

Study on the Rheological Behavior of the Hydrophobically Modified Hydroxyethyl Cellulose with 1,2-Epoxyhexadecane*

Lin Ye, Qin Li, Ronghua Huang

The State Key Lab. of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, People's Republic of China

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ABSTRACT: Through the macromolecule reaction method, the hydrophobically modified hydroxyethyl cellulose (EP16-HAHEC) was synthesized using 1, 2-epoxyhexadecane as the hydrophobic monomer. The solution properties of EP16-HAHEC were comprehensively investigated, which showed that the polymer with enhanced; viscosification property, thermal stability, shear resistance, and salt resistance was obtained. Amphiphilic structure of EP16-HAHEC molecules contributed to the surface activity of the polymer. By forming complex solution with surfactants or carboxymethyl cellulose (CMC), the viscosification property of EP16-HAHEC could be enhanced through the interactions of hydrophobic groups and hydrogen bonds. The viscosity-enhancing mechanism of HAHEC was studied by the environment scan electronic micro-

scope (ESEM) and the fluorescence spectrum measurements, which demonstrated that the formation of the supramolecular aggregation networks was coincident with the increase of the apparent viscosity of HAHEC. With the gradual formation of the complete polymer molecule networks, the apparent viscosity rised dramatically, and the associating aggregations of the polymer molecules appeared far before the great change of the macroproperty of the polymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2953–2959, 2006

Key words: hydrophobically-associating hydroxyethyl cellulose; rheological behavior; supramolecular aggregation; associating-viscosification mechanism

INTRODUCTION

Hydrophobically associating water-soluble polymers (HAWSP) have become of great interest in recent years, which are synthetic water-soluble polymers by incorporating a small amount of hydrophobic groups into the polymer molecules. When dissolved in water, the hydrophobic groups of the polymer molecules aggregate and result in intra and intermolecular associating. Above a critical associating concentration (C^*), the molecular network forms and causes a rapid increase in viscosity.¹ Such water-soluble polymers has proved to be of great technological importance, especially for tertiary oil recovery, latex paint systems, cosmetic formulation, drag reduction, flocculation, biological/medical purposes, etc.² However, the studies on HAWSP used in EOR almost concentrate on the acrylamide-based copolymers, which are easy to hydrolyze under high temperature, lose viscosity, and

show poor thermal stability. Hydroxyethyl cellulose, which has stable chemical structure, good biologic compatibility, and water solubility, and has been applied widely as thickeners in food, cosmetic products, and water-based paints, displaying application prospects in EOR.³

In this article, the hydrophobically modified hydroxyethyl cellulose (EP16-HAHEC) was prepared using 1, 2-epoxyhexadecane as the hydrophobic monomer. The viscosity of HEC was remarkably improved, and showed unique rheological behaviors.

EXPERIMENTAL

Materials

Hydroxyethyl cellulose (HEC), analytical purity, was purchased from Merck-Schuchardt Co. (Germany), where the molar substitution degree (M_s) is 2.5, and M_w is 118,000 g/mol. 1,2-Epoxyhexadecane (EP16) was purchased from Fluka (Germany). Carboxymethyl Cellulose, 90% purity, was purchased from Baiyun Cellulose Factory (Chongqing, China), where the degree of substitution (DS) is 0.75, and M_w is 76,000 g/mol. Both sodium dodecyl sulfate (SDS) and isopropanol (IPA), analytical purity, were purchased from Kelong Chemical Factory (Chengdu, China). All the agents were used as received.

Correspondence to: L. Ye (yelinwh@126.com).

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TABLE I
Apparent Viscosity of EP16-HAHEC in Aqueous Solution

Polymer concentration (g/dL)	0.1	0.2	0.25	0.3	0.4	0.5
Apparent viscosity (mPa s)	2.67	4.00	53.3	334.6	826.2	1969

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

HEC and appropriate amount of isopropanol (IPA) were added to a three-necked bottle, then agitated and purged with nitrogen. NaOH aqueous solution of a certain concentration was added dropwisely to the bottle. After HEC had been sufficiently swelled for 24 h, EP16 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 to PH 7–8, washed, and soaked with hexane and acetone. Finally the product was dried under the reduced pressure at 45°C for 6 h. The samples used in this study are listed in Table I.

Analysis and measurement

Solution viscosities were measured using a Brookfield DV-III rotator viscometer (USA). If there are no special statements, the measurement conditions were all as follows: temperature, 25°C; shear rate, 6 s⁻¹. Viscosity–shear rate relationship was measured at 25°C by a HAKKE RV20 rotator rheometer (Germany). Surface tension was measured by Kruss-Kiost a surface tensiometer (Germany) under 25 ± 0.1°C. FTIR analysis of the polymer composition was conducted with a Nicolet-560 infrared spectrometer (USA). The UV analysis of the intermolecular hydrogen bonding interaction for the complex polymer solution was performed with a Shimadzu UV-240 spectrometer (Japan). The environment scanning electronic microscope (ESEM) analysis was performed by an ESEM XL30 microscope from Philips Co. (The Netherlands) to study the micromorphology of the polymer solution with a 2.7–5 Torr of the measurement pressure and –2.8°C of the measurement temperature. TOSHIBA fluorimeter (Japan) was used to study the hydrophobic-microdomain formed by the polymer molecules. Samples were prepared by dissolving Pyrene (10⁻⁵ M) and Rhodamine B (10⁻⁶ M) in the polymer solution.

RESULTS AND DISCUSSION

The solution properties of EP16-HAHEC

The viscosification performance

As shown in Figure 1, the apparent viscosity of EP16–HAHEC rose abruptly at the polymer concentration of 0.2 g/dL, which can be determined as the critical associating concentration C* of the polymer. The ap-

parent viscosity can reach 826.2 mPa s at 0.4 g/dL of the polymer concentration, which was over 40 times of that for HEC at the same concentration. There exists intermolecular and intramolecular hydrophobical associations in the mean time for the aqueous solution of HAWSP. Below C*, the intramolecular associating dominates, the hydrodynamic volume of the polymer decreases due to the shrinkage of polymer molecule chains, and there is little change for the apparent viscosity with the increase of polymer concentration. Above C*, the intermolecular associating dominates. Wide-range dynamic crosslinking molecular networks form via nodes of hydrophobic microdomains, which significantly increases the hydrodynamic volume and leads to the sharp ascending of the apparent viscosity.⁴

Temperature effect

Figure 2 displayed the effect of temperature on the apparent viscosity of the polymer solutions. Before 50°C, a sharp decrease in viscosity was observed with increasing temperature, and then remained stable at the viscosity of about 10 mPa s. The temperature–viscosity relationship was complex, and different for different polymer solution systems. Temperature increase made the movement of water molecules and hydrophobic groups increase, and the hydration spheres of the hydrophobic groups change a great deal, which were unfavored for the interchain association of the copolymers. Hydrophobic hydration was exothermic while hydrophobe–hydrophobe interaction was endothermic, and the viscosity may increase upon heating by an entropy driven increase in hydrophobic bonding.⁵

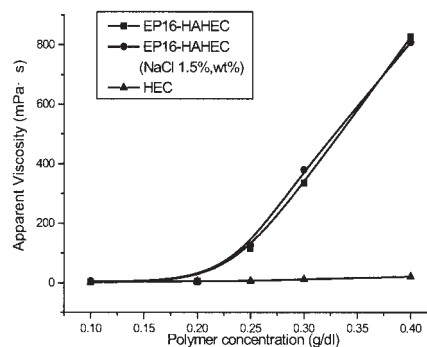


Figure 1 Effect of polymer concentration on the apparent viscosity of EP16–HAHEC at 25°C and 6 s⁻¹.

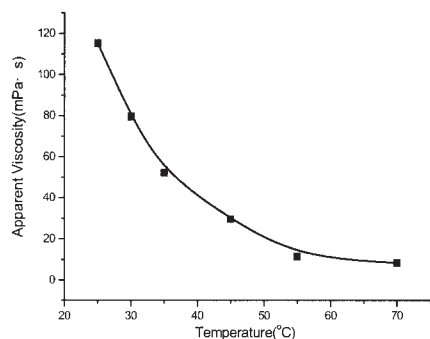


Figure 2 Effect of temperature on the apparent viscosity of EP16-HAHEC in 1.5% NaCl aqueous solution at 25°C and 6 s^{-1} .

Ionic strength effect

Addition of NaCl led to the increase of the polarity of the polymer solution and strengthening of the hydrophobic association. The crosslinking molecular networks formed in greater range, and the apparent viscosity of the polymer solution dramatically rose. As shown in Figure 3, the viscosity curve obtained a climax at about 5 wt % NaCl, and then above it the viscosity decreased, resulting from the too strong hydrophobically association, the phase separation of the polymer solution and the formation of some microhydrogels, which was coincident with the drop of the light transmittance rate.

The kinetic rheologic behavior

As shown in Figure 4, with the increase of the shear rate, EP16-HAHEC first behaved as a pseudoplastic behavior and the apparent viscosity decreased sharply, which indicated the rapid damages of molecular networks built up by the relatively weak hydrophobic association. When the shear application was removed, the hydrophobic association networks can

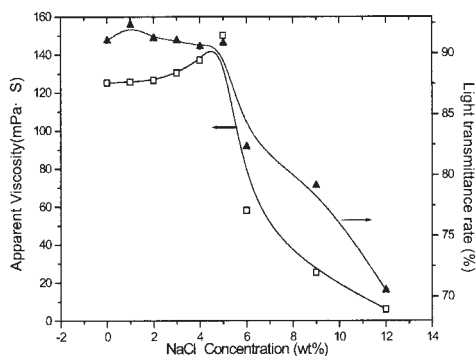


Figure 3 Effect of NaCl concentration on the apparent viscosity and light transmittance rate of EP16-HAHEC in aqueous solution at 25°C and 6 s^{-1} (polymer concentration: $0.25 \text{ g} \cdot \text{dL}^{-1}$).

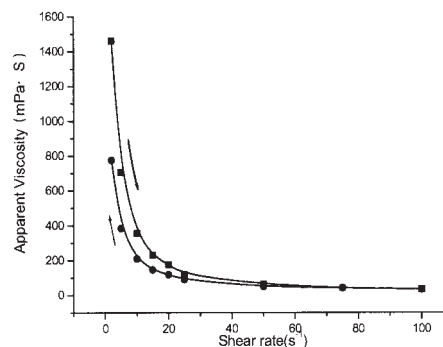


Figure 4 Effect of shear rate on the apparent viscosity of EP16-HAHEC at 25°C (NaCl concentration: 1.5 wt %, polymer concentration: 0.3 g/dL).

recover, but showed a stagnant of viscosity. During the shear process, there existed a kind of dynamic equilibrium between associating and unassociating of the polymer molecules,⁶ which has the character of time dependence. For the polymer molecules with long side chains, it needed more time for the molecule aggregations to form. The area formed by the two curves (viscosity increase and decrease with shear rate) can denoted the association degree of the polymer system. The larger the area, the stronger the association, and the more complex and complete the supramolecular aggregation networks.

As shown in Figure 5, at 5 s^{-1} of the shear rate, the apparent viscosity of the polymer solution decreased abruptly with time, and tended to be stable in 2 min; at 100 s^{-1} of shear rate, the apparent viscosity decreased with time at first, and becomes stable in 0.5 min; at 10 and 20 s^{-1} of the shear rate, the apparent viscosity reached the lowest value in 2.5 min, recovered to a certain value afterwards, and tended to be stable in 5 min. There were two situations for the hydrophobically associating polymer solutions during the shear process. The supramolecular aggregation networks were destroyed under shear application re-

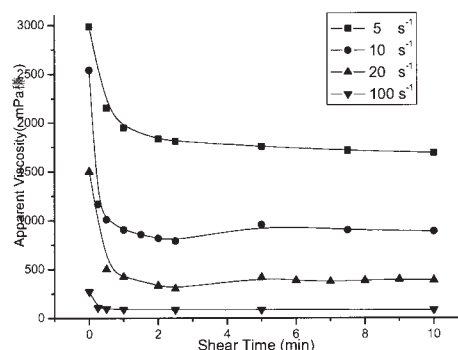


Figure 5 Effect of shear time on the apparent viscosity of EP16-HAHEC at 25°C (NaCl concentration: 1.5 wt %, polymer concentration: 0.5 g/dL).

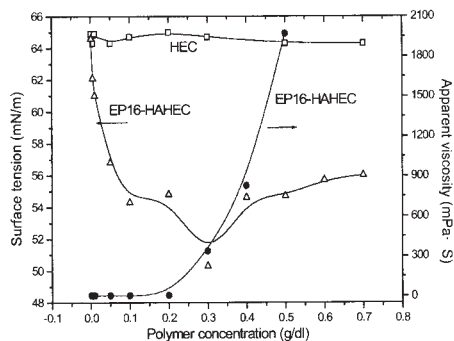


Figure 6 Effect of polymer concentration on the surface tension of EP16-HAHEC at 25°C.

sulting in the decrease of the hydrodynamic volume and the apparent viscosity. On the other hand, the entanglement of the molecules and the molecules in the state of intramolecule associations gradually extended, orientated, and the hydrophobic alkanes associated with each other under a certain shear rate leading to the increase of the hydrodynamic volume and the apparent viscosity.⁴ Therefore, this kind of polymer displayed very complex rheological behaviors.

Surface activity

Long-chain alkanes have a tendency to move to the surface of the aqueous solution and lead to the decrease of the surface tension. Amphiphilic structure of EP16-HAHEC molecules contributed to the surface activity of the polymer. As shown in Figure 6, both HEC and EP16-HAHEC solutions showed lower surface tension than that of the deionized water (about 71.8 mN/m). However, the former remained about 64–65 mN/m with the increase of polymer concentration, and the later showed a differently complex-changing tendency. The surface tension of EP16-HAHEC dropped first until it got to the lowest point of about 50.3 mN/m at the polymer concentration of 0.3 g/dL, then rose obviously, and kept about 55 mN/m;

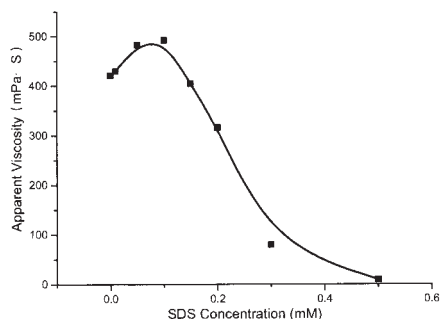


Figure 7 Effect of SDS concentration on the apparent viscosity of EP16-HAHEC at 25°C and 6 s^{-1} (polymer concentration: 0.25 g/dL).

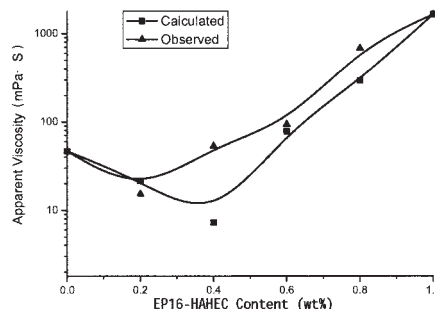


Figure 8 Apparent viscosity of EP16-HAHEC/CMC composite solution with 0.5 g/dL polymer concentration.

meanwhile, the apparent viscosity also increased sharply, and the intermolecular association dominated at this polymer concentration. The strong associations of EP16-HAHEC molecules may prevent carbon chains on them from transferring to the surface, and even drag some of the alkane chains back to the inner water system and result in a looser molecules arrange on the surface, which naturally led to the increase of surface tension.

The complex solution

EP16-HAHEC/surfactant

As shown in Figure 7, in the range of 0–0.1 mM SDS concentration, the complex micelle was formed by the interaction of the surfactant molecules with the hydrophobic groups of the polymer molecules, leading to the formation of the supramolecular crosslinking networks in the solution and the increase of the apparent viscosity. In the range of 0.2–0.5 mM SDS concentration, the complex micelle was formed by the interaction of the surfactant molecules with the hydrophobic groups of a single polymer molecule and inhibited the formation of the intermolecular associations, resulting in the dramatic decrease of the apparent viscosity of the polymer solution.

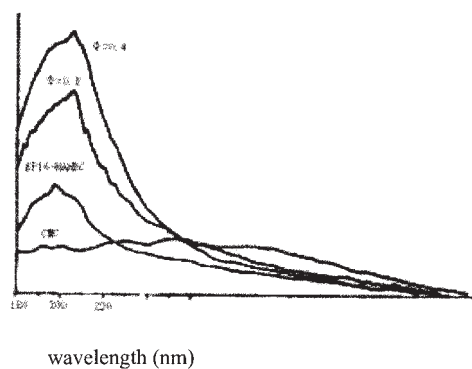


Figure 9 Ultraviolet spectrum of CMC/HAHEC.

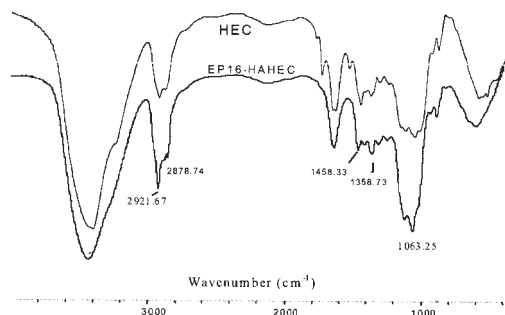


Figure 10 FTIR of HEC and EP16-HAHEC.

EP16-HAHEC/carboxymethyl cellulose (CMC)

According to the compounding principle for the double-composition polymer solutions,^{7,8} the relationship between the apparent viscosity of the compounding solutions and single-composition solution can be expressed as the following equation:

$$\lg \eta = x \lg \eta_1 + (1 - x) \lg \eta_2 \quad (1)$$

where η_1 and η_2 were the apparent viscosity of the first and second composition in the solution respectively, and x was the wt % of the first composition versus the whole compounding solution. Figure 8 displayed the comparison of the theoretical viscosity obtained from eq (1) and the actual viscosity of the EP16-HAHEC/CMC composite solution, and the ac-

tual viscosity of the composite solution was much higher than the theoretical value in the whole composite ratios except $\phi = 0.2$ (ϕ : the wt % of EP16-HAHEC in the composites), indicating that there maybe exist a certain amount of molecular complex in the composite solutions resulting in the increase of the hydrodynamic volume and the rise of the apparent viscosity.

The ultraviolet spectrum was measured for $0.5 \text{ g} \cdot \text{dL}^{-1}$ of EP16-HAHEC solution with composite ratio $\phi = 0.8$ and $\phi = 0.4$, and 0.5 g/dL of CMC solution, as shown in Figure 9. It was found that in the range of 190–220 nm, there was no absorption peak for CMC solution, and the absorption peak appeared at 197 nm for EP16-HAHEC solution and 204 nm for all the CMC/EP16-HAHEC composite solution. The red displacement of the absorption peak indicated that the molecular compound was formed by the hydrogen bonding interaction in the composite solution.¹⁹

The characterization of the supramolecular aggregations of EP16-HAHEC

FTIR spectrum analysis

To keep 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 made it much difficult for the structure and composition of the polymer to be ana-

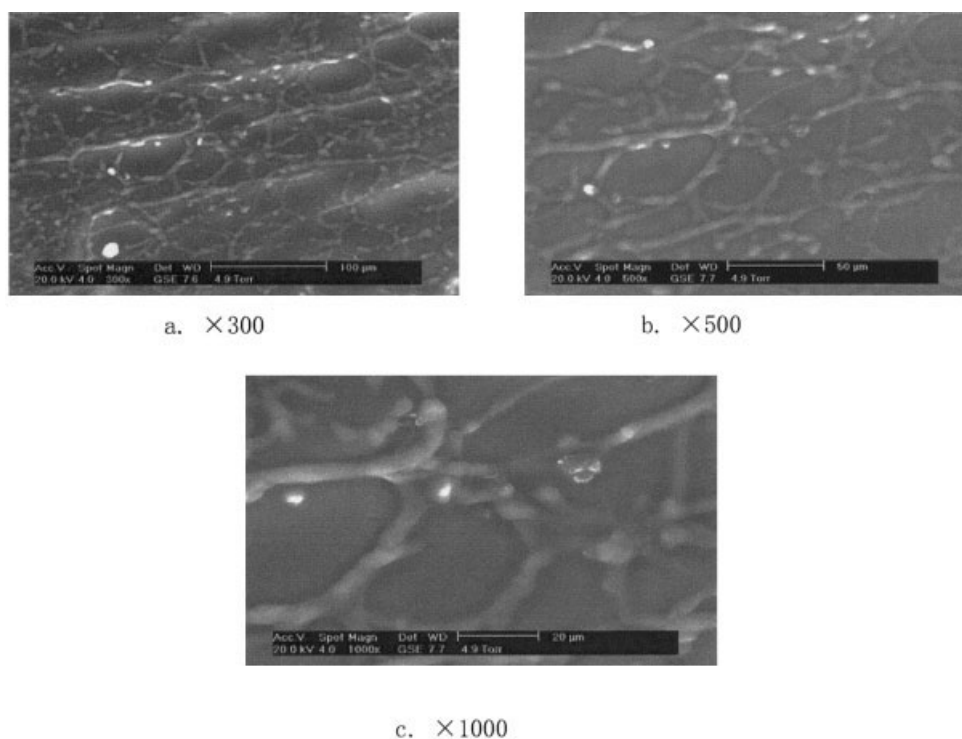


Figure 11 ESEM of 0.2 g/dL EP16-HAHEC in aqueous solution.

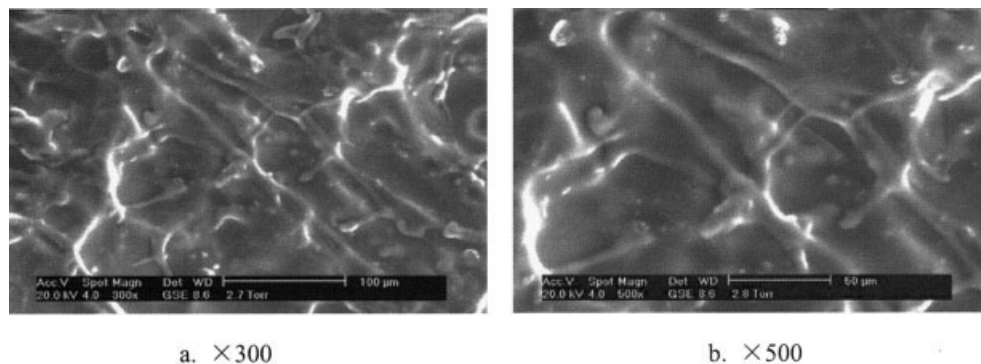


Figure 12 ESEM of 0.25 g/dL EP16-HAHEC in aqueous solution.

lyzed by normal methods. In this article FTIR was applied to qualitatively describe the change of the molecular structure of HEC by hydrophobically modification.

The difference of the infrared absorption peak intensity between HEC and EP16-HAHEC was shown in Figure 10. Although the peak at 3000–3600 cm^{-1} acted as an internal standard, compared with HEC, the absorption peaks of EP16-HAHEC at 1210–1000 and 2900 cm^{-1} were considerably enhanced, and the same as the peak at 1375 and 1450 cm^{-1} . The peaks at 1210–1000 cm^{-1} that represented the stretching vibration of C—O and the asymmetric stretching vibration of C—O—C was attributed to the increase of ether linkages at HEC molecules. The peaks at 2900 cm^{-1} that represented the stretching vibration of C—H was attributed to the increase of alkane structures of HEC molecules. The absorption peaks around 1375 and 1450 cm^{-1} , respectively, represented the symmetric bending vibration and asymmetric vibration of CH_3 and CH_2 . From the above description, it can be confirmed that the alkanes group was introduced to the HEC molecules.

ESEM analysis

The apparent viscosity of EP16-HAHEC at different concentrations was listed in Table I, indicating that the critical association concentration was around 0.2 g/dL. The polymer samples with polymer concentration of 0.2, 0.25, and 0.5 g/dL were applied to the study on the aggregation morphology in the solution.

As shown in Figure 11, the supramolecular aggregation networks were formed in the solution, but slender and not so complete at the polymer concentration of 0.2 g/dL. The string diameter of the networks is about 5 μm , and there was no dramatic increase of the apparent viscosity.

As shown in Figure 12, when the polymer concentration exceeded C^* and reaches 0.25 g/dL, the supramolecular aggregation networks become more dense and complete, the dimension of the crosslinking

structure increased, and the apparent viscosity increased dramatically, resulting from the hydrophobic associations of the polymer molecules. As shown in Figure 13, when the polymer concentration reaches 0.5 g/dL, the supramolecular aggregation networks became quite dense and complete, and the much high apparent viscosity was achieved.

The microphase viscosity of the polymer solution

Pyrene has very low solubility in water, and can dissolve in the micelle. The ratio of the pyrene fluorescence intensity of the first band to that of the third band (I_1/I_3) is related to the polarity of the local environment.¹⁰ As shown in Figure 14, the I_1/I_3 values decreased with the increase of the polymer concentration, indicating that HAHEC provides more hydrophobic microdomains for the pyrene molecules. At low polymer concentration, there was a rapid drop for I_1/I_3 , indicating that many hydrophobic associating aggregations have formed, although there was no supramolecular aggregation networks and dramatic increase of the apparent viscosity for the polymer solution. At high polymer concentration, the solution polarity and I_1/I_3 declined slowly due to the very slow formation of the new associating aggregations.

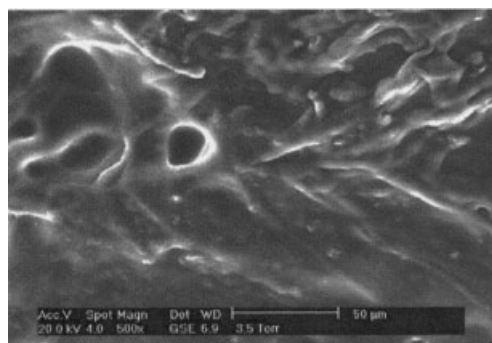


Figure 13 ESEM of 0.5 g/dL EP16-HAHEC in aqueous solution ($\times 500$).

The solution microphase viscosity can be characterized with the fluorescence vibration degree of Rhodamine B, which calculation formula is expressed as follows:

$$P_{\max}^{\lambda} = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$$

where, P_{\max}^{λ} denotes vibration degree, I_{\parallel} and I_{\perp} denote the fluorescence intensity parallel and vertical with the vibration direction of the inspection meter, respectively. As shown in Figure 15, the solution microphase viscosity increased with the increase of the polymer concentration, indicating the increase of the hydrophobic domains and associating aggregations. But only a small amount of aggregations and networks formed; the apparent viscosity of the solution can have a large ascending form. Therefore, the increase of

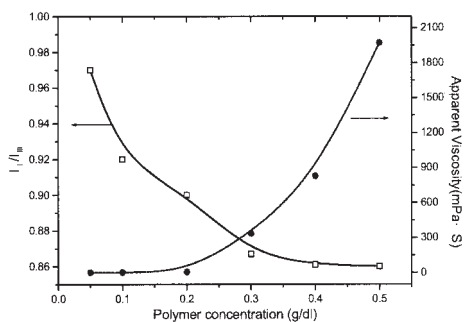


Figure 14 Effect of the polymer concentration on I_{\parallel}/I_{\perp} .

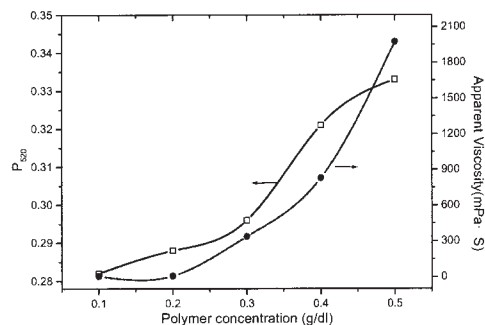


Figure 15 The microphase viscosity of EP16-HAHEC in aqueous solution.

the macrophase viscosity lagged behind the increase of the microviscosity.

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