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Polymer 41 (2000) 4357–4360

polymer

Polymer Communication

Phase diagram of water soluble semirigid polymers as a function of chain hydrophobicity

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Received 7 October 1999; received in revised form 18 October 1999; accepted 29 October 1999

Abstract

The phase behavior in water of hydroxypropylcellulose (HPC) and HPC partially esterified with methacryloyl chloride (HPCM) has been studied by measuring the variation of solution turbidity in the temperature range -5 to 46°C. The resulting phase diagram is compared to previous results on HPC/water system and a qualitative agreement is observed. The HPCM phase diagram shifts towards lower values of temperature and polymer concentration; which may be mainly explained by the presence of hydrophobic residues introduced along the HPC chain. The progressive loss of the structure of water molecules around these groups as temperature or concentration increase reduces the area of the isotropic region with respect to that of the anisotropic phase. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phase behavior; Hydroxypropylcellulose; Polymer liquid crystal

1. Introduction

In a recent paper [1], the phase behavior in aqueous solution of hydroxypropylcellulose (HPC) partially esterified with methacryloyl chloride (HPCM) was examined with respect to the trend of the cloud temperature T_c, at constant v_p, and the critical concentration $v_p{}'$, at room temperature, as a function of the amount of methacrylic groups introduced along the chain. As known from the underivatized polymer [2–5], T_c is the temperature at which a diluted isotropic solution or a concentrated anisotropic solution becomes cloudy entering a wide biphasic region, while $v_p{}'$ is the concentration, expressed as volume fraction of polymer, at which the anisotropic phase first appears at constant T. The above results suggested a shift of the phase diagram (v_p vs. temperature) of HPCM with respect to that of the original HPC. The aim of this paper is to quantitatively evaluate the shift of the phase diagram in a wide range of polymer concentration and temperature.

2. Experimental

A hydroxypropylcellulose (HPC) sample, supplied by Hercules Inc., molecular weight 60 000, molar degree of substitution $\mathrm{MS} = 4$, was used for the phase diagram determination and for the hydroxypropylcellulose methacrylate (HPCM) synthesis. MS is defined as the total number of molecules of propylene oxide that have combined with the original cellulose per anhydroglucose unit.

HPCM was synthesized according to the method described in a previous work [1]. HPCM esterification degree DS (mole of acylresidue per mole of HPC unit) was $0.14 + 0.01$. We used this low value of DS because samples with DS higher than $\cong 0.2$ are insoluble in water [1]. Doubly distilled water was used to prepare all the solutions.

3. Methods

3.1. Thermal analysis

Transition temperatures were measured by an optical apparatus assembled in our laboratory: it consists of a laser generator ($\lambda = 545$ nm), a holder, where a quartz cell 1×0.1 cm containing the polymer solution may be located and heated or cooled using a Peltier cell, a photometer connected to a computer, capable of measuring the intensity variation of a laser beam going straight through the cell. The temperature regulator allows specific heating or cooling programs to be selected. A thermocouple located inside the cell gives the actual solution temperature at any time. A jump in the intensity of transmitted light during T variation indicates the occurrence of a phase transition (see

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PII: S0032-3861(99)00795-8

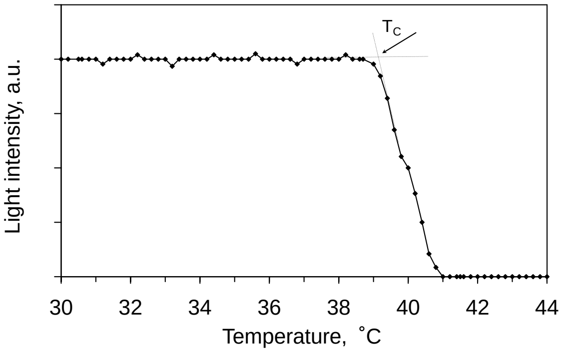

Fig. 1. Laser light intensity transmitted through a HPC solution ($v_p = 0.05$) as a function of the temperature. The heating rate is 0.2°C/min T_c cloud temperature.

Fig. 1) from a single phase to a biphasic system. The curve is reversible.

3.2. Optical microscopy

The critical volume fraction $v_p{}'$, at which anisotropy may initially be observed in a solution between crossed polarizers (at constant T), was determined at room temperature for both HPC and HPCM samples by using a Polyvar Pol Reichert polarizing microscope.

4. Results and discussion

An appropriate evaluation of the influence of the hydrophobic methacrylic groups on the phase diagram in water, needs to compare samples of HPC and HPCM having the same chain in terms of MS and hydroxypropyl substituents distribution. In fact the phase diagrams of HPC reported in the literature [2–5] show the same general behavior (wide biphasic region at $T > 40$°C, narrow biphasic region at lower T), but the agreement between these results from different authors is merely qualitative. Probably the actual nature of the samples in terms of average molecular weight, MS and hydroxypropyl substituents distribution, influences to a certain extent the area of stability of the different phases.

For this main reason, we decided to study the phase behavior of our HPC sample as well as that of its derivative HPCM.

An important preliminary point concerns the heating (or cooling) rate of the solutions under examination. It is in fact well known that the value of a transition temperature depends on that parameter, whatever the employed experimental method is. Fig. 2 gives the T_c trend of an HPC isotropic solution ($v_p = 0.05$) at different heating rates, from 0.1 to 1°C/min. In this range, T_c values vary from 39.2 to 48°C, however, when the rate is <0.2°C/min., T_c becomes practically constant. This result, together with the necessity to limit the measurement time, suggested the best rate for our determinations was 0.2°C/min. In general, this point should not be neglected when results of different authors are compared.

Fig. 3 shows the phase diagram of our HPC sample. Twelve solutions, isotropic at room temperature, were progressively heated and the values of T_c determined according to the described procedure. The volume fraction v_p was in the range 0.01–0.4. Moreover, each point on the diagram corresponds to the medium value of three determinations. Four solutions, anisotropic at room temperature, with a 0.45–0.7 v_p, showed, after heating, the T_c values reported on the right side of the figure. Owing to the limitations of our instrument, it was impossible to explore higher volume fraction. If we now compare the T_c trend for isotropic solutions with the results of literature there is a good agreement, despite the different experimental methods and the different HPC samples. The right side of T_c curve falls between the results obtained by Larez et al. [2] (line *b*) and those by Guido [3] (line *d*). Evidently, the curves agree only from a

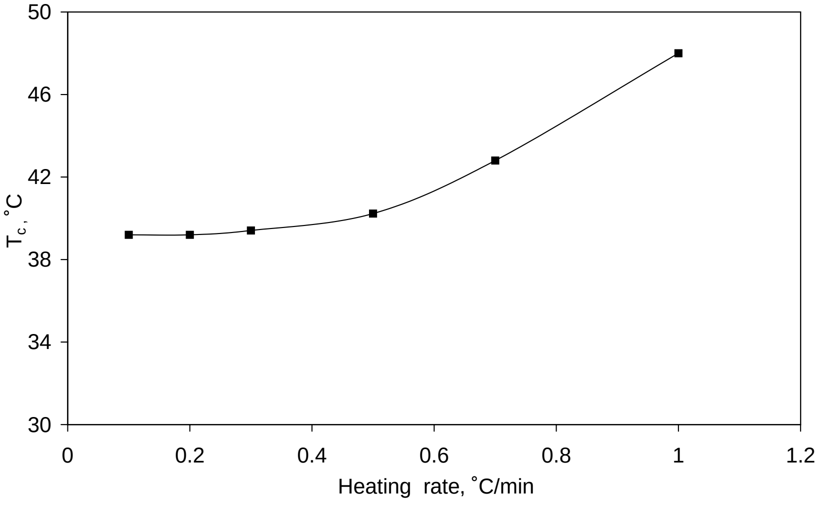

Fig. 2. Cloud temperature as a function of heating rate for HPC isotropic solution, $v_p = 0.05$.

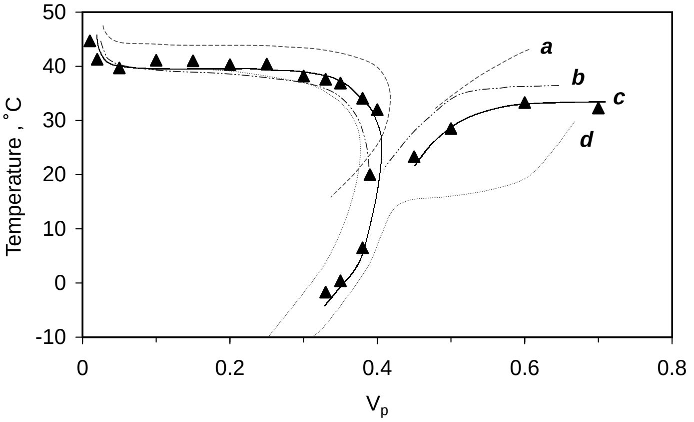

Fig. 3. Phase diagram of HPC in water: (a) from Ref. [4]; (b) from Ref. [2]; (c) our results; and (d) from Ref. [3].

qualitative point of view, probably because the cloud transition of anisotropic solutions is strongly dependent on the sample nature. With regard to the isotropic field, it is interesting to observe that three solutions having v_p equal to 0.33, 0.35 and 0.38, respectively, show a transition to the biphasic region when cooled. The transition points were confirmed by optical microscopy. Solutions at increasing concentration and constant T (20°C) were examined under polarized light between crossed nicols; the concentration at which the first traces of anisotropy appears was taken as $v_p{}'$ at the T of measurement. Fig. 3 shows a decrease of $v_p{}'$ vs T, a thermotropic effect that was previously observed by Conio et al. [6,7] in a non-aqueous solvent (dimethylacetamide) and more recently by Guido [3] in water.

The experimental methods used in this work are incapable of determining the values of $v_p{}''$ (volume fraction at which the isotropic phase is no longer stable); hence its trend as a function of T cannot be reported in Fig. 3.

The phase diagram of the HPCM sample was determined following the method used for HPC. Five solutions that were prepared and heated at 0.2°C/min fall in the isotropic region at 25°C. The T_c values are reported in Fig. 4 and their trend clearly follows the HPC curve of the wide region showing a shift of T_c of about 5°C lower.

Isotropic solutions at $v_p = 0.30$ and 0.33 were also cooled and crossed the narrow region at temperatures close to 0°C. This curve was compared with the measurement of $v_p{}'$ at 20°C. The T_c values of three anisotropic solutions, with a 0.4–0.6 v_p, were also measured and reported in the same figure. In this region, the gap of T_c related to HPC and HPCM is wider than that in the isotropic region and the difference ($T_{c,HPC} - T_{c,HPCM}$) is about 15°C. Moreover, the HPCM curve tends to cross that of HPC. So the HPCM diagram shifts toward lower values of T and v_p, according to the hypothesis advanced in our previous paper [1].

As anticipated, this behavior may be mainly explained by the presence of hydrophobic residues introduced along the HPC chain. The progressive loss of structure of water molecules around these groups as T or v_p increase reduces the area of the isotropic region more than that of the anisotropic phase.

We believe that this paper contributes further in understanding the role of the balance between hydrophobic and hydrophilic groups in water soluble polymers, and, consequently, in their derivatives like hydrogels. The synthesis

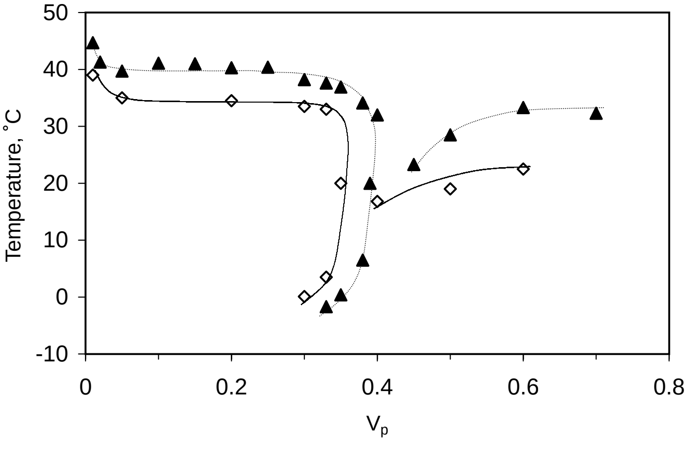

Fig. 4. Phase diagram of HPC (▲) and HPCM (◇) in water.

of new classes of HPC derivatives with side chain groups of different hydrophobicity is in progress.

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