

Study of Rheological Behavior of Hydrophobically Modified Hydroxyethyl Cellulose

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ABSTRACT: Hydrophobically modified hydroxyethyl cellulose (BD-HAHEC) was synthesized by the macromolecular reaction of hydroxyethyl cellulose (HEC) with bromododecane (BD). Study of the effects of polymer concentration, shear rate, temperature, and electrolytes on the rheological behavior of BD-HAHEC indicated that the polymers had high viscosity, excellent viscosity retention in brine water, good thermal stability, and surface activity. Furthermore, investigation of the

micromorphology of BD-HAHEC solutions revealed the close relationship of rheological behavior and a hydrophobically associating effect. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3346–3352, 2006

Key words: water-soluble polymers; solution properties, microstructure; morphology

INTRODUCTION

Hydrophobically associating water-soluble polymers (HAWSP) are synthetic water-soluble polymers that incorporate a small amount of hydrophobic groups into the polymer molecules. When dissolved in water, the hydrophobic groups of the polymer molecules aggregate, resulting in intra- and intermolecular associations. Above a critical associating concentration (C^*), the molecular network forms and causes a rapid increase in viscosity.¹ Such water-soluble polymers are widely used in a number of applications, including enhanced oil recovery (EOR), latex paint systems, cosmetic formulations, drag reduction, flocculation, and biological/medical purposes.² However, studies of HAWSP applied in EOR have mostly concentrated on acrylamide-based copolymers, which are easy to hydrolyze under high temperature and low viscosity, and they show poor thermal stability. Moreover, excess use of this kind of polymer may pollute the earth. Hydroxyethyl cellulose, which has a stable chemical structure, good biologic compatibility, and water solubility, is especially nontoxic and environmentally friendly and has been applied widely as thickeners in food and incosmetic products and water-based paints,³ has prospects for applications in EOR.

In this study, hydrophobically modified hydroxyethyl cellulose (BD-HAHEC) was prepared, and the viscosity of HEC showed remarkable improvement and unique rheological behaviors. The supramolecular morphology of BD-HAHEC was studied by atom force microscopy (AFM) and fluorescence spectrum analysis in order to understand the associating mechanism of such polymers.

EXPERIMENTAL

Materials

Hydroxyethyl cellulose (HEC) was purchased from Merck-Schuchardt Co. (Muchen, Germany) with a degree of molar substitution (M_s) of 2.5. 1-Bromododecane (BD) was purchased from Fluka (Buchs, Germany). Both of these and other chemical agents were all of analytical purity and used as received.

Synthesis of hydrophobically modified HEC (abbreviation: BD-HAHEC)

HEC and the appropriate amount of isopropanol (IPA) were added to a three-necked bottle and then agitated and purged with nitrogen. An NaOH aqueous solution of a certain concentration was added dropwise to the bottle. After HEC had been sufficiently swelling for 24 h, BD was added slowly, and the temperature was raised to 80°C. The reaction lasted for about 10 h. Then the product was filtrated, neutralized with HCl, washed, and soaked with hexane and acetone. Finally the product was dried under

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TABLE I
Effect of Temperature on Apparent Viscosity
of BD-HAHEC

T(°C)	40	45	50	55	60
η (mPa S)	22.6	21.3	19.5	18	16.8

Polymer concentration: 0.3g/dl; shear rate: 100s^{-1} .

reduced pressure at 45°C for 5 h. The samples used in this study are listed in Table I.

Analysis and measurement

Solution viscosities were measured with a Brookfield DV-III rotator viscometer (U.S.A.). If there were no special statements, the conditions for all measurement were: temperature, 25°C; shear rate, 6 s^{-1} . Viscosity–shear rate relationship was measured by a HAKKE RV20 rotator rheometer (Germany). Surface tension was measured by a Kruss-Kiost surface tensiometer (Germany) at 25°C. Polymer molecular weight was measured with an Agilent-HP1100 liquid chromatogram (U.S.A.). FTIR analysis of the polymer composition was conducted with a Nicolet-560 infrared spectrometer (U.S.A.), and the glass-transition temperature (T_g) was measured by a Netzsch DSC 204 (Germany). AFM micrographs were acquired by an SPA 400 atom force microscope (Japan) in order to study the micromorphology of the polymer solution. The samples were prepared as follows. Polymer solutions were coated on the mica substrate first and then dried at room temperature in a desiccator. A Toshiba fluorimeter (Japan) was used to study the hydrophobic microdomain formed by the polymer molecules, and samples were prepared by dissolving Pyrene (10^{-5} M) and Rhodamine B (10^{-6}) in the polymer solution.

RESULTS AND DISCUSSION

Rheological properties of BD-HAHEC

Effect of polymer concentration on apparent viscosity of BD-HAHEC

As shown in Figure 1, the apparent viscosity of BD-HAHEC rose abruptly at a polymer concentration of 0.25 g/dL, which was determined as the critical associating concentration, C^* , of the polymer. Generally speaking, in the meantime, there exist intermolecular and intramolecular hydrophobic associations in the aqueous system of the hydrophobically associating polymers (HAPs).⁴ Below C^* , intramolecular associating dominates, the hydrodynamic volume of the polymer decreases because of the shrinkage of polymer molecules chains, and there is little change in apparent viscosity with increased polymer concentration. Above C^* , intermolecular associating dominates. A

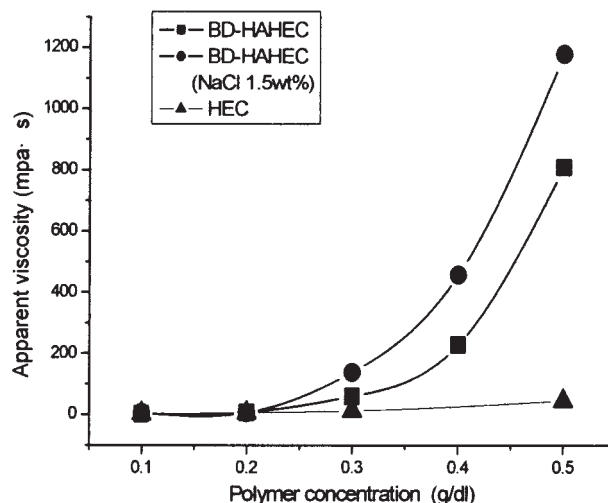


Figure 1 Effect of polymer concentration on apparent viscosity of BD-HAHEC and HEC at 25°C and 6 s^{-1} .

wide range of molecular networks forms via nodes of hydrophobic microdomains, which significantly improves the hydrodynamic volume and leads to a sharp increase in the apparent viscosity. It was reported⁵ that the same kind of HAHEC reaches a apparent viscosity of 450 mPa S at a concentration of 2 g/dL, whereas BD-HAHEC can reach 450 mPa s at a concentration of 0.45 g/dL under the same measurement conditions and shows remarkable improvement in the viscosity of HEC.

Effect of shear rates on apparent viscosity of BD-HAHEC

As shown in Figure 2, with an increase in shear rate, BD-HAHEC first behaved like a pseudoplastic prop-

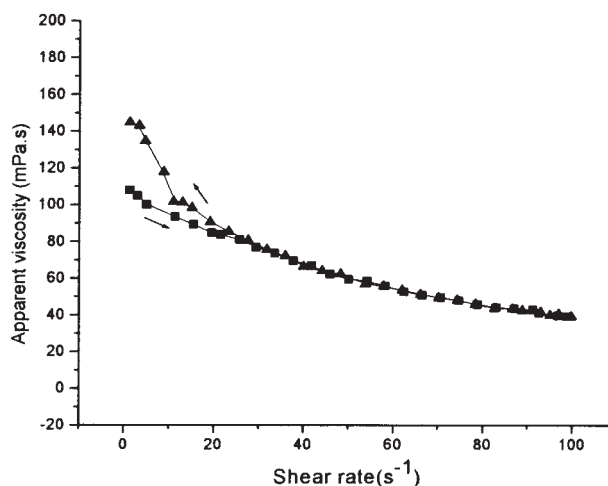


Figure 2 Effect of shear rate on current viscosity at 25°C (polymer concentration: 0.3 g/dL, NaCl concentration: 1.5 wt %).

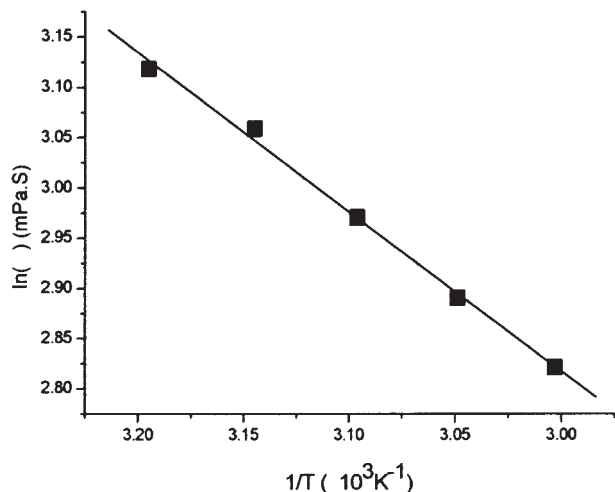


Figure 3 Dependence of apparent viscosity on temperature.

erty, and the apparent viscosity decreased sharply, indicating rapid damage to molecular networks built up by the relatively weak hydrophobic association. When the shear rate was higher than 80 s^{-1} , apparent viscosity did not change obviously anymore and remained at about $40 \text{ mPa} \cdot \text{s}$. When the shear application was removed, the hydrophobic association networks could recover and were enhanced, which indicated that during the shear process, there was a kind of dynamic equilibrium between associating and not associating in the polymer molecules.⁶

Effect of temperature on apparent viscosity of BD-HAHEC

Viscous activation energy (E_a) can be used to characterize the ability of BD-HAHEC to retain apparent viscosity under high temperatures. The Arrhenius formula can be used to express the relationships between E_a and viscosity:

$$\eta = A \cdot \exp[E_a/(RT)]$$

It can also be written as:

$$\ln(\eta) = \ln A + (E_a/R)(1/T)$$

The $\ln(\eta) - 1/T$ curve (Fig. 3) was plotted from apparent viscosity values under various temperatures (Table I), and the equation could be deduced from it:

$$\ln(\eta) = 1.5867(1/T) - 1.9429$$

Combining with the Arrhenius formula, the E_a of the polymer could be calculated,

$$E_a = 13.2 \text{ kJ/mol}$$

where the E_a of polyacrylamide (PAM; $M_n = 3.0 \cdot 10^6$) was about 24 kJ/mol .

For an individual polymer, a higher E_a meant higher sensitivity of the polymer to temperature and greater loss of viscosity under high temperatures. Therefore, to some degree, the lower E_a of BD-HAHEC showed better thermal stability than PAM.

Effect of additional electrolytes on apparent viscosity of BD-HAHEC

The addition of NaCl led to increased polarity of the polymer solution and much stronger hydrophobic association. The crosslinking molecular networks formed in the greater range and the apparent viscosity of the polymer solution dramatically rose. As shown in Figure 4, the highest viscosity was reached at about 6 wt % NaCl, after which it decreased. A too-strong hydrophobic association resulted in phase separation, loss of viscosity, and a decreased rate of light transmission in the polymer solution.

Surface activity of BD-HAHEC

Because long-chain alkanes have a tendency to move to the water's surface, leading to decreased surface tension,⁷ the HEC and BD-HAHEC solutions both showed lower surface tension than did deionized water (about 71.8 mN/m). However, HEC remained at about $64\text{--}65 \text{ mN/m}$ with an increase in polymer concentration, but BD-HAHEC showed a different, complex tendency to change (Fig. 5). The surface tension of BD-HAHEC first dropped to its lowest point, about 56.8 mN/m , at a polymer concentration of 0.2 g/dL . This phenomenon could be explained by the number of nonpolar long alkane chains arrayed on the surface of the water gradually increasing with increasing polymer concentration.

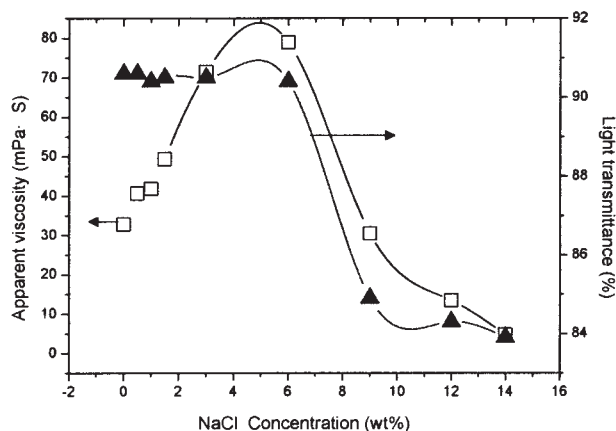


Figure 4 Effect of NaCl concentration on apparent viscosity and light transmittance of BD-HAHEC in an aqueous solution at 25°C and 6 s^{-1} .

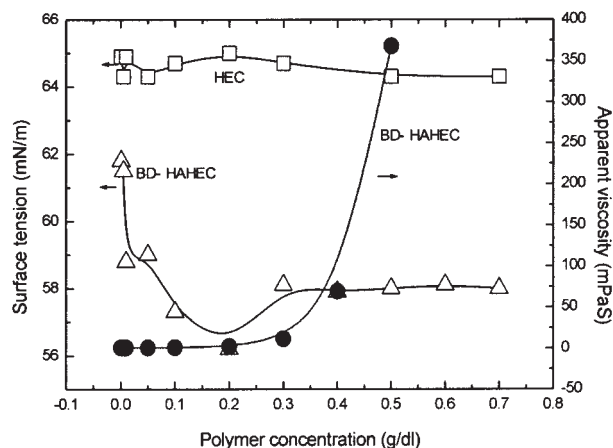


Figure 5 Effect of concentration on surface tension of polymer solution at 25°C.

Interestingly, after reaching its lowest point, above a polymer concentration of 0.3 g/dL, the surface tension increased to and remained at about 58 mN/m; meanwhile the apparent viscosity also increased sharply at about the same concentration, at which intermolecular association dominated. So the strong associations of BD-HAHEC molecules may have prevented their carbon chains from transferring to the surface and even dragged some of the alkane chains back to the inner water system, resulting in a looser arrangement of molecules on the surface, which naturally led to increased surface tension. Moreover, because of the hindrance of crosslinking molecular networks formed by the hydrophobic associating of the polymer molecules, it was more difficult at higher polymer concentrations for the alkane chains to move up to the water's surface, and so the surface molecular density and the surface tension remained fixed.

Microstructure of BD-HAHEC aqueous solution

To maintain the good water solubility of the hydrophobically modified polymers, usually not more than 1 mol % hydrophobic groups were introduced into the polymer molecules,⁴ which makes it much more difficult for the structure and composition of the polymers to be analyzed by normal methods. In this study, FTIR and DSC were used to qualitatively describe the change in the molecular structure of HEC after hydrophobic modification.

Polymer molecular weight measurement

As shown in Figure 6, the liquid chromatogram analysis indicated that HEC and BD-HAHEC had almost the same molecular weight, 1.18×10^5 and 1.17×10^5 , respectively, which means that very small changes in the composition and structure of HEC occurred after the hydrophobic modification reaction. The molecular weight distribution of BD-HAHEC became slightly wider than that of HEC, and the polymer with the lowest molecular weight increased because very little decomposition of the polymer occurred during the macromolecular reaction in strong alkali and at high temperature.

FTIR spectrum analysis

The differences in infrared absorption peak intensity between HEC and BD-HAHEC are shown in Figure 7. Although the peak at $3000\text{--}3600\text{ cm}^{-1}$ acted as an internal standard, compared with HEC, the absorption peaks of BD-HAHEC-1 and BD-HAHEC-2 at $1210\text{--}1000$ and 2900 cm^{-1} were considerably higher. The peaks at $1210\text{--}1000\text{ cm}^{-1}$, which represent the stretching vibration of C—O and the asymmetric stretching vibration of C—O—C, were attributed to

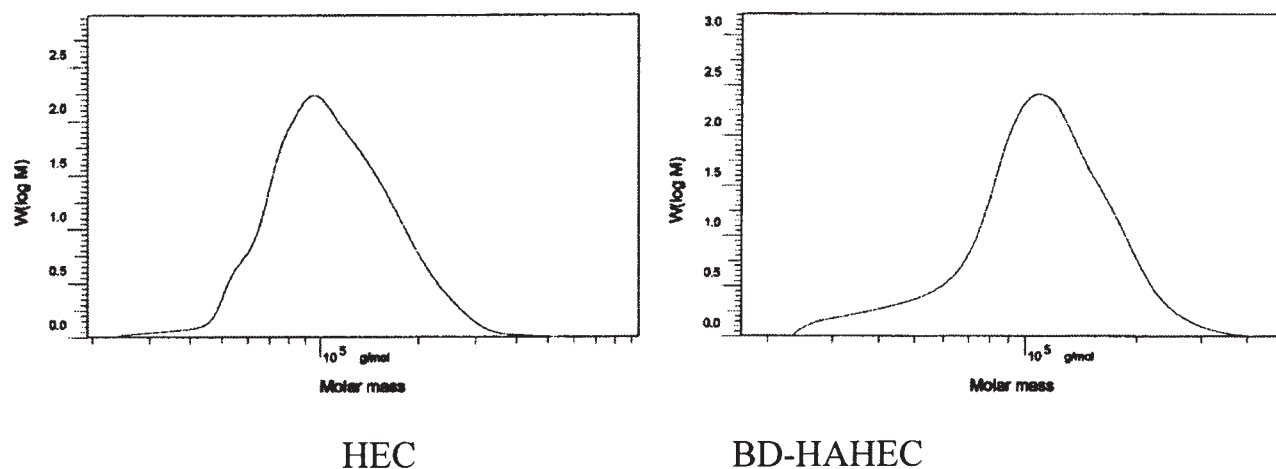


Figure 6 Molecular weight of HEC and BD-HAHEC measured by liquid chromatogram.

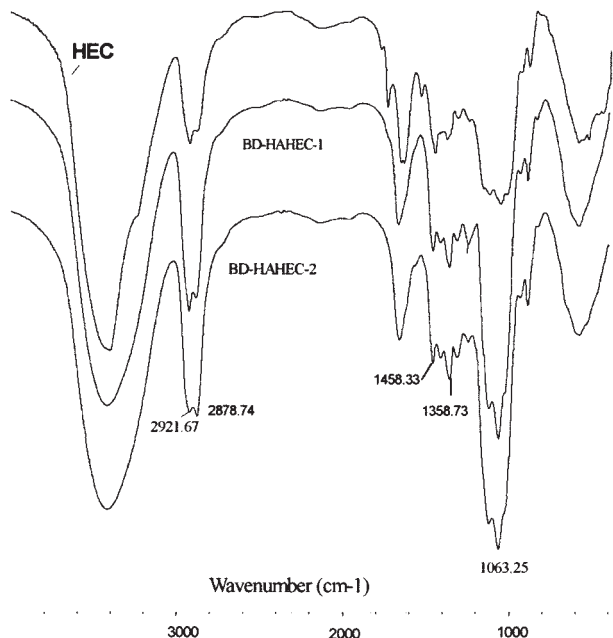


Figure 7 FTIR of HEC and BD-HAHEC.

the increase in the ether linkages of the HEC molecules. And the peaks at 2900 cm^{-1} , which represent the stretching vibration of C—H, were attributed to the increased number of alkane structures in the HEC molecules. The absorption peaks around 1375 and 1450 cm^{-1} represent the symmetric bending and asymmetric vibrations of CH_3 and CH_2 , respectively. From the above description, we could safely draw the conclusion that alkanes groups were introduced into the HEC molecules.

DSC analysis

As shown in Figure 8 and Table II, BD-HAHEC displayed a higher glass-transition temperature (T_g) and

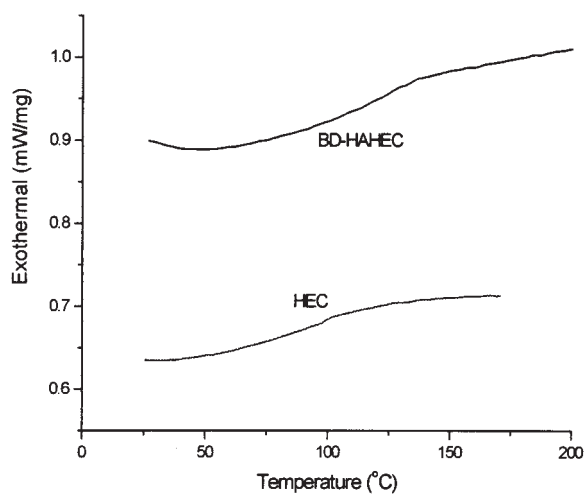


Figure 8 DSC of HEC and BD-HAHEC.

TABLE II
Glass-Transition Temperature and Enthalpy
of HEC and BD-HAHEC

Sample	T_g ($^{\circ}\text{C}$)	ΔC_p ($\text{J g}^{-1} \text{K}^{-1}$)
HEC	98.51	0.162
BD-HAHEC	124.17	0.208

more enthalpy than did HEC, which shows that the movement of the chain segments of BD-HAHEC was more difficult after incorporation of the long alkane chains.

AFM study

The viscosity of the BD-HAHEC solution was closely related to its micromorphology, such as degree of aggregation, size and density of aggregate particles, manner in which particles arrayed, and so on.

At a polymer concentration of 0.1 g/dL , the polymer molecules formed aggregates of small particles, about 100 nm in diameter, as highlighted in Figure 9. The particles further linked with each other and formed mountainlike structures (shown as circled domains in Fig. 9). With the increase of the polymer concentration to 0.4 g/dL of the polymer solution and with $1.5\text{ wt } \%$ NaCl, a great number of much larger aggregates ($3\text{--}4\text{ }\mu\text{m}$) appeared, as shown in Figure 10. Some of them were sticklike aggregates, some composed of at least two “sticks,” whereas others were flowerlike aggregates. Also observed were many small particles about $100\text{--}200\text{ nm}$ in size, which tended to approach the aggregates. More delicate structures can be observed in Fig. 10(c1–c3). It is clear that the slim sticklike structures were composed of particles about 100 nm in size. Such transformations of microstructures were coincident with the remarkable increase in the apparent viscosity of the polymer solution.

Fluorescence spectrum study. The ratio of peak I_{\parallel} to peak I_{\perp} (I_{\parallel}/I_{\perp}) in the pyrene emission spectrum was used to characterize the polarity of the local

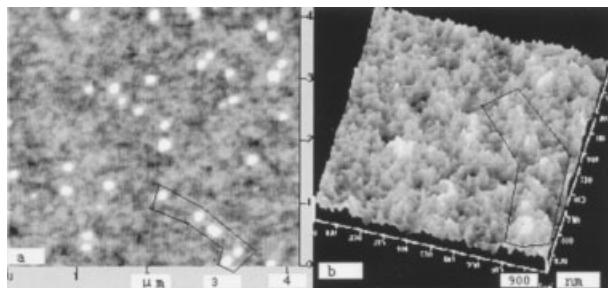


Figure 9 AFM image of BD-HAHEC at 0.1 g/dL polymer concentration.

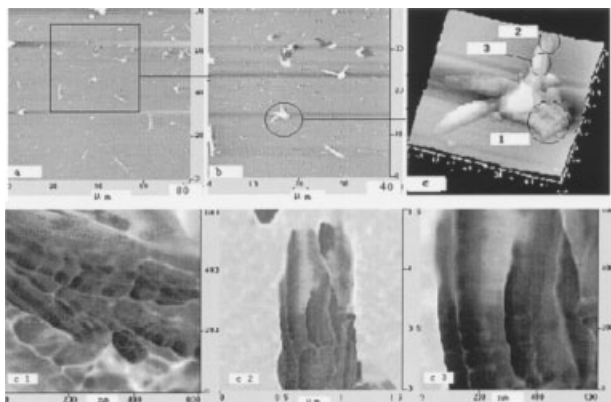


Figure 10 AFM image of BD-HAHEC at 0.4 g/dL polymer concentration and 1.5 wt % NaCl.

environment of the solution.⁸ It can be seen in Figure 11 that with an increase in polymer concentration, I_{\perp}/I_{\parallel} continued to decrease, indicating the reduced polarity of the hydrophobic microdomain. It was suggested⁹ that at relatively low polymer concentrations, associations of polymer molecules form when no network forms. Therefore, below C^* (0.3g/dL), I_{\perp}/I_{\parallel} decreased greatly, whereas the apparent viscosity of the polymer solution changed only a little. Moreover, the trend of decreasing polarity, from 0.1 to 0.4 g/dL, was just coincident with the increasing aggregation shown in the AFM micrograph. Above C^* , extensive intermolecular association led to the formation of network structures and a great increase in the viscosity of the polymer solution, while I_{\perp}/I_{\parallel} decreased slowly and solution polarity tended to be stable.

The degree of fluorescent polarization of RhB can be defined as the following formula:

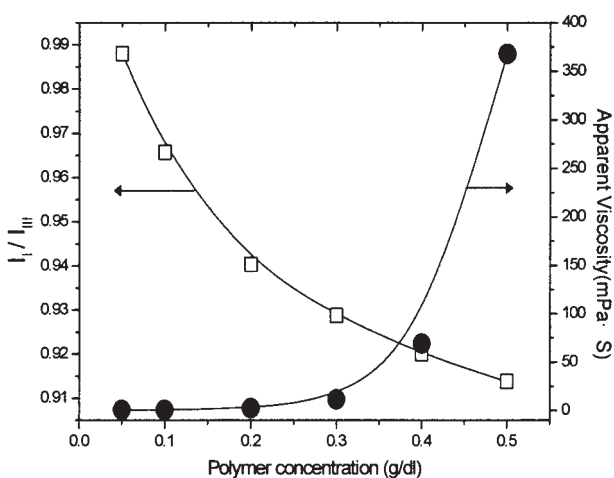


Figure 11 Effect of polymer concentration on I_{\perp}/I_{\parallel} of pyrene fluorescence.

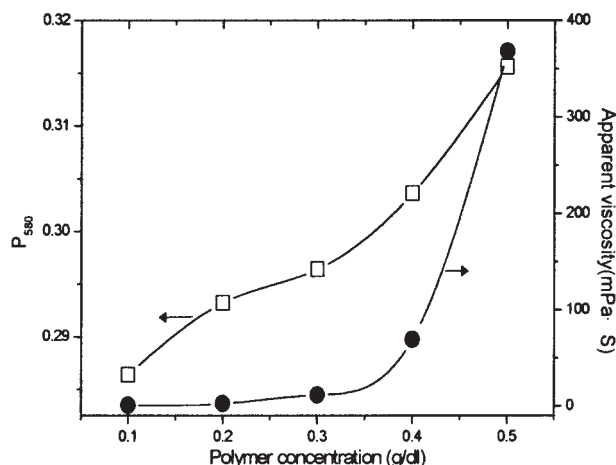


Figure 12 Microphase viscosity of BD-HAHEC.

$$P\lambda_{\max} = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$$

where I_{\parallel} and I_{\perp} are the intensity of the parallel light and the vertical light, respectively, of the excitation spectrum. This formula is commonly used to characterize the local viscosity of a solution.¹⁰ Figure 12 shows that with an increase in the polymer concentration, the local viscosity of the solution microenvironment continued to increase, which also indicated aggregation of the hydrophobic groups. However, only when a enough such microaggregations had formed could the macroviscosity begin to increase. This explains why the apparent viscosity of the polymer solution increased more slowly than did that of the local viscosity of the polymer solution.

CONCLUSIONS

Hydrophobically modified hydroxyethyl cellulose (BD-HAHEC) with remarkably enhanced viscosity was prepared. It showed unique rheological behavior such as excellent retention of viscosity in brine water, good thermal stability, and surface activity. FTIR and DSC analysis indicated the incorporation of hydrophobic long alkane chains. The supramolecular morphology and associating mechanism of BD-HAHEC were studied by the atom force microscopy and fluorescence spectrum analysis, which further demonstrated that transformations of microstructures from small particles to large sticklike aggregates were coincident with the remarkable increase in the apparent viscosity of the polymer solution, and the hydrophobic associating of the polymer solution, both inter- and intramolecularly, started much earlier than did the drastic change in macrorheological behavior. These changes are favorable for improvement of the proper-

ties and the increased use of natural polymers such as hydroxyethyl cellulose.

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