid Crystallinity of CDA-AA Solutions

Molecular weight	CDA-AA Concentration (wt%)		
	40	45	50
30,300	LC domains, I matrix	I domains, LC matrix	LC
56,000	LC domains, I domains	LC	LC

<sup>a</sup>LC = liquid crystalline; I = isotropic.

TABLE IV  
Effect of CDA Molecular Weight on Liquid Crystallinity  
of CDA-AA Solutions

Molecular weight	CDA-NV-2-P concentration (wt%)*		
	40	45	50
30,300	I	I	LC domains, I matrix
56,000	I	LC domains, I matrix	LC

\*LC = liquid crystalline; I = isotropic.

Temperature was found to have a significant impact on the anisotropy of all solutions. As the temperature of the solutions increased, anisotropy decreased. Increases of 10–20°C were sufficient to destroy the anisotropy of biphasic solutions. The anisotropic solutions retained some anisotropy up to 60°C but became completely isotropic by 70°C. Upon cooling to room temperature after heating to 70°C, an equivalent anisotropic texture reappeared after several hours or more. These long relaxation times made it possible to polymerize samples possessing identical concentrations and different degrees of anisotropy.

#### Polymerization of CDA-NVP and CDA-AA Solutions

The 56,000 molecular weight CDA was chosen over the 30,300 molecular weight CDA for polymerization studies owing to its lower critical concentration and its greater solution viscosity at a given concentration. The temperature sensitivity of the mesophase makes thermally induced free radical initiation impractical. Consequently, room temperature UV initiators were utilized in all polymerizations.

The initial polymerizations were performed on microscope slides in an attempt to study the effect of polymerization on composite anisotropy to determine the potential for preparing large-scale molecular composites. Microscope slide polymerizations were performed by pressing a small quantity of the desired CDA-monomer solution between a UV-transparent quartz coverslip and a microscope slide. The coverslip edges were sealed with silicon grease and the solutions observed under crossed polarized light to determine, qualitatively, the degree of liquid crystallinity prior to polymerization. The slides were then inserted into a UV source at  $\lambda_{\max} = 300$  nm for sufficient time to completely polymerize the monomer solvent, and the final composite was observed under crossed polarized light.

Completely anisotropic 45 wt% CDA-AA solutions containing 1 mol% benzoin butyl ether were subjected to the microscope polymerizations already discussed. The clear BBE containing CDA-AA solutions polymerized completely in 1 min to give clear, hard films that were found to maintain a substantial degree of the anisotropy in the starting solutions. The fast polymerization rates and high initial viscosities of the CDA-AA solutions ensured that the AA polymerized around the CDA to freeze in the anisotropy before phase separation occurred.

In contrast to the rapid polymerizations observed with CDA-AA solutions, 50 wt% CDA-NVP solutions containing 1 mol% BBE required over 10 min of UV exposure to polymerize, and the resulting films exhibited a considerable loss of anisotropy. In view of the long polymerization time and the heat generated by the UV source, the loss of anisotropy was not surprising. During exposure times of this length, the slides were found to warm to temperatures in excess of 50°C, which is sufficient to destroy the anisotropy of the solution. Apparently, the liquid crystallinity of the solutions was thermally destroyed simultaneously with the polymerization of monomer.

To decrease polymerization times and thus decrease the heating effects caused by the UV source for the CDA-NVP solutions, 1 mol% 2,2-dimethoxy-2-phenylacetophenone (DMPA) was employed in place of BBE. The resulting polymerizations were complete in less than 2 min and yielded clear, hard films that completely retained the anisotropy present in the initial solutions. The importance of the polymerization rate suggests that the anisotropic morphology must be frozen in before phase separation occurs. BBE and DMPA (1 mol%) were used in all further polymerizations of AA and NVP composites, respectively.

To prepare larger scale films, CDA-monomer-initiator solutions were pressed between quartz plates to a  $4 \times 3 \times \frac{1}{16}$  inch solution film. The plates were placed in the UV source for 10 min to ensure complete polymerization. The polymerization of both 50 wt% CDA-AA and CDA-NVP solutions resulted in clear, hard films that exhibited virtually complete retention of initial anisotropy when viewed under crossed polarized light. In addition, isotropic 50 wt% CDA-NVP composites were prepared by thermally quenching the liquid crystallinity from anisotropic solutions before polymerizing. This was accomplished by heating the anisotropic solutions in the quartz plates for 30 min at 70°C before UV polymerizing at room temperature. The relaxation times needed to regain anisotropy was found to be of the order of 12 h at room temperature. The polymerization of these 50 wt% isotropic solutions were performed immediately upon cooling to room temperature and resulted in completely isotropic composites.

### Solubility and Thermal Properties

Solubility studies were conducted to determine whether the anisotropic morphology obtained in the composites was attributable to the intertwining of the polymerizing monomer with the CDA or whether the morphology was a result of cross-linking via reaction with CDA. Dioxane and pyridine were chosen for the CDA-AA and CDA-NVP systems, respectively, as these solvents were found to be good solvents for both polymers in the composites. With both systems, the composites were completely soluble, indicating that negligible cross-linking occurred during polymerization. The CDA chains, therefore, were not chemically tied together but physically entangled in the matrix of the random coil polymer. When viewed under crossed polarized light, the composites were found to slowly lose anisotropy on swelling but did not become completely isotropic until entirely dissolved. Once dissolved, the anisotropy could not be restored by casting a film of the solution. The resulting solution-cast composite blends were white, phase-separated films

devoid of the anisotropy initially present before dissolution. The phase separation exhibited on casting is an indication of the incompatibility of the polymers used and further exemplifies the importance of the polymerization technique in preparing homogeneous composites.

To determine the stability of the anisotropic morphologies of the CDA-AA and CDA-NVP composites to elevated temperatures, samples were heated on a Mettler microscope hot stage and observed under crossed polarized light. The anisotropy of the CDA-PAA composite was found to be stable up to 224°C, at which point the sample began decomposing. The sample never flowed and was insoluble in dioxane. The absence of flow and insolubility of the brown film suggested that cross-linking had occurred during the heating. This effect was studied further by heating another sample at 120°C in a nitrogen atmosphere for 1 h and then placing it in a beaker containing dioxane. The sample swelled slightly but never dissolved nor lost anisotropy. It is likely that the cross-linking is attributable to a transesterification between the poly(acrylic acid) (PAA) carboxyl groups and the CDA acetate groups to produce ester linkages between the CDA and PAA. It is interesting to note that the sample retained its anisotropy upon cross-linking and that the swollen sample also exhibited some degree of anisotropy.

The 50 wt% CDA-NVP mesophase was stable up to 130°C, at which temperature the sample began to flow and lose anisotropy. This temperature corresponds closely with the  $T_g$  calculated for this composite. The heat treatment did not cause any significant cross-linking, as indicated by the solubility of the composite in pyridine upon cooling.

The  $T_g$  of the composites and their respective homopolymers were determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). These techniques are commonly employed as a probe of the homogeneity of polymer blends. Both large-scale 50:50 CDA-PNVP and 50:50 CDA-PAA molecular composites showed single  $T_g$  and had values that fell between the  $T_g$  of the homopolymers of the respective composite (Table V). This indicates that the molecular composites are quite homogeneous. The competition between phase separation and polymerization is evidenced, however, in that polymerizations that progressed sluggishly resulted in phase-separated composites (2  $T_g$ ). For example, polymerization of 50 wt% CDA-NVP solutions containing BBE instead of DMPA typically required over 10 min to

TABLE V  
Glass Transition Temperatures of PAA, PNVP, CDA,  
and Their Respective Composites

Polymer	$T_g$ (°C)
PAA	99 <sup>a</sup>
PNVP	82 <sup>a</sup>
CDA	187 <sup>a</sup>
CDA-PAA	137–138 <sup>a, b</sup>
CDA-PNVP	130–132 <sup>a, b</sup>

<sup>a</sup>DSC.

<sup>b</sup>DMA.

obtain high conversions of the NVP. These materials showed two  $T_g$ 's (i.e., 100 and 148°C) instead of the single  $T_g$  obtained with the quickly polymerized DMPA-initiated composites.

### CONCLUSIONS

Cellulose diacetate (CDA) was found to be soluble in several commercially available monomers, including NVP and AA. The onset of liquid crystallinity was dependent on the polymer molecular weight, temperature, and solvent type. Polymerization of anisotropic CDA-AA and CDA-NVP occurred with considerable retention of the solution anisotropy as monitored by crossed polarized light. Unlike previous attempts with PHIC-styrene solutions,<sup>1</sup> both microscope-scale and larger scale CDA-AA and CDA-NVP polymerizations produced homogeneous, anisotropic molecular composites. The homogeneity and degree of anisotropy retained in the final composite depended on the rate of polymerization relative to the rate of phase separation of the polymerizing monomer solvent with the dissolved liquid crystalline polymer. High initial solution viscosities and fast polymerization times favor the formation of homogeneous molecular composites with retention of solution anisotropy. Cross-linking of an anisotropic composite occurs with retention of anisotropy. These cross-linked systems can be swollen by solvent without completely losing anisotropy.

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