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RIGID BACKBONE POLYMERS, XIII: EFFECTS OF THE NATURE OF THE SOLVENT ON THE LYOTROPIC MESOMORPHICITY OF CELLULOSE ACETATE.

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ABSTRACT. The behavior of cellulose acetate was studied in over 30 solvents. It was found that the concentration C* at which the anisotropic phase appears, is dependent on the nature of the solvent. In strong or moderately strong acids, C* is linearly dependent on pK, that is, the stronger the acid the lower the concentration at which anisotropy makes its first appearance. In other solvents, C* is inversely dependent on the molar volume of the solvent.

INTRODUCTION. It has been recently discovered that many cellulose derivatives exhibit liquid crystalline behavior in solutions above a critical concentration C* characteristic of the polymer-solvent pair[1-4]. In the following, results of cellulose acetate alone will be described. It will be shown that the concentration C* is dependent on parameters characteristic of the solvent, such as its acidity or molar volume. Theoretical explanation of the reported observations will be published elsewhere.

EXPERIMENTAL. Cellulose acetate, 39.8% acetyl content (D.S. = 2.45), was obtained from Aldrich Chemicals (#18,095-5) and was used as received. Its intrinsic viscosity at 25°C was determined to be $[\eta] = 0.96$ dL/g in acetone. Using the relationship[5] $[\eta] = 0.45\text{x}10^{-4} M_v^{0.9}$, the viscosity average molecular weight of the cellulose acetate was calculated to be $M_v = 64\ 000$.

Cross polarized light microscopy was performed with the aid of a Reichert microscope equipped with a hot stage and operating at x100 magnification. The microscopic observations were all conducted at 25°C except when chloroacetic acid (m.p.=63°C) was the solvent. In this case the observations were conducted at 65°C. The samples were placed between two microscope coverglasses and sealed all around with high viscosity silicone grease to avoid solvent evaporation or absorption of air humidity. When positioned on the microscope stage, the assembly allowed a modest shearing of the sample by slight movements of the top coverglass.

Wide angle X-ray diffraction (WAXD) patterns were obtained from the "as received" cellulose acetate and from a 1:1 cellulose acetate/phenol highly viscous solution (dope), using copper radiation in a Norelco diffractometer in a parafocus geometry. All concentrations are reported in weight of polymer to volume of solvent. In cases where the solvent is solid at room temperature, the mixing was effected by heating to above its melting point. In the cases of naphthols and dihydroxy solvents, the polymer and solvent were dissolved in acetone, and after the mixing was effected the acetone was stripped off by the application of high vacuum and gentle heat. In all cases, the samples were allowed to equilibrate at room temperature for several hours before being mounted on the microscope stage for observation.

RESULTS. A large number of solvents were found to be capable of dissolving cellulose acetate and maintain highly concentrated solutions. In most cases, the solution concentration surpassed C* and a mesomorphic state was easily observable as a highly birefringent viscous fluid by means of cross-polarized light microscopy. In several solvents no liquid crystallinity was observed even though the polymer concentration surpassed 50%. Benzyl alcohol was one such solvent. Its apparent failure to foment liquid crystallinity may be a reflection of weak interactions with the polymer. It should be noted that cellulose acetate is insoluble in hydroxy-containing solvents such as water, methanol and ethylene glycol. Three additional solvents in which no liquid crystallinity was manifested were o-cresol, 2,6-xylenol and p-tert-butylphenol. From space-filling models it was found that in these cases steric hinderance interferes with a close fit of the solvent molecule and the polymer chain; a fit necessary for close interaction between the solvent hydroxy group and the acetate carbonyl or the residual glucose hydroxy of the polymeric chain.

WAXD patterns of the solid polymer and its liquid crystalline dope in phenol, indicated that the latter contained no polymeric crystallites. In no case was solid crystalline polymer observed in the anisotropic solutions in the concentration range of interest.

The concentration C* was chosen as a means to evaluate the effectiveness of solvents in fomenting liquid crystallinity; the smaller is C* the more effective is the corresponding solvent. Data points were obtained by dilution from the fully anisotropic state, and C* was defined as the last concentration at which the anisotropic phase was observed in the quiescent state. The next dilution resulted in a situation in which the solution appeared to be isotropic when relaxed at rest, but highly birefringent when sheared on the microscope stage by moving the cover glass. From the incremental dilutions an error of less than 2% concentration is possible.

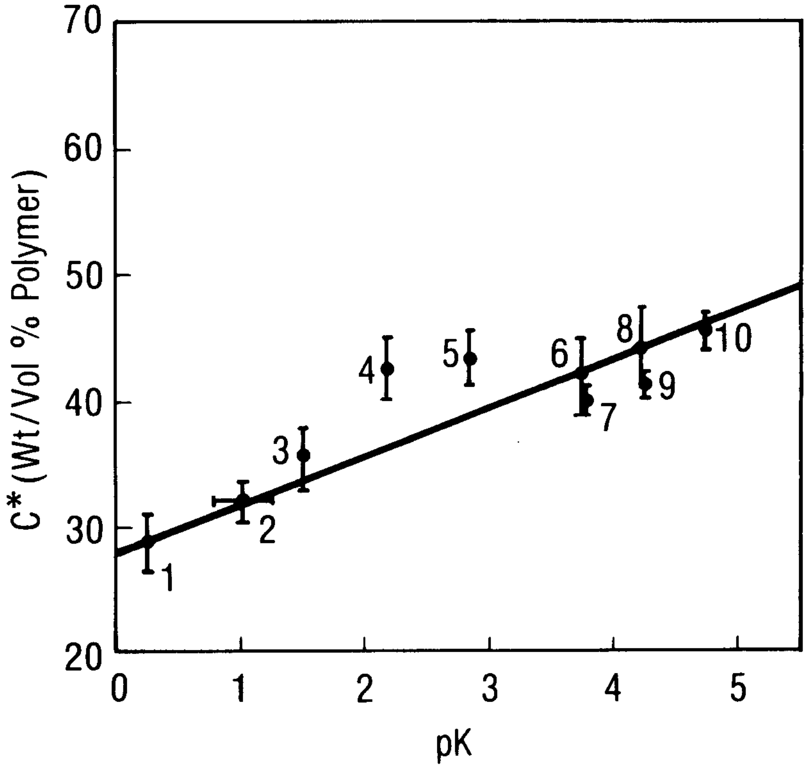

FIGURE 1: Concentration C* at which an anisotropic phase appears as a function of pK of the following acids: (1) Trifluoroacetic acid (2) Difluoracetic acid (3) Dicloroacetic acid (4) Phosphoric acid (5) Chloroacetic acid (6) 1-Naphthol (7) Formic Acid (8) 2-Naphthol (9) Acrylic acid (10) Acetic acid

The obtained results are presented graphically in Figures 1 and 2. In Fig. 1, the results for solvents which are considered to be strong organic acids (except for phosphoric acid in point 4) are displayed. We have found that an acceptable correlation exist between the dissociation constant of the acid and C*, the more dissociated (the stronger) the acid the smaller is C*. The phosphoric acid is inorganic and contains some water. Both may contribute to the fact that C* for this solvent is higher than expected. The datum point for chloroacetic acid (number 5 in Fig. 1) was obtained at 65°C, which may explain the higher than expected C* value for this solvent. It is of interest to note that 1-naphthol and 2-naphthol exhibited the same relationship between pK and C* as the organic acids in Fig. 1, and were not hindered in the formation of liquid crystalline state by the size of the condensed aromatic rings. Conversely, we found the polymer to be insoluble or sparsely soluble in cyclohexylacetic acid. This acid, liquid at room temperature, should have a pK similar to acetic acid and other alkyl acids, of the order of $4.75 \leq pK \leq 4.90$[6]. We believe the insolubility of cellulose acetate in cyclohexylacetic acid to be a consequence of the hinderance of the bulky cyclohexyl group.

In figure 2 are shown the results obtained with weakly acidic, neutral and organic base solvents. Except for p-cresol and trifluoroethanol, they all appear to follow rather closely an inverse and linear relationship between C* and the molar volume of the solvent, V. Attempts to fit the stronger acids, in Fig. 1, to a V-C* relationship failed. Weakly acidic solvents, such as phenol, m-cresol, o-chlorophenol, resorcinol, hydroquinone and pyrocatechol, that follow rather well the V-C* relationship, could not be fitted to a pK-C* relationship. In the latter case their data points were grouped more or less together in a small region centered around a C* value of about 40% and pK value of about 10. To avoid clutter, the data points of hydroquinone and pyrocatechol were omitted from Fig. 2. They both fall practically on point 6 for resorcinol.

Organic bases, such as aniline, pyridine and the two picolines, showed no dependence of their C* values on the corresponding pK_a, the values of C* remaining more or less constant even though the pK_a changed by more than a whole pK_a unit. The fit of the organic bases to the molar volume curve in Fig. 2 is far superior than a fit to pK_a values, especially when it is recognized that some experimental scatter is bound to occur in the experimental determination of C*. The very high C* for the p-cresol and the very low C* for trifluoroethanol solvents, both out of line with respect to the V-C* and pK-C* relationships, are not understood by us as yet.

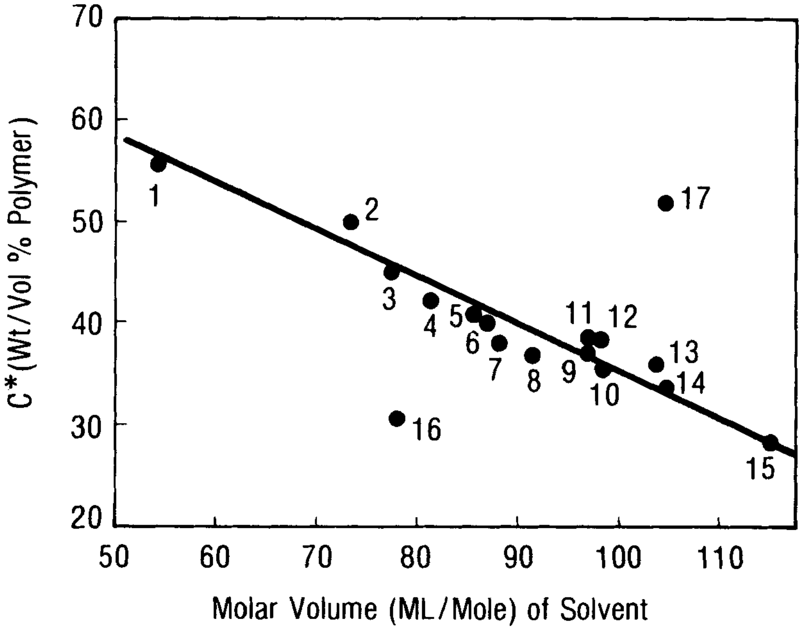

FIGURE 2: Concentration C* at which an anisotropic phase appears, as a function of the molar volume of the following solvents:
(1) Nitromethane (2) Acetone (3) N,N'-Dimethylformamide (4) Pyridine (5) 1,4-Dioxane (6) Resorcinol (7) Phenol (8) Aniline (9) N-Methyl-2-pyrrolidinone (10) Ethyl acetate (11) 3-Picoline (12) 4-Picoline (13) o-Chlorophenol (14) m-Cresol (15) Hexafluoroacetone sesquihydrate (16) Trifluoroethanol (17) p-Cresol

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