

# A Study on the Solution Behavior of IPBC-Hydrophobically-Modified Hydroxyethyl Cellulose

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**ABSTRACT:** Through the macromolecule reaction method, a series of 4-isopropylbenzyl chloride (IPBC) hydrophobically-modified hydroxyethyl cellulose (HAHEC) were synthesized. The use of suitable amount of hydrophobic monomer can ensure both the strong intermolecular association and good water-solubility of HAHEC. Effects of polymer concentration, shear rates, temperature, and electrolytes on the solution behavior of HAHEC were comprehensively studied, which indicated that the polymers show high viscosification property, excellent viscosity retention in brine water, and surface activity. FTIR, DSC, and UV measurements were applied to characterize the molecular structure and composition of HAHEC to

confirm the incorporation of hydrophobic group into the polymer chain. Atomic force microscope (AFM) and fluorescence spectrum measurements were applied to study the formation of the molecule aggregation and hydrophobic microdomain of HAHEC, and revealed the close relationship between the rheological behaviors and the hydrophobic viscosification effect. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2824–2831, 2006

**Key words:** hydroxyethyl cellulose; association–viscosification effect; hydrophobic-modification; critical associating concentration; solution behavior; characterization

## INTRODUCTION

Hydrophobically associating water-soluble polymers (HAWSP) are synthetic water-soluble polymers<sup>1</sup> that incorporate 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 the intra- and intermolecular associating. Above a critical associating concentration ( $C^*$ ), the molecular network forms and causes a rapid increase in viscosity<sup>2</sup>. Such water-soluble polymers are widely used in a number of applications, such as flocculation, enhanced oil recovery (EOR), latex paint system, and drag reduction. 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 paint<sup>3</sup>, displays application prospects in EOR.

In this study, 4-isopropylbenzyl chloride (IPBC) was applied as the hydrophobic monomer for the modification of hydroxyethyl cellulose, because the benzyl group in its molecule can stabilize the hydrophobic associations and have the advantage of being UV- and fluorescence-active. The solution behavior and the supramolecular structure of the polymers were investigated.

## EXPERIMENTAL

### Materials

HEC was purchased from MERCK-Schuchardt Co. of Germany, which molar substitution degree ( $M_s$ ) is 2.5 and  $M_w$  is 110,000. IPBC was purchased from Tokyo Kasei Kogyo Co., Ltd. Both of the agents and other chemical agents are all of analytical purity and used as received.

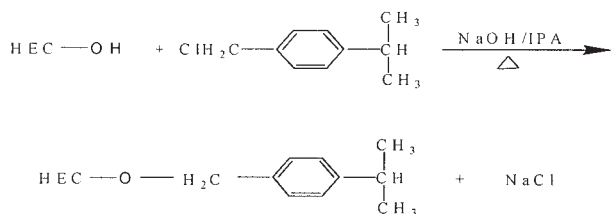
### Synthesis of the polymers

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 dropwise to the bottle. After HEC had been sufficiently swelling for 24 h, IPBC was added slowly and the temperature was raised to 80°C. The reaction lasted for about 8 h. Then the product was neutralized with HCl, filtrated, washed and soaked with hexane and acetone. Finally

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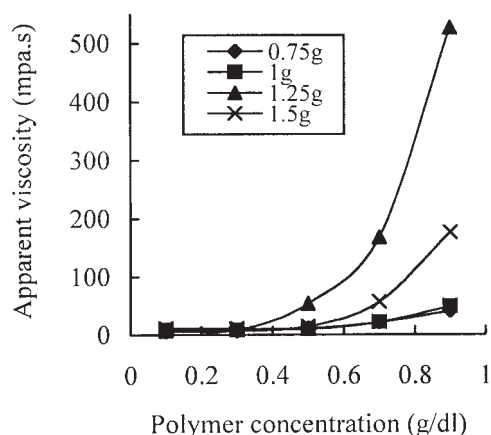
the product was dried under reduced pressure at 45°C for 5 h. The principle of the reaction was as shown in Scheme 1.

### Measurements

The solution viscosities were measured by the Brookfield DV-III rotator viscometer of U.S.A under 25°C and 6 s<sup>-1</sup>. Viscosity-temperature characteristic was measured from 25°C to 70°C. The light transmittance was measured by 722 grating spectrophotometer under room temperature, and the wavelength was  $\lambda = 460$  nm. The viscosity-shear rate relationship was measured by the HAKKE RV20 rotator rheometer of Germany under 25°C. The surface tension was measured by the Kruss-Kiost surface tension meter of Germany under 25°C. The glass transition temperature ( $T_g$ ) was measured by the Netzschdsc 204 of Germany from -25 to 200°C, and the temperature elevating rate was 20 k/min. The FTIR analysis of the polymer composition was conducted with Nicolet-560 infrared spectrometer of USA. The Japanese Shimadzu UV-240 was used to measure the hydrophobic group content in the polymer. AFM micrographs were acquired by the SPA 400 atomic force microscope (AFM) of Japan to study the micro-morphology of the polymer solution and the samples were prepared as follows: polymer solutions were coated on the mica substrate first, and then dried under room temperature in a desiccator. The Toshiba fluorimeter of Japan was used to study the hydrophobic microdomain formed by the polymer molecules, and samples were pre-

**TABLE I**  
Effect of IPBC Dosage on the Water Solubility of HAHEC

IPBC dosage (g)	Transmittancy (%)	Water-solubility of the product
0.5		Good
0.75	97.7	Good
1	97.1	Good
1.25	98.2	Good
1.5	87.7	Phase separation
1.75	84.0	Phase separation
2		Insoluble



**Figure 1** Effect of IPBC on the apparent viscosity of HAHEC in aqueous solution at 25°C and 6 s<sup>-1</sup>.

pared by dissolving pyrene (10<sup>-5</sup>M) in the polymer solution<sup>4</sup>.

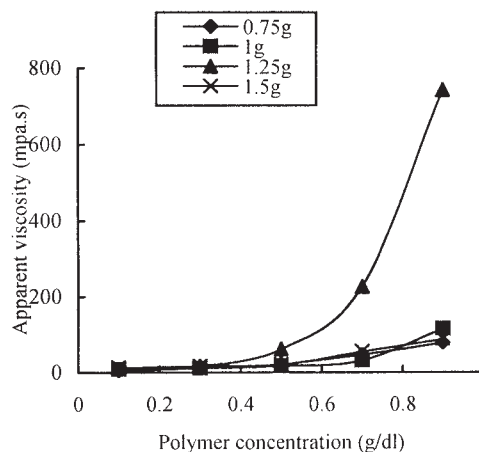
## RESULTS AND DISCUSSION

### The solution properties of HAHEC

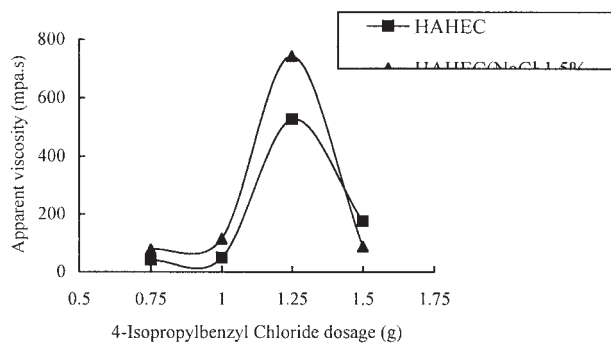
Effect of polymer solubility and concentration on the apparent viscosity of HAHEC

Different hydrophobic monomer content led to different water solubility of the polymer and also affected the viscosity of the polymer solution remarkably, and the high hydrophobic monomer content may not certainly bring high viscosity for the polymer. As Table I and Figures 1-3 show, the best sample should have both suitable hydrophobic monomer content and ideal water solubility.

For the small amount use of the hydrophobic monomer such as 0.75 g and 1g IPBC with high light trans-



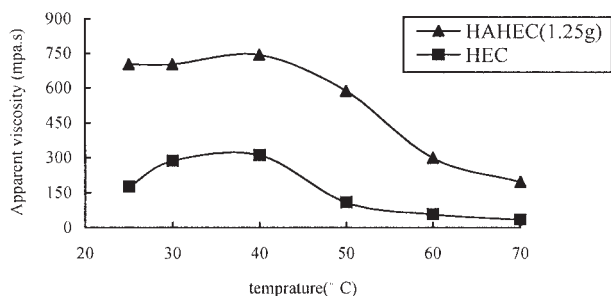
**Figure 2** Effect of IPBC dosage on the apparent viscosity of HAHEC in 1.5 wt % NaCl aqueous solution at 25°C and 6 s<sup>-1</sup>.



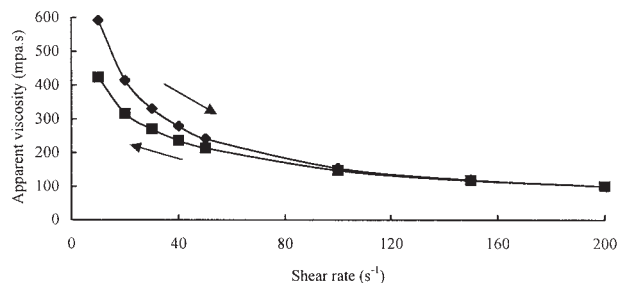
**Figure 3** Effect of IPBC dosage on the apparent viscosity of HAHEC in aqueous solution at 25°C and 6 s<sup>-1</sup> (Polymer concentration 0.9 g/dL).

mittance and good water-solubility, the apparent viscosity of the sample was very low, and when the IPBC amount increased to 1.25 g, the viscosification performance was enhanced remarkably and the polymer solution still kept good water-solubility. However, when the IPBC amount further increased to 1.5 g and 1.75 g, the apparent viscosity decreased because of the too many hydrophobic groups on the polymer molecular chains led to the too strong intermolecular associations, the phase separation of the polymer solution, the drop of the water-solubility of the polymer, and decrease of the apparent viscosity.

For the polymer with 1.25 g IPBC, the apparent viscosity rose abruptly at the polymer concentration of 0.5 g/dL, which can be determined as the critical associating concentration  $C^*$  of the polymer (Figs. 1 and 2). Generally speaking, there existed intermolecular and intramolecular hydrophobic associations in the aqueous solution. Below  $C^*$ , intramolecular association dominated. Above  $C^*$ , intermolecular association dominated, and the hydrodynamic volume and the apparent viscosity of the polymer solution were improved remarkably. The apparent viscosity of HAHEC can reach 734.6 mpa s at 0.9 g/dL polymer concentration and 1.5% NaCl concentration, while the apparent viscosity of HEC was only 174 mpa s at the same condition.



**Figure 4** Effect of temperature on the apparent viscosity of the polymer in 1.5 wt % NaCl aqueous solution at 6 s<sup>-1</sup> (Polymer concentration 0.9 g/dL).



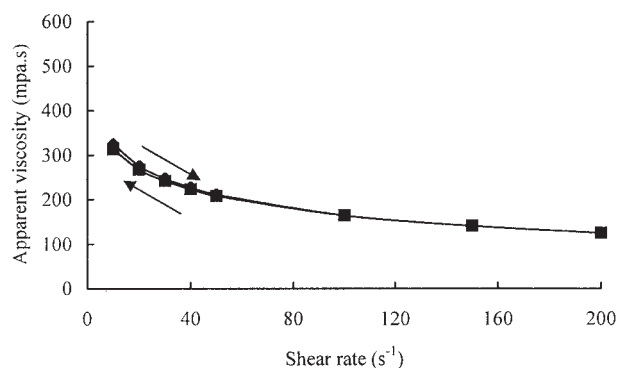
**Figure 5** Effect of shear rate on the apparent viscosity of HAHEC (1.25 g) in 1.5 wt % NaCl aqueous solution at 25°C and 6 s<sup>-1</sup> (Polymer concentration 0.9 g/dL).

#### Effect of temperature on the apparent viscosity of HAHEC

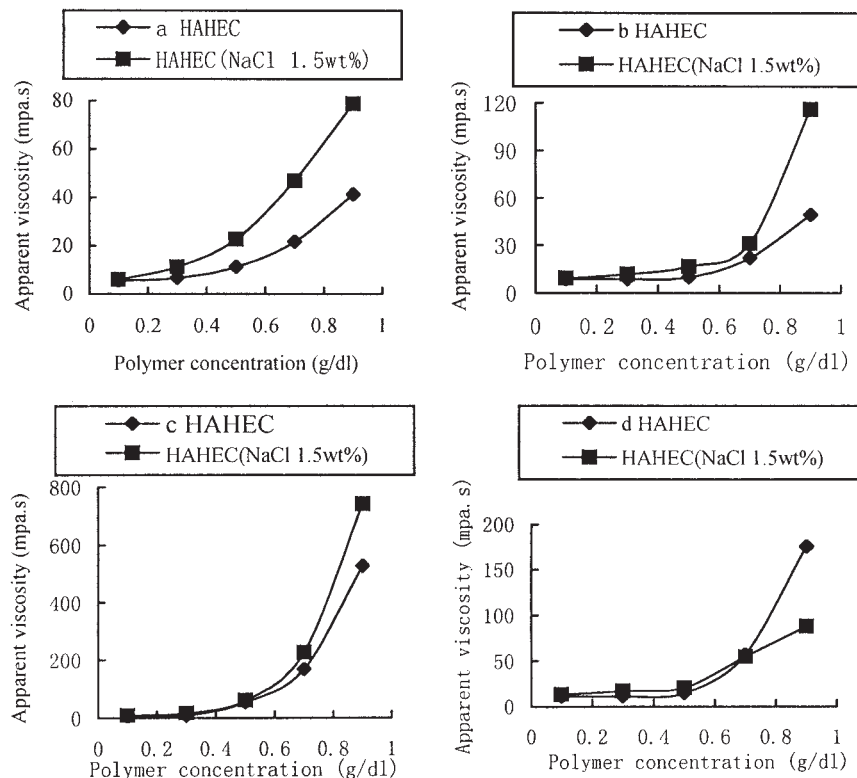
There are two aspects for the effect of the temperature on the hydrophobic association of the polymers<sup>5</sup>. On one hand, the hydrophobic association is an endothermic process and the association will be enhanced as temperature increases. In the meantime, the strengthening of the molecular movement with temperature results in the expansion of the hydrophilic molecular chain, which is favored for the increase of the hydrodynamic volume. On the other hand, the hydrophobic hydration is exothermic, the temperature rise makes the movement of water molecules and hydrophobic groups increase, and the hydration spheres of the hydrophobic groups changes greatly, resulting in the weakening of the hydrophobic association. As shown in Figure 4, the apparent viscosity change of HAHEC was not obvious below 40°C, then decreased sharply between 40 and 60°C, and the trend became slower above 60°C. The viscosity-temperature effect was so complex and different for various kinds of polymer systems.

#### Effect of shear rates on the apparent viscosity of HAHEC

As shown in Figure 5, HAHEC firstly behaved as a pseudoplastic property and the apparent viscosity de-



**Figure 6** Effect of shear rate on the apparent viscosity of SEC in 1.5 wt % NaCl aqueous solution at 25°C and 6 s<sup>-1</sup> (Polymer concentration 0.9 g/dL).



**Figure 7** Effect of NaCl on the apparent viscosity of HAHEC in aqueous solution at 25°C and 6 s<sup>-1</sup> (a) 0.75 g, (b) 1 g, (c) 1.25 g (d) 1.5 g.

creased sharply with the increase of the shear rate, which indicated the rapid damages of the molecular network built up by the relatively weak hydrophobic association. When the shear rate was above 80 s<sup>-1</sup>, the apparent viscosity did not change obviously any more and kept at about 150 mpa s. When the shear application was removed, the hydrophobic association networks can recover but showed a stagnant of viscosity, indicating that during the shear process there existed a kind of dynamic equilibrium between associating and unassociating of the HAHEC molecules, which was time-dependent and can not terminate immediately. Ostwald model<sup>6</sup> evaluation of this system, whose relation parameter  $R^2$  can reach 0.99, can be expressed as follows

$$\tau = a \gamma^n$$

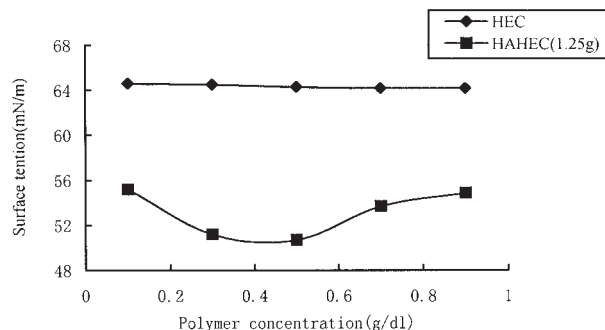
where  $a = 1123$ ;  $n = -0.5167$ , the flow index;  $\gamma$ , the shear rate.

The area formed by the two curves (viscosity increase and decrease with shear rate) can denote 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.

Figure 6 showed the viscosity–shear rate relationship of HEC at the same polymer concentration and salt concentration as HAHEC. There was almost no stagnancy for the shear recover, and no intermolecular association existed, which demonstrated indirectly that the hydrophobic groups had been incorporated into HEC chain for HAHEC.

#### Effect of additional electrolyte on apparent viscosity

Addition of NaCl led to the increase of the polarity of the polymer solution, and the crosslinking molecular



**Figure 8** Effect of polymer concentration on the surface tension of the polymer solution at 25°C.

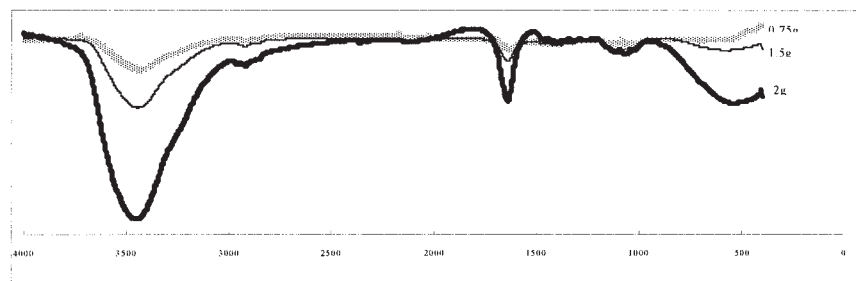


Figure 9 Effect of IPBC dosage on the FTIR absorption of HAHEC.

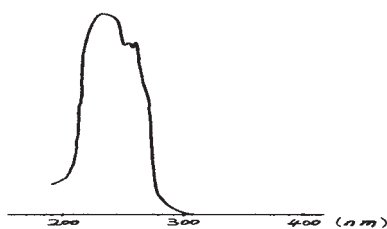


Figure 10 UV-vis spectra of IPBC.

networks formed in greater range and the apparent viscosity of the polymer solution rose dramatically because of the stronger hydrophobic association<sup>7</sup>. As shown in Figure 7, the viscosity curve got to an obvious enhancement in 1.5 wt % NaCl aqueous solution for Figures 7(a–c). For Figure 7(d) the hydrophobically too-strong association resulted in the phase separation of the polymer solution, and the drop of the viscosity.

#### The surface activity of HAHEC

As shown in Figure 8, both HEC and HAHEC solution showed lower surface tension than that of the deionized water (about 72 mN/m). However, the former kept at about 64–65 mN/m with the increase of polymer concentration and the latter showed a differently complex changing tendency. The surface tension of HAHEC dropped firstly till it got to the

lowest point of  $\sim 50.7$  mN/m at the polymer concentration of 0.5 g/dL, and then it rose obviously and kept at  $\sim 54.5$  mN/m above 0.7 g/dL of polymer concentration. The amphiphilic structure of HAHEC molecules contributed to the surface activity of the polymer<sup>8</sup>.

#### The composition and structure characterization

##### FTIR measurement

The difference of the infrared absorption intensity between HEC and HAHEC was shown in Figure 9. The absorption peaks of HAHEC at  $3000\text{--}3700\text{ cm}^{-1}$  and  $1450\text{--}1650\text{ cm}^{-1}$  attributed to the benzene group absorption, and the fingerprint region ( $650\text{--}1300\text{ cm}^{-1}$ ) attributed to the vibration of ether bonds were considerably enhanced compared with HEC, indicating that

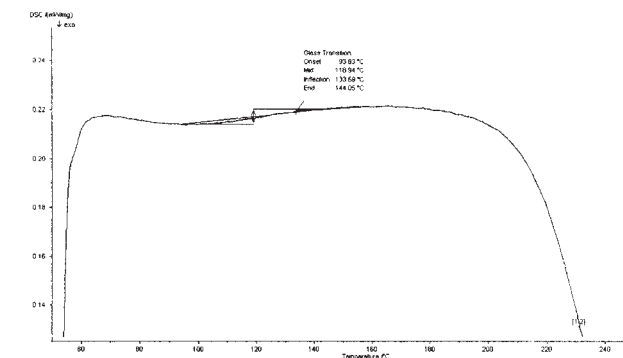


Figure 12 DSC of HAHEC.

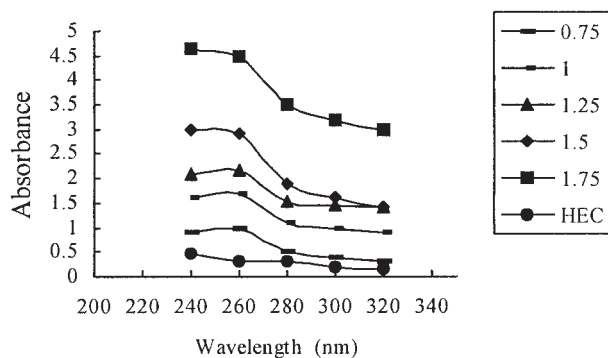


Figure 11 The UV-vis absorbance of HAHEC and HEC.

IPBC dosage (g)	Actual content (wt %)
0.75	5.35
1	8.56
1.25	12.04
1.5	15.52
1.75	24.09



**TABLE III**  
Glass Transition Temperature of the Polymer

Sample	$T_g$ (°C)
HEC	98.15
HAHEC	118.94

the hydrophobic groups were introduced to the HEC molecule<sup>9</sup>.

### UV measurement

As shown in Figures 10 and 11, because the hydrophobic monomer IPBC contained the benzene group, and had the advantage of being UV-active, HAHEC had an obvious UV absorption at 260 nm at which the benzene group had characteristic absorption, while there was no absorption for HEC. The absorption intensity of HAHEC increased with the increasing amount use of IPBC.

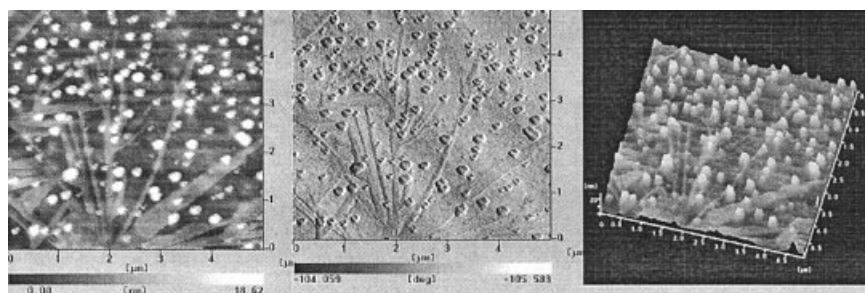
The actual content of the hydrophobic group in HAHEC molecules can be calculated according to the Lambert–Beer law, as shown in Table II.

### DSC measurement

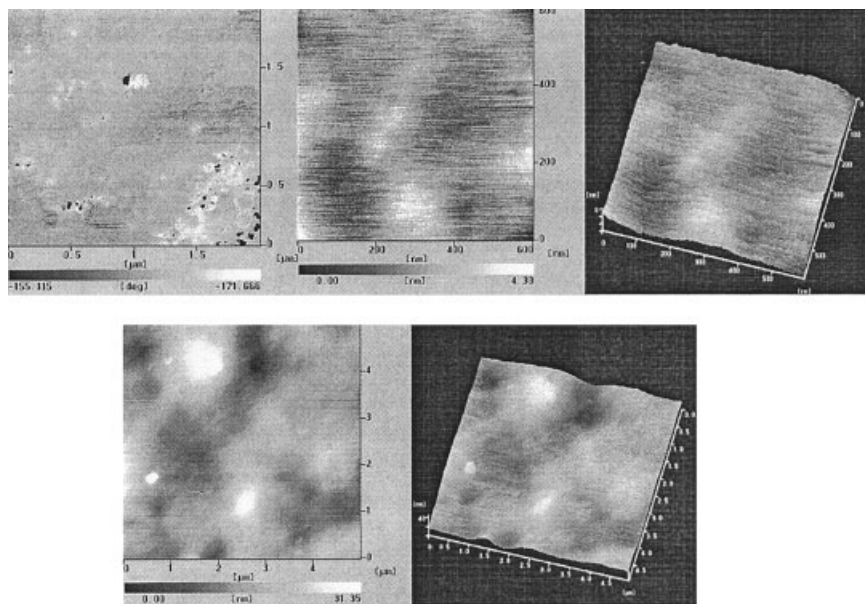
As shown in Figure 12 and Table III, the  $T_g$  of HAHEC was enhanced compared with HEC, because the aromatic hydrophobic groups were brought into the macromolecule, resulting in the bigger space hindrance.

### AFM measurement

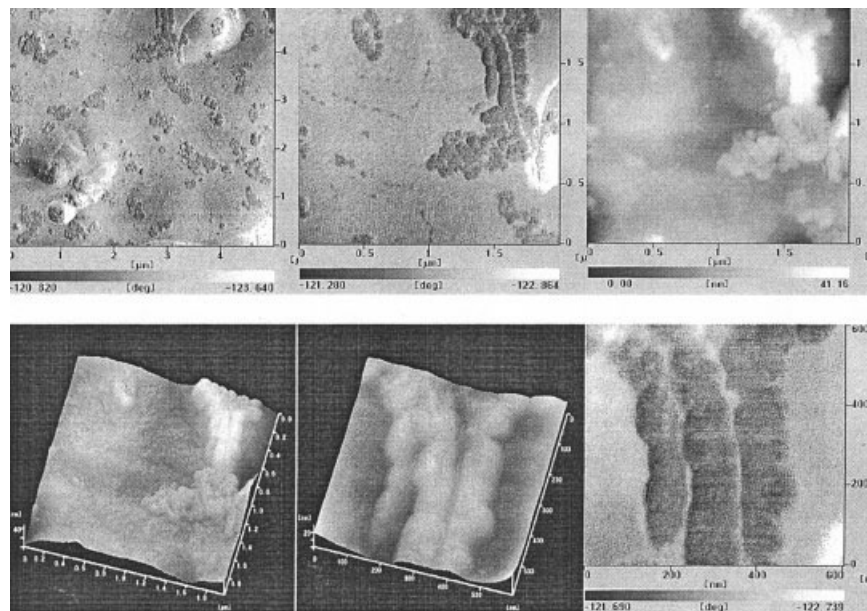
For the understanding of why the HAHEC polymer solution showed high viscosity, the aggregation morphology of the polymer molecules in aqueous solution was investigated by AFM. The supramolecule structure of HEC in 1.5% NaCl aqueous solution was displayed in Figure 13. The well-distributed small particles aggregations of HEC (shown as the bright spots in the image), and no complex supramolecular aggrega-



**Figure 13** AFM micrograph of HEC in 1.5 wt % NaCl aqueous solution at 0.9 g/dL polymer concentration.

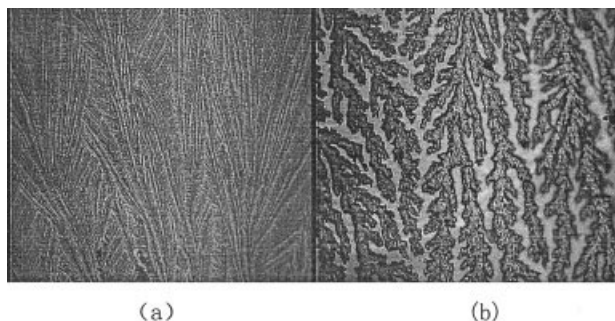


**Figure 14** AFM micrograph of HAHEC (1.25 g IPBC) in 1.5 wt % NaCl aqueous solution at 0.3 g/dL polymer concentration.



**Figure 15** AFM micrograph of HAHEC (1.25 g IPBC) in 1.5 wt % NaCl aqueous solution at 0.9 g/dL polymer concentration.

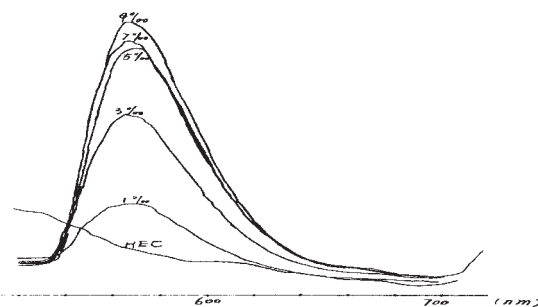
tion networks can be observed. In Figures 14 and 15, for HAHEC, the molecular aggregation dimension increased obviously, and changed with the polymer concentration, from small particle aggregations at 0.3 g/dL polymer concentration to string-like aggregations at 0.9 g/dL polymer concentration, which was composed of many spherical aggregations, resulting from the formation of the intermolecular hydrophobic association networks<sup>10</sup>. The morphology of NaCl crystal in the brine aqueous solution was also influenced by the polymer concentration and supramolecular aggregations. As shown in Figure 16 the salt crystal was very small and slender in the solution with low polymer concentration (0.3 g/dL) and it became much larger, tree-like crystal in the solution with high polymer concentration (0.9g/dL), and the NaCl concentration was the same (1.5 wt % NaCl) for both cases. The polymer aggregations perhaps had the induction effect of the salt crystallization.



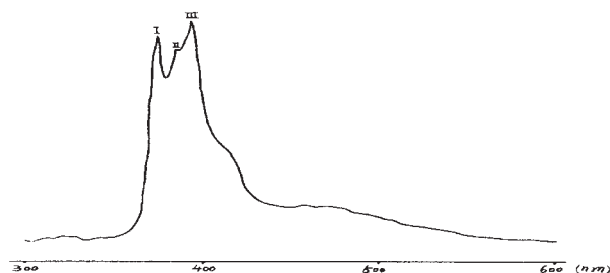
**Figure 16** Effect of polymer concentration on the morphology of NaCl crystal (Polymer concentration: (a) 0.3 g/dL (b) 0.9 g/dL, 1.5 wt % NaCl).

### Pyrene fluorescense studies

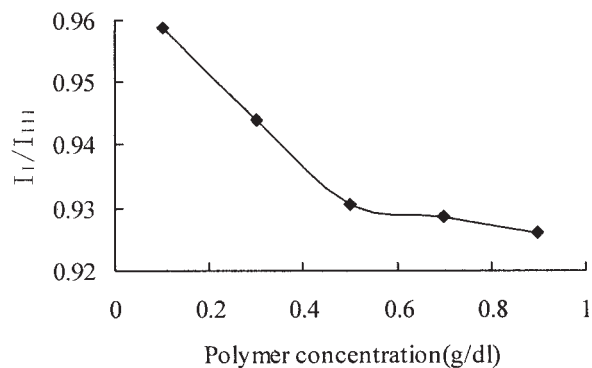
As shown in Figure 17, because that benzene group in HAHEC molecules was fluorescence-active, fluorescence absorbance of HAHEC in aqueous solution became stronger with the increase of the polymer concentration with higher hydrophobic group con-



**Figure 17** Effect of the polymer concentration on the fluorescence absorbance of the polymer in 1.5 wt % NaCl solution.



**Figure 18** Pyrene fluorescence spectrum of HAHEC in 1.5 wt % NaCl aqueous solution (Polymer concentration: 0.9 g/dL).



**Figure 19** Effect of HAHEC (1.25 g IPBC) concentration on  $I_1/I_{iii}$  (1.5 wt % NaCl).

centration, which further demonstrated that the hydrophobic groups had been successfully incorporated into HEC molecules.

Pyrene probe experiments were also performed to investigate the aggregation of the polymer molecules<sup>11</sup>. The ratio of the of 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<sup>4</sup>. As

shown in Figures 18 and 19, the  $I_1/I_3$  values decreased with the increase of the polymer concentration, indicating that HAHEC provided more hydrophobic microdomains for the pyrene molecules formed through the association of the hydrophobic groups.

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