

Phase Studies of a Liquid Crystalline Polymer: Hydroxypropyl Cellulose

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ABSTRACT

Phase diagrams for the isotropic-anisotropic phase transition in solutions of a thermotropic cellulose derivative, hydroxypropyl cellulose are presented. The effect of the molecular weight is demonstrated. A comparison to the theory of semi-rigid liquid crystalline polymers is given.

INTRODUCTION

Liquid crystalline polymers behave in many ways in a manner remarkably similar to the conventional, small molecule liquid crystals. The same nematic and cholesteric textures due to disclinations of the director are observed under the polarizing microscope and, in light scattering, the Bragg type reflections of cholesteric structures are found (FRIED et al. 1982). In external fields, distortion of the director axis (PATEL et al. 1979), magnetic birefringence (MARET et al. 1980) and even hydrodynamic instabilities (KRIGBAUM et al. 1982) have been reported. Circular dichroism (LEMATRE et al. 1982), optical rotary dispersion (TSENG et al. 1980) as well as visual observation of typical iridescent colors are used to indicate cholesteric ordering of the mesophase.

Phase studies of these materials are also available. Systematic investigations of the effect of molecular weight (SHIMAHURA 1981), of degree of substitution and of the solvent (AHARONI 1980, BHEDA et al. 1980, TSU-TSUI and TANAKA 1980, DAYAN et al. 1982) have been initiated.

In small molecule liquid crystals, dilution in a simple isotropic solvent consisting of molecules with spherical symmetry leads to a rapid linear decay of the phase transition temperature in agreement with predictions of mean field theory (HUMPHRIES et al. 1971). In polymer liquid crystals, new effects may occur due to molecular flexibility and high

molecular weight.

The purpose of this paper is to investigate the presence of such effects in the case of a thermotropic cellulose derivative, hydroxypropyl cellulose (HPC).

EXPERIMENTAL

Sample preparation:

The hydroxypropyl cellulose samples were obtained from Aldrich chemical Co., and had nominal M_w values of respectively 100 000, 300 000 and 1 000 000. The sample of $M_w = 60\ 000$ is manufactured by Polysciences.

Several series of solutions containing from 10% to 90% by weight of hydroxypropyl cellulose in dimethylacetamide (Aldrich) are prepared by weighting appropriate quantities of polymer and solvent and allowing the solutions to stand for several days. The mixing process was accelerated by warming slightly the solutions for a few hours.

Dilute solutions were clear viscous liquids and on increasing the polymer concentration to above 65%, iridescent colors are observed.

Optical microscopy:

An Olympus polarizing microscope was used to investigate the birefringent characteristics of the systems. The solutions were placed between two microscopic slides, and were studied both at room temperature and at elevated temperatures using a hot stage equipped with accurate temperature regulation (Mettler). Transmitted light intensities were measured via a photomultiplier.

Our experimental transition points correspond to the complete disappearance of birefringence and the appearance of a dark field.

The microscope is equipped with a photographic apparatus which allows photography of textures during heating and cooling cycles.

DISCUSSION OF THE THEORY

Recently, we have proposed a theory for semi-rigid liquid crystalline polymers (TEN BOSCH et al. 1982). Extended from the molecular model for the phase transition in membrane lipids (JAHNIG 1979), the polymer is described by a deformable elastic chain. By including orientation dependent intermolecular interactions (steric, dispersion) arising from the axial symmetry of the polymer segments, a first order transition to an

ordered, liquid crystalline phase is shown to occur. The method of calculation follows JAHNIG (1979) and the main results are summarized here.

In an isotropic solvent, the orientation dependent interactions between polymer chains are diluted by a factor given by the volume fraction x occupied by the polymers. The "pseudotransition temperature" $T_C(x)$, the temperature at which the transition would take place in absence of biphasic separation, is determined by the strength of the mean field interaction and by the chain flexibility. If the persistence length q of the worm-like chain is assumed temperature independent, we obtain linear phase diagrams $T_C(x) = xT_C$. If, on the other hand, the bending elastic constant governing intrachain interactions is constant in temperature, then $q \propto 1/kT$ and $T_C(x) = \sqrt{x} T_C$. We also find (TEN BOSCH 1982), that the phase transition temperature T_C of the thermotropic polymer is a function of molecular weight, slowly increasing from the monomer to reach saturation at high degrees of polymerization. This is due to screening of the quadrupolar interactions.

COMPARISON TO EXPERIMENT

The effect of the molecular weight on the transition temperature is shown for pure HPC in fig. 1. Experimental results for different molecular weights are plotted and are in good agreement with published results (SHIMAHURA et al. 1981, SUTO et al. 1982). In the range studied, saturation has not yet been reached.

The isotropic-anisotropic phase diagrams for a solution of HPC in dimethylacetamide (DMAC) are given in fig. 2 for different molecular weights. In fig. 3, we plot the comparison between these experiments and the results of the theory. The pure transition temperatures are taken from fig. 1. For the low molecular weight samples, good agreement between theory and experiment is found for $T_C(x) = \sqrt{x} T_C$. Using 100 \AA for the room temperature persistence length, we obtain an average interchain interaction energy of the order of 0.4 kcal/mol .

Note, that whereas volume fractions of the polymer are used in the theory, experimental concentrations (fig. 2) are given in weight %. In a first approximation, from the density data of BHEDA et al. 1980, using the variation with temperature given by SAMUELS 1969, we find a shift of the experimental phase diagram on transformation to volume fractions of around 4 % (fig. 4).

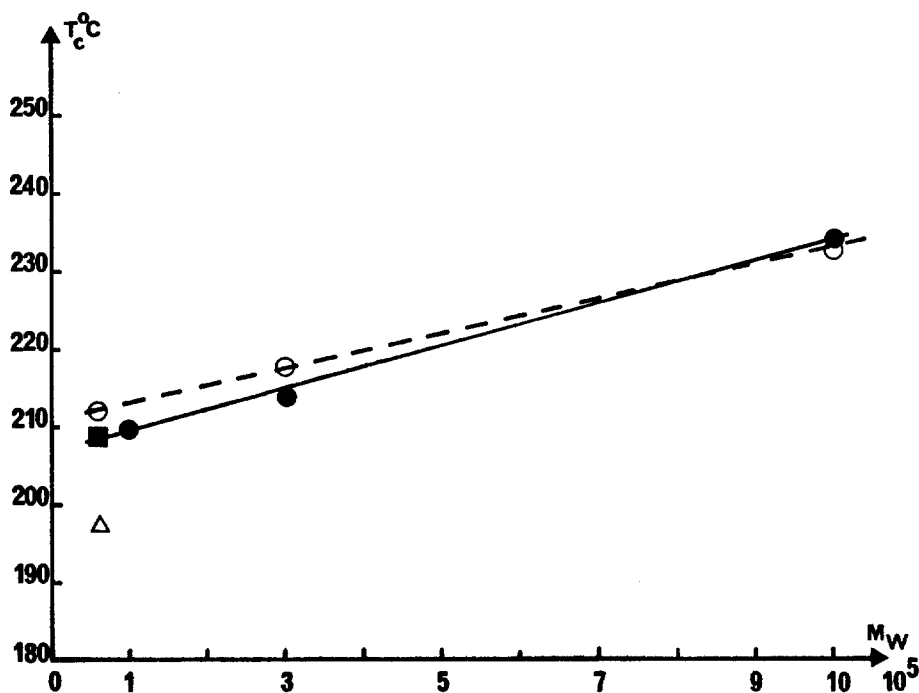


Fig. 1 : Mesomorphic transition temperature of pure hydroxypropyl cellulose as a function of molecular weight M_w .

- HPC (SHIMAHURA et al. 1981)
- HPC Aldrich
- HPC (SUTO et al. 1982)
- △ HPC Polysciences

We do not plot the biphasic regions in the vicinity of the first order mesomorphic phase transition. These regions are not readily observed under the polarizing microscope, possibly due to slow nucleation dynamics, small size of the biphasic domains or narrowness of the temperature range involved. The curves in fig. 1 and 2 plot the temperature of total extinction between crossed polarizers and correspond to the upper limit of the biphasic region.

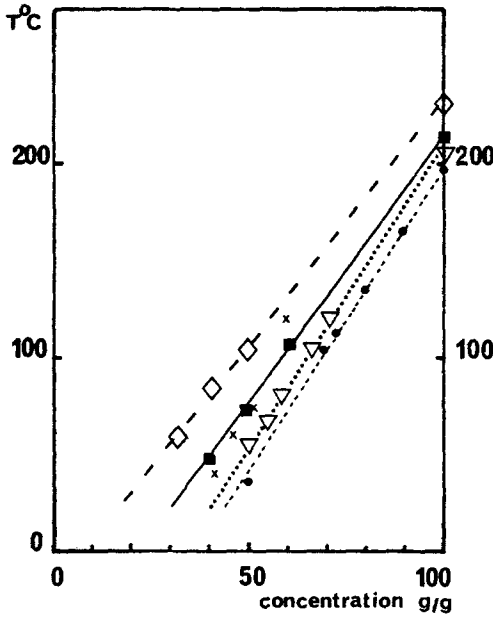


Fig. 2 : Experimental phase diagram for hydroxypropyl cellulose in dimethylacetamide for different molecular weights M_w .

- ◇ - - $M_w = 1\ 000\ 000$
 - — $M_w = 300\ 000$
 - ▽ ··· $M_w = 100\ 000$
 - - · - $M_w = 60\ 000$
 - X - - $M_w = 100\ 000$
- (BHEDA et al. 1980)

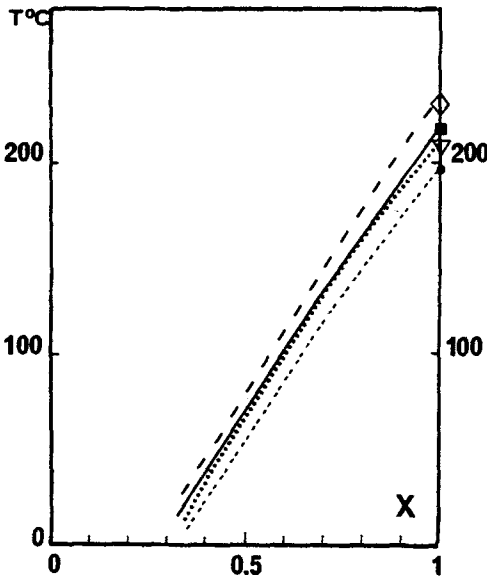


Fig. 3 : Theoretical phase diagram for hydroxypropyl cellulose in dimethylacetamide for different molecular weights M_w .

- ◇ - - $M_w = 1\ 000\ 000$
- — $M_w = 300\ 000$
- ▽ ··· $M_w = 100\ 000$
- - · - $M_w = 60\ 000$

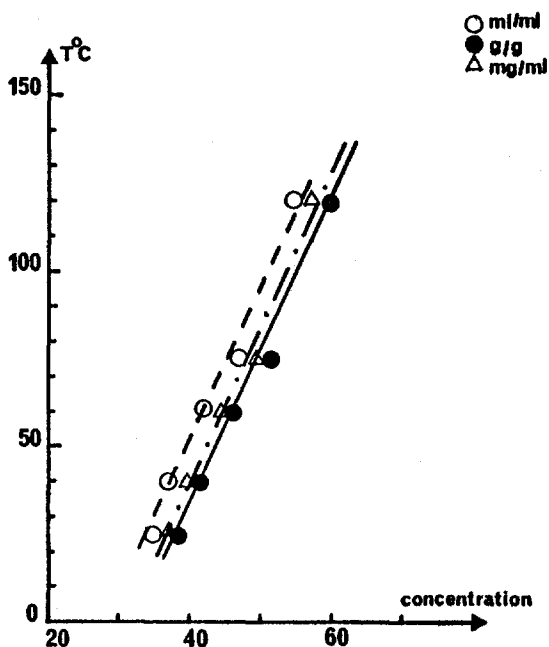


Fig. 4 : Transformation of experimental phase diagram (polymer concentration in wt. %) to polymer concentration in vol. % for hydroxypropyl cellulose ($M_w = 100\ 000$) in dimethylacetamide solution

An example of completely anisotropic (focal conic) texture is given in fig. 5 .

In conclusion, a variation with molecular weight of the phase transition temperature of the thermotropic polymer predicted by the theory is found in HPC. The experimental phase diagrams HPC/DMAC are also in qualitative agreement with the theoretical predictions. On the other hand, specific solvent interactions may effect the critical concentration. Strong interchain hydrogen bonds and polarity of the solvent could help to stabilize the ordered phase. It would be of interest to investigate these effects further and to extend these studies to other solvents and to a range of molecular weights not investigated here.

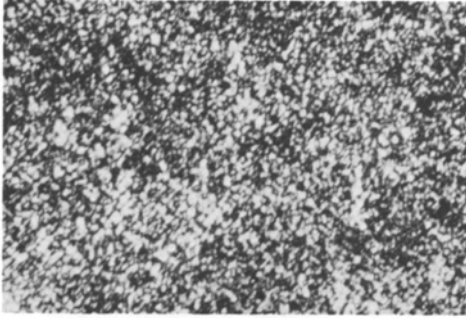


Fig. 5 : Texture (focal conic)
of hydroxypropyl cellulose in
dimethylacetamide
69.37% polymer (by wt.)
 $M_w = 100\ 000$

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