

A Study on P(VP-VA) Hydrophobically Associating Behaviour of Water-soluble Copolymers

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ABSTRACT

Vinylpyrrolidone-vinyl acetate (VP-VA) hydrophobically associating water-soluble copolymers were synthesized by free radical copolymerization. The effects of hydrophobic content and temperature on the viscosity and refractive index behaviour were investigated in detail. The critical concentration C^* of the hydrophobically associating water-soluble copolymers was studied in the static state and in flowing solution by refractometry and viscosimetry, respectively. A dramatic decrease in solution viscosity of P(VP-VA) copolymers is observed with increasing the VA content at all temperatures. Also as the VA content in the copolymer increased, the solution refractive index of the copolymer decreased. The lowering in viscosity and refractive index reflects the contraction of the polymer coil because of intramolecular hydrophobic interactions. Variation of the dynamic and static critical concentration as a function of the temperature for P(VP-VA) copolymer in water has been investigated. The critical concentrations are lower when determined by refractive index measurements in the static state compared to the critical concentrations determined in the dynamic state using viscometer.

Key Words:

hydrophobically associating polymer;
viscosity;
refractive index;
critical concentration;
vinylpyrrolidone-vinyl acetate copolymer.

INTRODUCTION

The study of hydrophobically associating polymers has been received a great deal of attention recently [1-11]. Hydrophobically associating polymers consist of water-soluble polymer containing a small number of hydrophobic groups [12-14]. In

aqueous solution, the hydrophobic groups aggregate and result in intra- and intermolecular association.

Above a certain polymer concentration, C^* , the intermolecular hydrophobic interactions lead to the formation of polymolecular associa-

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tions. As a consequence, these copolymers exhibit thickening properties equivalent to those observed for higher molecular weight homopolymers.

The type and content of the hydrophobic groups restrict the solubility of hydrophobically associating water-soluble polymer. Depending on the method of synthesis, the hydrophobes can be distributed anywhere in the copolymer, for example, at each end of the backbone or within the chain as pendant groups in a random or blocky arrangement. Recently, it is demonstrated that distribution of hydrophobic unit along the chain affects the solution properties of copolymer containing hydrophobic monomer [15]. From the theoretical aspect, the influence of distribution of monomer units along the chain on the phase behaviour of statistical copolymers have been studied by Foroutan [16,17].

In the present work, a series of poly(vinyl pyrrolidone-vinyl acetate) hydrophobically associating water-soluble copolymers with homogeneity in backbone distribution and different monomer ratios were synthesized in the absence of surfactant, which made the copolymerization process and post-treatment of the product convenient and easy to be conducted. Copolymers of vinyl pyrrolidone (VP) and vinyl acetate (VA) monomers have significant utility in the pharmaceutical, cosmetic industries and in the food industry as well as numerous other technical fields [18]. These copolymers can be synthesized in different ways resulting in the different homogeneity of backbone monomer distribution and the solubility of copolymer in different solvents, but for some uses, however, it is necessary that the copolymer be present as clear aqueous solutions.

The aim of this work is to demonstrate, the existence of the critical concentration, C^* , in a copolymer having a substantial homogeneous structure. Also in this paper, we have tried to determine C^* not only by viscosity measurement but also for first time by refractive index measurement.

EXPERIMENTAL

The source and the purification of the monomers and other reagents have been reported in our previous paper [19].

Copolymerization

Vinyl pyrrolidone (VP) and polyvinyl pyrrolidone

(PVP) are soluble in water because they can form hydrogen bonds between nitrogen atoms and water molecule, whereas vinyl acetate (VA) monomer does not form hydrogen bond with water. Therefore, some difficulties in the copolymer synthesis arise from the insolubility of the hydrophobic monomer in water. To overcome the insolubility of the hydrophobic monomer and to provide a P(VP-VA) homogeneous copolymer that is soluble in water, a suitable process was applied. The method of P(VP-VA) synthesis was described in detail in the United State Patent [20]. To provide a P(VP-VA) homogeneous copolymer that is soluble in water, it was proposed to use a process involving precharging VP and VA monomers in a predetermined ratio and then feeding VP and VA at a predetermined rate. The ratio of the components in the initial charge and the feeding rate for the monomers being selected in accordance with the reactivity ratios of the monomers towards copolymerization as opposed to homopolymerization.

Here we describe the Zhong's copolymerization method [20] for synthesis of homogeneous P(VP-VA) copolymer. Starting from the copolymerization equation [21];

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

and the equivalent equation for F_2 , after derivation, we can obtain the following equation:

$$\left(\frac{f_1}{f_2}\right) = \frac{(F_1 - F_2) + [(F_2 - F_1)^2 + 4F_1 F_2 r_1 r_2]^{1/2}}{2F_2 r_1} \quad (2)$$

where F_1 and F_2 are the mole fractions of monomer 1 and monomer 2 in the copolymer; r_1 and r_2 are the reactivity ratios for monomer 1 and monomer 2; f_1 and f_2 are the mole fractions of unreacted monomer 1 and monomer 2, respectively, in the reactor. It should be noted that r_1 and r_2 are assumed to be equal to 1.89 and 0.227 according the literature [18], although there is difference between these values and the true values of r_1 and r_2 (Table 2).

By using eqn(2) and that $f_1 + f_2 = 1$, we can decide the initial monomer composition (f_1 and f_2) to make the initial copolymer having the instantaneous composition of F_1 and F_2 . Therefore, the initial monomer concentration is established based on the monomer reactivity

ratios (r_1 and r_2) and F_1 and F_2 .

As the reaction progresses, the monomers should be supplemented continuously based on their consumption ratios to maintain the instantaneous monomer composition to be constant at f_1 and f_2 , therefore, the instantaneous copolymer composition can be maintained constant at F_1 and F_2 and equal to the cumulative copolymer composition. The description of the synthesis route of the Zhong's copolymerization method has been reported [20] and will not be presented here.

Viscosity Measurement

Viscosity measurements were carried out at various temperatures by an Ubbelohde viscometer with internal dilution, suspended in a thermostat at the required temperature (-0.01 C). The solution was kept about 20 min prior the measurements for temperature equilibrium. The efflux time was determined with an accuracy of -0.01 s. For any errors that could have originated from concentration inaccuracies more than once, we have observed almost identical values.

Refractive Index Measurements

The refractive index of each solution was measured in triplicate using a Quartz-RS-232 digital refractometer having a precision of -0.0001 . Before initiation of each measurement run at a given temperature, the calibrations of refractometer were made using distilled water as reference material.

RESULTS AND DISCUSSION

Characterization of P(VP-VA) Homogeneous Copolymers

The mole fractions of VP and VA in the feed composition and in the copolymers of various compositions that are calculated by using elemental analysis and NMR spectroscopy data are listed in Table 1. The reactivity ratios of VP and VA; r_{VP} and r_{VA} which are obtained from Extended Kelen-Todous method are given in Table 2. The characterization and spectroscopy studies and calculation of reactivity ratios of these copolymers have been reported in our previous paper [19].

Choice of Experimental Condition

In the general synthetic methods of P(VP-VA) copoly-

Table 1. Composition of VP (1) and VA (2) in the feed and copolymers.

Copolymer	f_1	f_2	N (%)	F_1	F_2
A	0.285	0.715	8.02	0.576	0.424
B	0.515	0.485	10.62	0.793	0.207
C	0.603	0.397	10.84	0.832	0.168
D	0.713	0.287	11.68	0.890	0.110
E	0.767	0.233	11.91	0.931	0.069
F	0.821	0.179	12.15	0.950	0.050

f_1 and f_2 are the mole fractions of VP and VA in the feed.

F_1 and F_2 are the mole fractions of VP and VA in the copolymer.

mers, because VP is a more active monomer during the polymerization than the VA monomer, VP will react faster and go into the copolymer chains first as VP units. The VA will react later leading to formation of VA blocks in the copolymer [15]. The presence of VA blocks in this heterogeneous copolymer will reduce its water solubility appreciably.

As mentioned before, during the synthesis of P(VP-VA) copolymer, each monomer and solvent must be added into the reactor separately. Therefore, each monomer feeding rate can be adjusted independently to keep the monomer conversion ratio constant and the solvent feeding rate can be adjusted independently, according to the monomer feeding rates. This well-organized distribution of VP and VA units in the macromolecule chain maximizes the copolymer's aqueous solution solubility [15]. The homogeneity in the backbone monomer distribution of synthesized copolymers was demonstrated by their solubility in water and their clear aqueous solutions [15].

In spite of the homogeneity of P(VP-VA) copolymers which is the result of homogeneous distribution of

Table 2. Monomer reactivity for copolymerization VP and VA.

	Elemental analysis	NMR Spectroscopy
VP(r_1)	5.730	4.357
VA(r_2)	0.170	0.083
$r_1 r_2$	0.974	0.360

(a) Measured at a concentration of 0.5 g/dL in DMF at 25°C.

the hydrophobic monomer units along the backbone (that is required for solubility P(VP-VA) copolymer in water), as we will show in the next section, the hydrophobically associating behaviour has been observed. As a consequence, hydrophobically associating behaviour depends on the existence of hydrophobic monomer content, and therefore the homogeneous distribution of the hydrophobic monomer cannot prevent the formation of hydrophobic association.

Effect of Copolymer Concentration on Viscosity

In Figure 1 we present the variation of the reduced viscosity (η_{sp}/c) versus the concentration for copolymers A, B, C, E and F at 25 C, 35 C and 45 C. As shown in Figures 1a-1c, in all curves, the reduced viscosity does not increase linearly with copolymer concentration and a maximum solution viscosity of P(VP-VA) copolymer appeared with increasing copolymer concentration in the range of 0-2.5 g/dL. In aqueous solution of these copolymers, the formation of the molecular network above a certain polymer concentration, C^* , causes a rapid increase in solution viscosity. Hydrophobically associating behaviour of this copolymer is so strong that there is no need to add salt for intensifying its effect.

Each curve in the Figure 1 can be divided into three regions with regards to P(VP-VA) concentrations:

- Polymer solution viscosities increase dramatically above a certain concentration (C^*), which correspond to the formation of three-dimensional network in solution.

- Higher concentration of P(VP-VA) makes the viscosities to decrease, and in this region, the association breaks and molecular chains will orientate in the fluid field.

Finally, the higher the P(VP-VA) concentration, the higher viscosities for solution can be observed.

Figure 2 shows the concentration dependence of the solution reduced viscosity (η_{sp}/c) for P(VP-VA) copolymers and polyvinyl pyrrolidone (PVP) in water in the range of 1-2.5 g/dL at 25 C, 35 C and 45 C. For the sake of clarity of this Figure, this range is chosen. An important point which is observed, is that as the VA content in the copolymer increases (from F to C), the solution viscosity obviously decreases. A dramatic decrease in solution viscosity of P(VP-VA) copolymers is observed with increasing the VA content from

polymer P(PVP) to copolymer F at all temperatures.

This figure demonstrates that the existence of a small quantity of hydrophobic monomer changes viscosity enormously. The lowering in viscosity reflects the contraction of the polymer coil because of intramolecular hydrophobic interactions. As expected, this

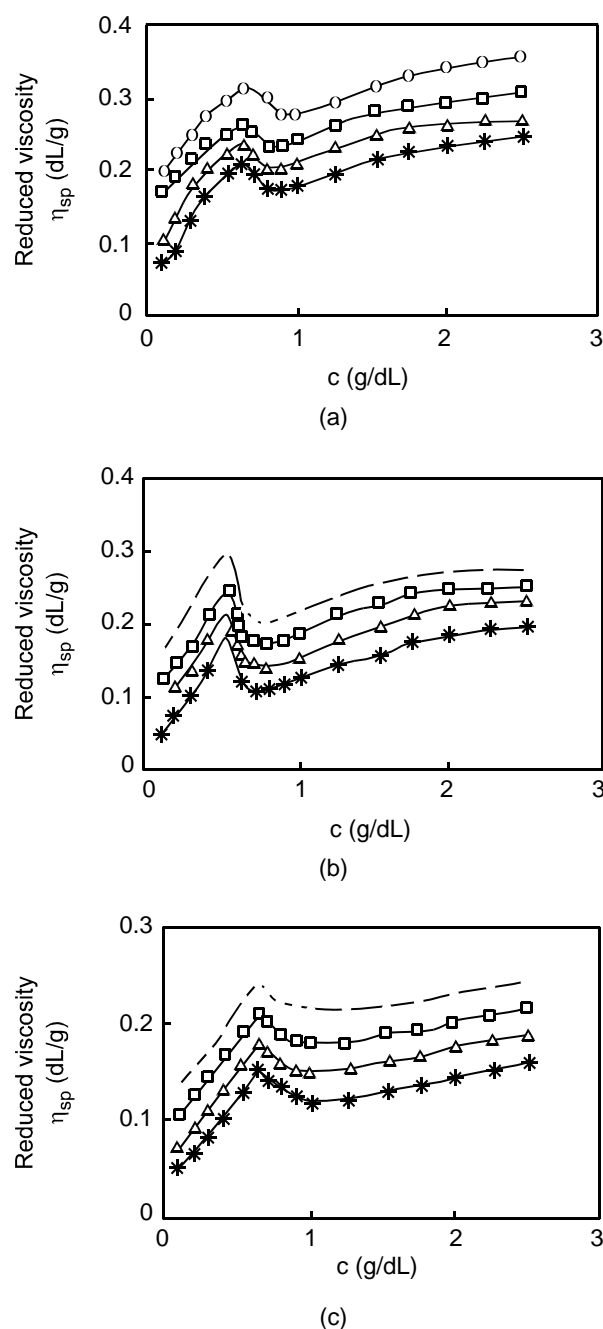
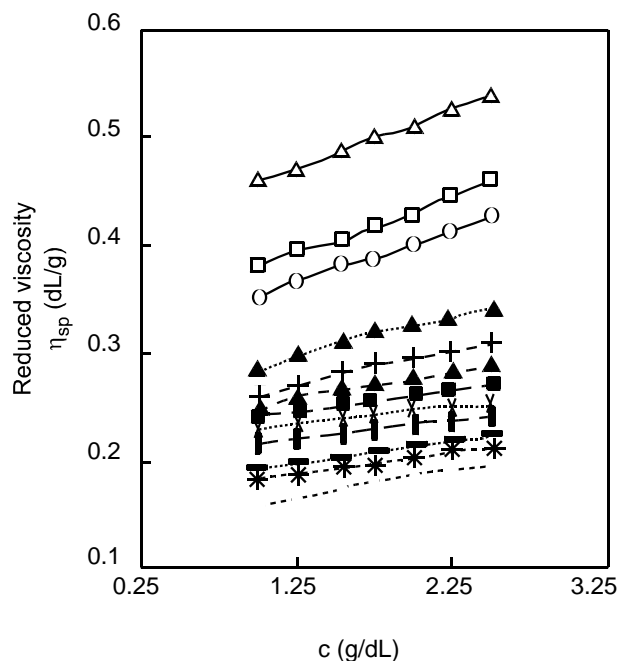


Figure 1. Variation of the reduced viscosity as a function of the concentration for P(VP-VA) copolymers: A(*), B(Δ), E(\square) and F (\circ) at (a) 25°C, (b) 35°C and (c) 45°C, respectively.



(▲) C1, (■) C2, (●) C3, (▲) F1, (■) F2, (●) F3, (+) E1, (x) E2, (*) E3, (Δ) P1, (□) P2, (○) P3.

Figure 2. Variation of the reduced viscosity as a function of the concentration for PVP polymer (P) and P(VP-VA) copolymers (C, E and F) at 25°C, 35°C and 45°C, indices 1, 2 and 3 represent 25°C, 35°C and 45°C, respectively.

effect is strong upon increasing the hydrophobic level.

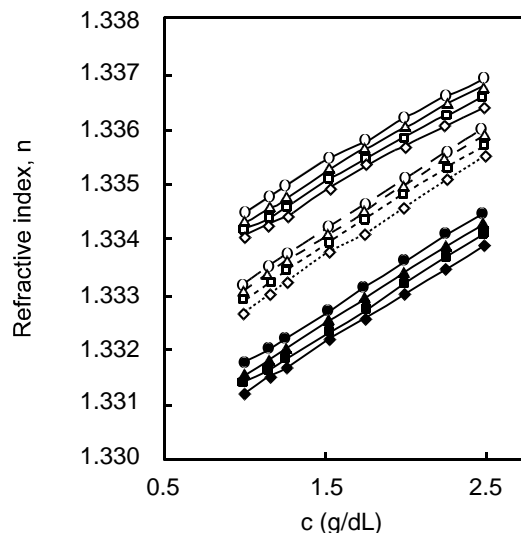
Temperature Dependence of Viscosity

The effect of temperature on the viscosity when temperature changes from 25 C to 45 C is shown also in Figure 2 for PVP and P(VP-VA) copolymers. With increasing temperature, there is a viscosity decrease. The viscosity behaviour of all copolymers is similar, but for clarity of this Figure, only some copolymers are presented.

Temperature increase makes the movement of water molecules and hydrophobic groups faster and the hydration spheres of the hydrophobic groups change a great deal, which are unfavourable for the interchain association of the copolymers. Also, Figure 2 shows that the values of viscosity of polymer P at different temperatures are very close to each other and the hydrophobic monomer content in copolymer is very influential on viscosity.

Refractive Index Study

Figure 3 shows the variation of refractive index (n) as



(—○—) P1, (---○---) P2, (●) P3, (▲) F1.

Figure 3. Plot of the refractive index versus concentration for PVP polymer (P) and P(VP-VA) copolymers (C, E and F) at 25°C, 35°C and 45°C, the numbers 1, 2 and 3 represent 25°C, 35°C and 45°C, respectively.

a function of concentration for PVP polymer (P) and P(VP-VA) copolymers (F, E and C) in water in the range 1-2.5 g/dL at 25 C, 35 C and 45 C. It appears from this Figure that as the VA content increased, the solution refractive index obviously decreased. In Figure 5 we present the variation of refractive index (n), versus the concentration, for copolymer A and F at

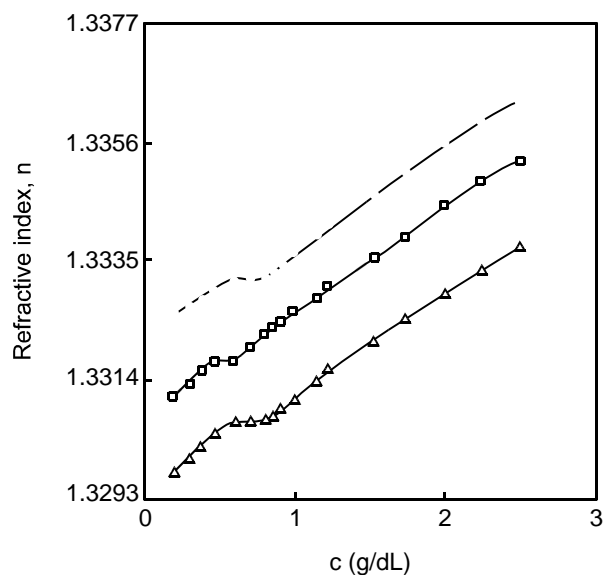


Figure 4. Plot of the refractive index versus concentration for copolymer C at 25°C (○), 35°C (□) and 45°C (Δ).

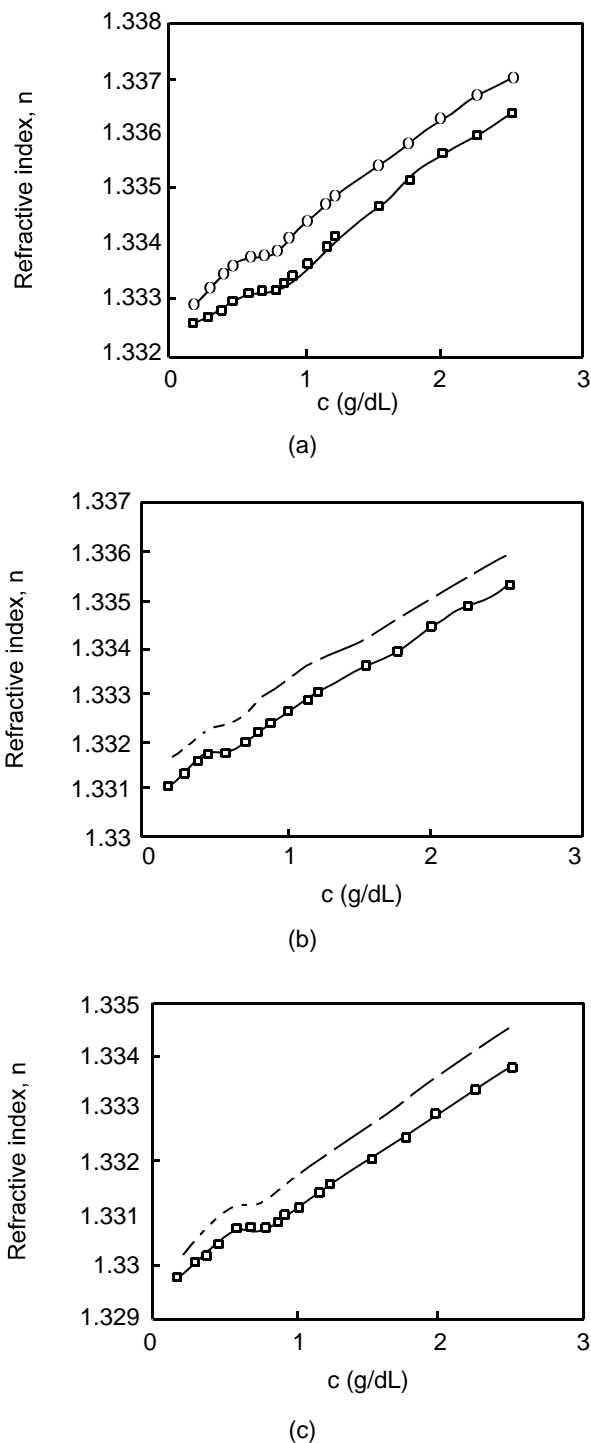


Figure 5. Plot of the refractive index versus concentration for P(VP-VA) copolymers: F (○) and A (□) at (a) 25°C, (b) 35°C and (c) 45°C, respectively.

25 C, 35 C and 45 C. As the VA content in the copolymer increased, the solution refractive index of the copolymer decreased. As shown in Figures 4 and 5, at

each certain temperature, there is a straight line consisting of few points so that in this range, the refractive index remains constant. The starting point of this range can be considered as the critical one, which corresponds to the formation of three-dimensional network in solution. After that, the higher the content of hydrophobic monomer in copolymer structure, the higher refractive index of solution can be observed.

Temperature Dependence of Refractive Index

Figure 3 shows the temperature dependence of the refractive index of polymer PVP and P(VP-VA) copolymers so that its values for polymer and all copolymers in a certain temperature are very close to each other. It should be reminded that the temperature dependence of the refractive index of the copolymer solutions should be mainly due to the temperature dependence of the refractive index of water although the effects of copolymer are important. The refractive index behaviour of all copolymers is similar and for more clarity, only copolymers C, E and F are given in Figure 3. For the sake of clarity of the effects of temperature on refractive index, we present plot of the refractive index versus concentration for P(VP-VA) copolymer C at different temperature in the Figure 4.

With increasing the temperature, the solution refractive index of copolymer C decreases.

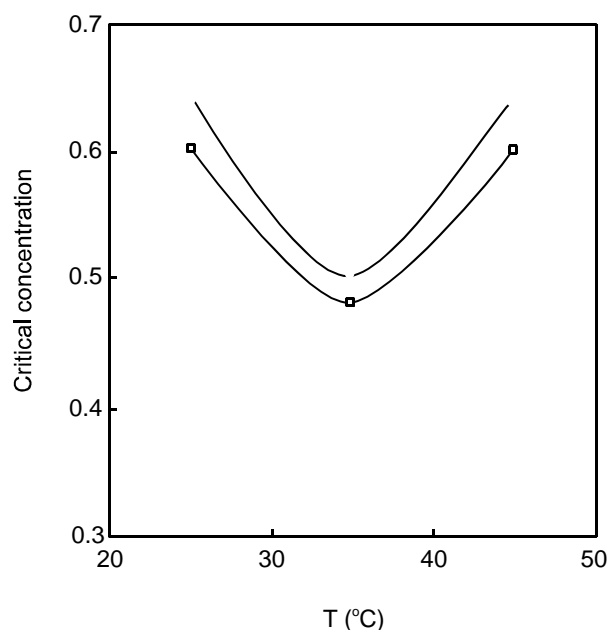


Figure 6. Variation of the dynamic (○) and static (□) critical concentration as a function of the temperature.

Figure 6 illustrates variation of the dynamic and static critical concentration as a function of the temperature for P(VP-VA) copolymer in water. There is a minimum critical concentration of copolymer appearing with increasing temperature at 35 C. The critical concentrations are lower when determined by refractive index measurements in the static state compared to the critical concentrations determined in the dynamic state using viscometer.

CONCLUSION

The hydrophobically associating behaviour of homogeneous P (VP-VA) water-soluble copolymers has been studied. The homogeneity in backbone monomer distribution of synthesized copolymers has been demonstrated by their solubility in water and their clear aqueous solutions.

The effects of hydrophobic content and temperature on the viscosity and refractive index behaviour were investigated in detail. The critical concentration C^* of the copolymers was studied in the static state and in flowing solution by refractometry and viscosimetry, respectively. The results obtained show that with increasing the hydrophobic monomer content and temperature, the viscosity and refractive index obviously decreased. The results presented in this paper show that the refractive index measurement can be a suitable method for detecting the critical concentration C^* of hydrophobically associating water-soluble polymers.

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