

Note

INTERMOLECULAR AND INTRAMOLECULAR INTERACTIONS OF POLYMER GUAR GUM IN SOLUTIONS

Yun-fei Yan^a, Hai-yang Yang^{a, b*}, Wen-yong Liu^a, Ping-ping Zhu^a and Ping-sheng He^a

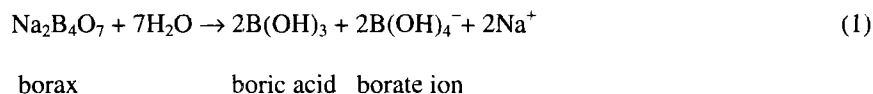
^aDepartment of Polymer Science and Engineering, ^bStructure Research Laboratory, University of Science and Technology of China, Hefei 230026, China

Abstract The tetrahedral borate ion can crosslink with polymer guar gum in aqueous solutions. If the concentration of guar gum is less than 0.045 g/dL, the intramolecular interaction between guar gum and borate ion increases due to the formation of crosslinks. As a result, the polymer chains of guar gum in solution shrink in size and the reduced viscosity of polymer solution decreases accordingly. On the other hand, if the concentration of guar gum is greater than 0.045 g/dL, the intermolecular interaction becomes apparent due to the same reason. The polymer chains, therefore, associate together and the reduced viscosity of polymer solution increases considerably. According to this technique, the critical concentration c^* , presented by de-Gennes^[1], is determined successfully.

Keywords: Guar gum; Crosslink reaction; Critical concentration c^* .

INTRODUCTION

In dilute polymer solution, polymer chains are separated and only intramolecular interaction exists. In concentrated polymer solution, however, polymer chains become crowded and the intermolecular interaction of polymer chains in solution becomes apparent. The concentration c^* at which polymer chains contacted was defined by de-Gennes as the boundary concentration between dilute and semi-dilute polymer solution^[1]. In good solvents, the repulsive force of polymer chains is strong. As a result, polymer chains shrink in size before they contacted and overlapped. The concentration at which polymer chains shrink in size was defined by Qian as the dynamic contact concentration c_s ($< c^*$)^[2]. In the present study, c^* of polymer guar gum in aqueous solution was determined successfully by a specially designed technique. It is well known that borax (or sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$) is a good buffer. At lower concentrations, it is totally dissociated into equivalent amount of boric acid and borate ion^[3–5].



Polymer guar gum is a water-soluble polyhydroxy polymer, the typical structure unit of which is shown in Fig. 1. The ratio of methyl α -D-galactopyranoside/methyl α -D-manno-pyranoside is approximately 1/2. The cross linking reaction of borate with guar gum^[3, 5], as outlined in Scheme 1, should increase intra- and inter-molecular interaction of polymer chains greatly.

Of peculiar importance is that the influence of intra- and inter-molecular interaction of polymer chains upon the viscosity of polymer solution is completely different. In dilute polymer solution ($c < c^*$), polymer chains are separated and the intramolecular interaction originated from the cross linking reaction of borate with guar gum

* Corresponding author: Hai-yang Yang (杨海洋), E-mail: yhy@ustc.edu.cn

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dominates. As a result, polymer chains shrink in size and the viscosity of guar gum solution decreases accordingly. On the contrary, in semi-dilute polymer solution ($c > c^*$), polymer chains become crowded together and the intermolecular interaction predominates, different polymer chains, therefore, associate together and the viscosity of polymer solution increases significantly. This demonstrates that the influence of cross-linking reaction of borate with guar gum upon the viscosity of aqueous solution of guar gum should be greatly associated with the concentration of polymer solution (dilute or semi-dilute).

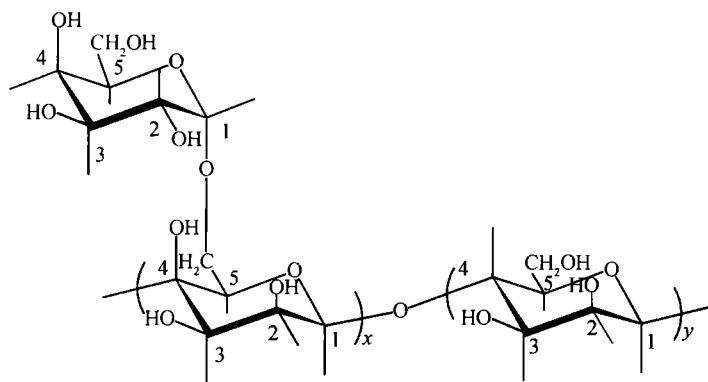
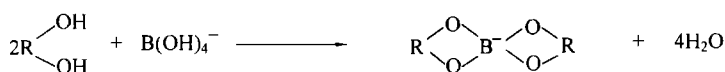


Fig. 1 Typical structure unit of polymer guar gum



Scheme 1 Reaction of borate with polyhydroxy polymer

EXPERIMENTAL

Guar gum was kindly supplied by Zhao-feng Zhuang, the engineer of Zhongyuan Oilfield (Puyang 457001). The viscosity-average molecular weight of guar gum was 2.3×10^6 , calculated according to the following equation^[6].

$$[\eta] = 7.76 \times 10^{-6} M_{\eta}^{0.98} \quad (2)$$

$[\eta]$ is the intrinsic viscosity of guar gum in pure water. Borax (or sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$) was A.R. grade and used as received. Both the solvent and the solution of guar gum were filtered with 0.45 μm filters prior to use.

The viscosity measurements were carried out using a conventional Ubbelohde viscometer. The capillary diameter of the viscometer was 0.55 mm. The viscosity measurement was performed according to the following procedure. (1) The flow time of guar gum solution, namely t , was measured using a thoroughly cleaned viscometer. The polymer solutions with different concentrations were prepared by adding pure solvent into the viscometer successively. (2) After the flow time of guar gum solution was measured, the solution was poured out and the viscometer was washed thoroughly with pure solvent for 3–5 times. The flow time of pure solvent, namely t_0' , was then measured. The relative viscosity of guar gum, η_r , was determined according to Eq. (3).

$$\eta_r = t/t_0' \quad (3)$$

In our previous studies^[7–12], we have presented that the measuring conditions for flow time corresponding to either polymer solution or the pure solvent are not the same due to the adsorption of polymer molecules on the viscometer capillary wall. For water-soluble polyhydroxy polymer molecules, however, the adsorbed molecules only decrease the effective diameter of capillary^[8]. As a result, the relative viscosity of polymer solution can be determined precisely according to Eq. (3)^[7,8].

RESULTS AND DISCUSSION

Figure 2 shows the plot of reduced viscosity versus concentration of guar gum in aqueous solutions at 30°C. The concentrations of borax in aqueous guar gum solution are indicated in the legend. It can be seen in the inset that the slope of curve changes considerably at the concentration greater than 0.045 g/dL. It is therefore of interest to make certain whether 0.045 g/dL can be referred to as the contact concentration c^* of guar gum in aqueous solution or not. In our experiments, the borax aqueous solution is selected as the mixed solvent and the viscosity of guar gum in borax aqueous solution is measured. The result is also shown in Fig. 2. It can be seen that if $c < 0.045$ g/dL, the reduced viscosity of guar gum in borax aqueous solution is less than the reduced viscosity of guar gum in pure water. In particular, the reduced viscosity of guar gum decreases considerably as the concentration of borax increases from 0.10 g/dL to 0.50 g/dL. The reasonable interpretation is that the intramolecular interaction in borax aqueous solution increases due to the crosslinking reaction of borate with guar gum. The polymer chains of guar gum, therefore, shrink in size and the reduced viscosity of guar gum solution decreases consequently. On the other hand, if $c > 0.045$ g/dL, the reduced viscosity of guar gum in borax aqueous solution is larger than that of guar gum in pure water as shown in Fig. 2. The expected experimental results indicate clearly that at higher concentrations ($c > 0.045$ g/dL) polymer chains of guar gum in borax aqueous solutions associate due to the increased intermolecular interaction also originated from the crosslinking reaction of borate with guar gum. We believe, therefore, that 0.045 g/dL is the contact concentration c^* of polymer guar gum in aqueous solution.

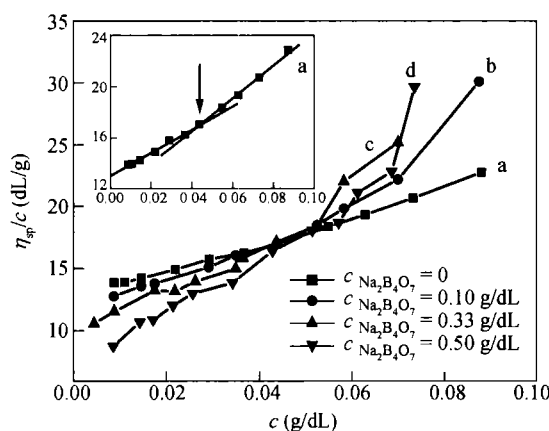


Fig. 2 The reduced viscosity η_{sp}/c versus c for guar gum at 30°C

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