Rheological Studies of Cellulose Derivatives Solutions

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Synopsis

The rheological behavior of solutions of cellulose derivatives, acetate, and hydroxypropyl was studied as a function of different parameters; molecular weight, concentration, . . . , at $T = 25°C$ in the vicinity of the liquid crystal phase transition. A variation of the strain rate sensitivity parameter with concentration is found. A degradation of the solution in trifluoroacetic acid is demonstrated.

INTRODUCTION

Many cellulose derivatives exhibit liquid crystalline behavior in solution at high concentration (20–50%) and the number of studies in these systems has continued to grow[1-4] in the search for high modulus and tensile strength fibers other than aromatic polyamides.[5-9]

There is now an extensive literature concerning the cholesteric nature of the mesomorphic phase of these systems,[1,10,11] the effect of the solvent on the critical concentration,[12] phase diagrams as a function of parameters characteristic of the polymer–solvent system.[13-15] Little information is available on the rheology[16-18] or on the cellulose-N-methylmorpholine N-oxide (NMNO) system.[19]

The aim of this paper is to support the optical and differential scanning calorimetry experiments on mesomorphic cellulose derivative solutions with rheological measurements in the vicinity of the critical concentration C^{**}.

EXPERIMENTAL

Materials

Three different cellulose derivatives were used in this study: cellulose diacetate (CDA) (Tennessee Eastman, Kingsport, Tenn., molecular weights $M_w \sim 56{,}000$, $M_w \sim 30{,}300$) and hydroxypropyl cellulose (HPC) [Polysciences, $M_w = 60{,}000$ and Aldrich ($M_w = 100{,}000$)]. Reagent-grade trifluoroacetic acid (TFA) and water were used. All samples were used without further purification.

Solution concentrations are given in weight ratios (polymer wt/solution wt × 100).

Optical Observations

Small amounts of solution, placed between glass slides, were observed with a Reichert microscope on a hot stage between crossed polarizers. Transmitted
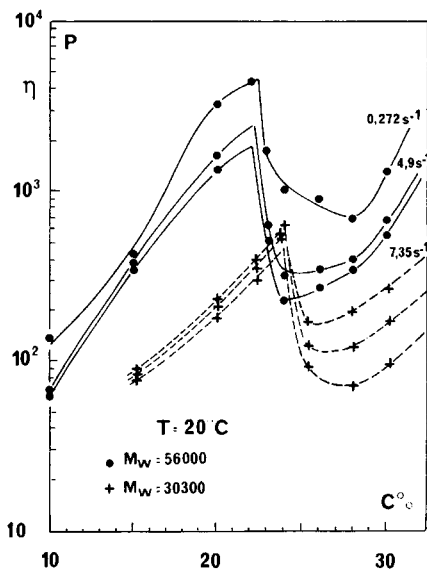
Fig. 1. Concentration dependence of viscosity η of CA/TFA solutions, at different shear rates for two molecular weights: (●) M_w = 56,000; (+) M_w = 30,300; T = 20°C.

light intensity, measured by photometer, was used to determine the critical concentration.

Rheological Measurements

The rheological properties were determined with a Rotovisco Viscosimeter for a shear rate (D) range of 0.27–10 s^{-1} and 6–40 s^{-1}. For low shear rate, a couette flow was used and for high shear rate and high viscosity a cone to plate. Good agreement was obtained in the intermediate range of D in the two systems. All measurements were made at a stabilized temperature 20 ± 0.5°C.

RESULTS AND DISCUSSION

Studies were made for the polymer–solvent systems at different concentrations and for different molecular weights (M_w). As predicted by theory[20,21] and found in previous experiments,[14] at a given temperature there is a concentration C^{**}, where a liquid crystalline phase appears. This concentration increases with temperature and depends strongly on the polymer–solvent systems.

Determination of the Critical Concentration

The change in viscosity in the isotropic and anisotropic phases enables us to observe the transition. The plot of the viscosity η vs. polymer concentration C shows the peak characteristic of lyotropic polymer solutions.[22] The viscosity first increases with concentration C up to a critical concentration C^{**} corresponding to the appearance of the anisotropic phase, also observed in optical microscopy between crossed polarizers. After this concentration, there is a competition between ordering due to shear and packing of the molecules in so-
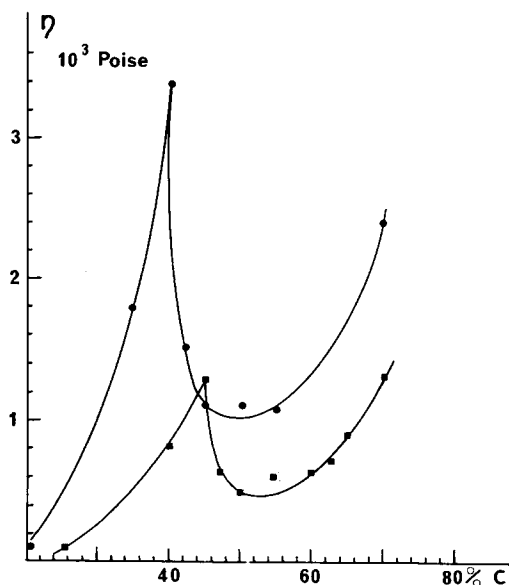
Fig. 2. Concentration dependence of viscosity η of HPC/H_2O solutions at different shear rates for two molecular weights: ($\bullet$) M_w = 100,000; ($\blacksquare$) M_w = 60,000.

lution. The viscosity first decreases as shear ordering dominates. It then increases as packing effects become important (Figs. 1 and 2). The theoretical approach proposed by Aharoni[23] to analyze the peak of viscosity in nematic solutions of polyisocyanates does not give good agreement with our experimental results, but the mesomorphic solutions obtained with the cellulosic derivatives under investigation are cholesteric and not nematic as in the polyisocyanate solutions. We find no significant difference between the critical concentration of the anisotropic phase determined by the maximum of the peak of viscosity and by other experimental techniques, for example, optical microscopy, and we do not observe a biphasic regime with quasi spherical inclusions which deform under shear. A characteristics optical micrograph of a mesomorphic solution is shown in Figure 3.
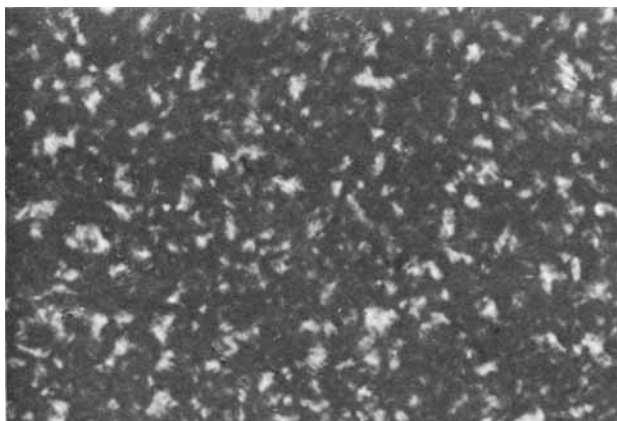

Fig. 3. Optical micrography of a CA/TFA solution (C = 28%).

We show, in Figures 1 and 2, the increase of C^{**} with the polymer molecular weight M_w, as predicted by theoretical investigations.[20,21] The maximum of the viscosity decreases with M_w as in the aromatic polyamides,[22] probably due to an increase of entanglements. For the range of shear rates considered here no variation of C^{**} is observed, although the shape of η vs. C curves is altered (Fig. 1).

Shear Flow Characterization

For each concentration shear stress–shear rate curves were plotted over a range of 0.27–10 s^{-1} for the cellulose acetates and of 6–100 s^{-1} for the cellulose hydroxypropyl (Figs. 4 and 5).

The shear stress τ is described by a power law:

$$\tau = kD^m \tag{1}$$

in the range of shear rate investigated (Figs. 6 and 7). Non-Newtonian behavior ($m \neq 1$) of macromolecular solutions is generally assumed to be due to chain entanglements and Papkov et al.[22] explain the flow behavior of the PBA solution using the concept of a fluctuating entanglement network. This concept is described in detail in a review by Graessley,[24] and may also be applicable to our case.

The rheological curves η (D) demonstrate the rheofluidifing character of CA/TFA solutions. The viscosity of constant concentration decreases under
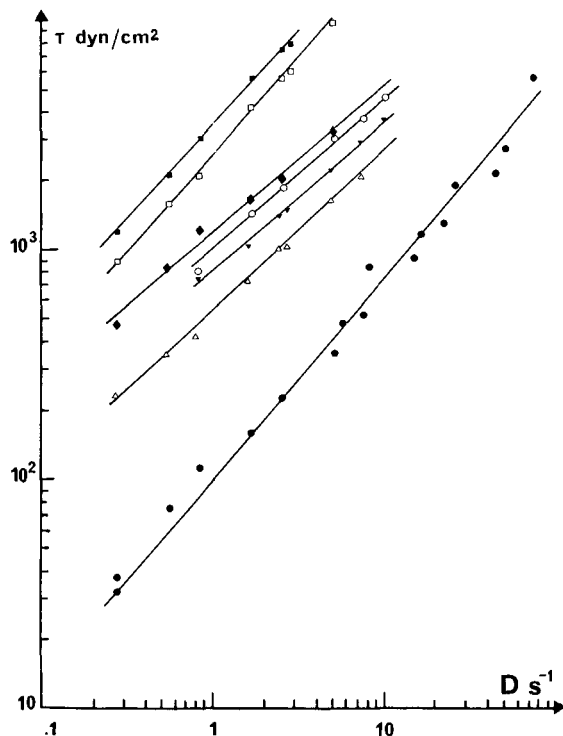

Fig. 4. Shear stress τ vs. shear rate D curves for a CA/TFA solution at different concentrations ($M_w = 56,000$). (●) 10%; (□) 20%; (■) 22%; (◆) 23%; (△) 26%; (▼) 28%; (○) 30%.
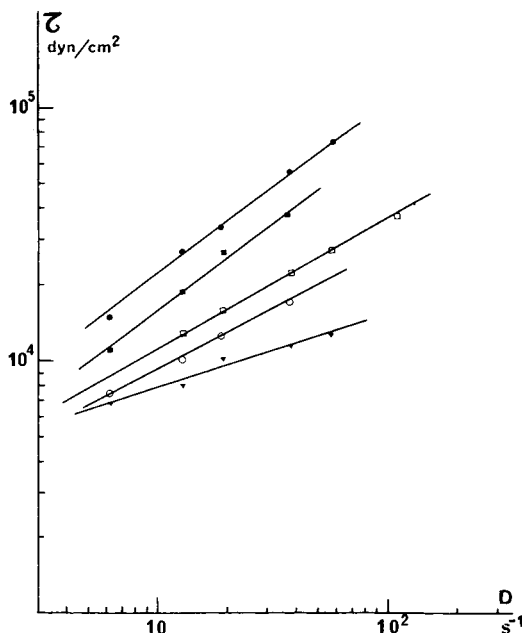
Fig. 5.   Shear stress τ vs. shear rate D curves for a HPC/H$_2$O solution at different concentrations (M_w = 100,000).   ($\blacksquare$) 35%; ($\blacktriangledown$) 45%; (O) 50%; ($\square$) 60%; ($\bullet$) 70%.

the action of a shear rate (Fig. 8).   This behavior is probably due to orientation of rigid segments of macromolecular chain under the flow.

Variation of m with Concentration

In Figs. 4 and 5, we note a variation of the slope of the lines log τ vs. log D with concentration.   This gives a variation with concentration of the power law of eq. (1).   In fact, (Figs. 6 and 7) at low concentration, m = 1 (Newtonian behavior), and then decreases linearly with concentration as the rheofluidifing character becomes evident until, at C^{**}, m decreases drastically.   A further increase of
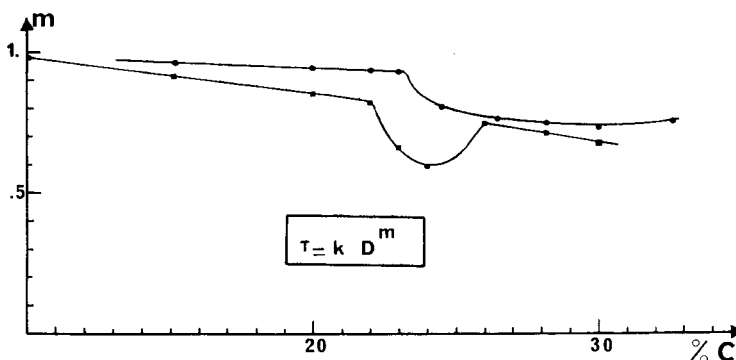

Fig. 6.   Concentration dependence of the strain rate sensitivity parameter m for CA/TFA solution. ($\bullet$) M_w = 30,300; ($\blacksquare$) M_w = 56,000.
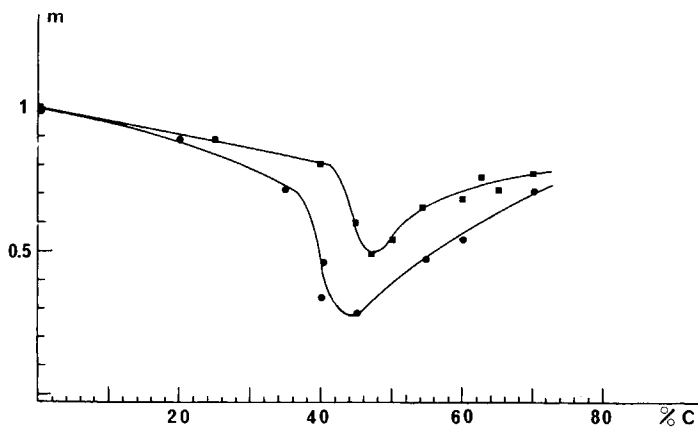
Fig. 7. Concentration dependence of the strain rate sensitivity parameter m for HPC/H_2O solutions. (■) $M_w = 60,000$; (●) $M_w = 100,000$.

polymer concentration causes an increase of m. This power law can therefore be used to demonstrate the appearance of the anisotropic phase. The concentration range where m decreases seems to correspond to the range where the drastic drop of the viscosity vs. concentration shows the appearance of an anisotropic phase. The variation of m with concentration is greater in high molecular weight samples. A similar result for m as a function of temperature has also been observed for cellulose-N-methylmorpholine N-oxide solutions.[19]

Influence of Degradation

When trifluoroacetic acid is used as a solvent, a temporal degradation of mesomorphic solutions is observed, with the disappearance of the selective reflexions of light related to the cholesteric structure and lowering of the enthalpic peak of the isotropic–anisotropic transition in differential scanning calorimetry.

In Figure 9, the viscosimetric measurements on CA/TFA solutions for a molecular weight $M_w = 56,000$ are shown. For a freshly prepared solution, we obtain
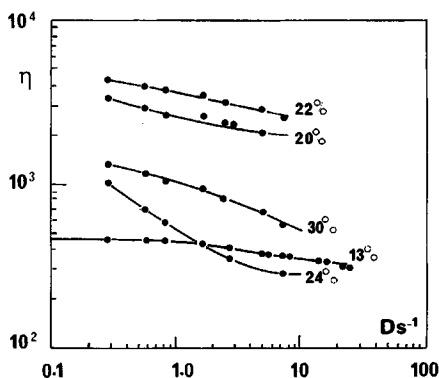

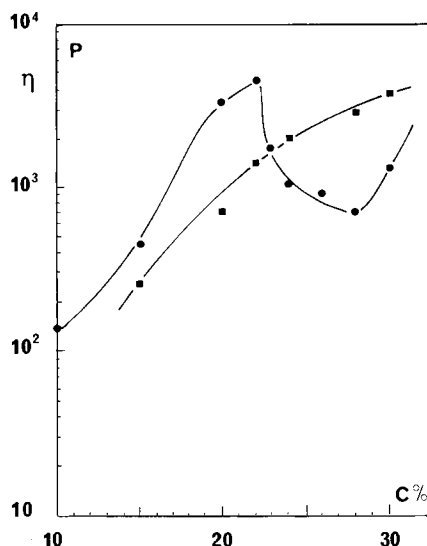Fig. 8. Rheological curves for a CA/TFA solution ($M_w = 56,000$) at different concentrations.

Fig. 9. Concentration dependence of viscosity η of CA/TFA solution of $M_w = 56{,}000$: (●) solutions recently prepared; (■) aged solutions (45 days).

a peak of the viscosity as a function of concentration. In the aged solution (45 days) only continuous increase of the viscosity is found, probably due to a truncation of molecular chains by the trifluoroacetic acid.

CONCLUSION

In this first step towards the spinning of mesomorphic cellulose solutions, we have investigated the transition between anisotropic and isotropic phases of CA/TFA and HPC/H$_2$O solutions. The experimental results demonstrate the need for a molecular model to explain viscosity and shear flow behavior in liquid crystalline polymer solutions.

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