

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Effect of pH on Gelation Behavior of Hydrolyzed Polyacrylamide and *O*-carboxymethyl Chitosan Mixed System

Jie Cao^a; Yebang Tan^{ab}; Yuju Che^a; Haipeng Xin^a

^a School of Chemistry and Chemical Engineering, Shandong University, Jinan, P. R. China ^b The Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, Jinan, P. R. China

Online publication date: 26 April 2010

To cite this Article Cao, Jie , Tan, Yebang , Che, Yuju and Xin, Haipeng(2010) 'Effect of pH on Gelation Behavior of Hydrolyzed Polyacrylamide and *O*-carboxymethyl Chitosan Mixed System', *Journal of Macromolecular Science, Part A*, 47: 6, 595 – 601

To link to this Article: DOI: 10.1080/10601321003742170

URL: <http://dx.doi.org/10.1080/10601321003742170>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Effect of pH on Gelation Behavior of Hydrolyzed Polyacrylamide and *O*-carboxymethyl Chitosan Mixed System

JIE CAO¹, YEBANG TAN^{1,2,*}, YUJU CHE¹ and HAIPENG XIN¹

¹School of Chemistry and Chemical Engineering, Shandong University, Jinan, P. R. China

²The Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, Jinan, P. R. China

Received September 2009, Accepted December 2009

The effect of pH on gelation behavior of hydrolyzed polyacrylamide (HPAM) and *O*-carboxymethyl chitosan (CMCH) were investigated by rheological measurements. The steady state shear experiments showed that the variation of apparent viscosity of each system had a similar tendency in the process. In basic environment, with the decrease of pH value, the apparent viscosity increased markedly, and in an acidic environment, the apparent viscosity decreased with the decrease of pH value. The results from oscillation experiments indicated the storage modulus (G') was higher than the lose modulus (G'') in the whole frequency investigated when pH was nearby 7, which indicated that gel formed in this condition. The critical angular frequency (ω^*) could also be affected by pH, which implied that the viscoelastic property of the sample was influenced by pH. All results implied that there was a sol-gel transition when pH was nearby 7 for all HPAM and CMCH systems investigated.

Keywords: Sol-gel transition, viscoelastic property, amphoteric, water soluble polymer

1 Introduction

Hydrolyzed polyacrylamide (HPAM) is one kind of important water soluble polymer due to its wide applications in many fields, such as flocculants for wastewater treatment, oil recovery, soil conditioning, agriculture, and biomedical applications (1–4).

O-carboxymethyl chitosan (CMCH), which is one of chitosan amphoteric derivatives, has attracted increasingly more researchers because of its intensive multiple bioactivities, excellent moisture-retention ability, biodegradability, biocompatibility, antibacterial and antifungal activities (5–7). The opposite ionizable groups, carboxyl and amine, could coexist on the same CMCH chains because of the carboxymethylation. This conversion not only provides CMCH the super solubility, but also provides some special chemical, physical and biological properties, all of which make CMCH an attractive option in connection with its use in food products, cosmetics and pharmaceuticals (7–10).

In the past few years, the gelation behavior of polymer in solution has attracted much attention due to its theoretical and practical applications (11–13). The gelation behavior

could be affected by many factors. The thermo-responsive polymer is one of the most researched materials in this area. The basic feature shared by thermo-responsive copolymers is that aqueous solutions of these polymeric systems display low viscosity at room temperature, and exhibit a sharp viscosity increase as temperature rises within a very narrow temperature interval, producing a gel at body temperature (13). A number of thermo-responsive polymers have been studied during the last decades, with much work focusing on poly(ethylene oxide-*co*-propylene oxide)(14–15), poly(*N*-isopropyl acrylamide) and its derivatives (16–18), poly(ethylene glycol) and biodegradable polyester (19–21). Although, pH-responsive polymers could also be widely used for many applications (22–24), there is much less research on the gelation behavior of pH-responsive polymers in aqueous solution. As a result, the rheological property study on the pH-responsive system might probably be helpful for a better understanding on the gelation behavior of this system.

In this work, four systems with different concentrations of HPAM and CMCH were prepared and the pH effects on the rheological property of four systems were studied. The results implied that there was a sol-gel transition when pH approximated 7 for all systems, and the CMCH was a good tackifier for HPAM solution in proper pH value. The aim of this study is to offer basic data for the formation of HPAM and CMCH gel.

*Address correspondence to: Yebang Tan, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China. E-mail: ybtan@sdu.edu.cn

2 Experimental

2.1 Materials

Hydrolyzed polyacrylamide (HPAM) was prepared by inverse emulsion polymerization. 0.7 g sorbitan monooleate (Span 80) and 0.1 g nonylphenol polyoxyethylene ether (OP 10) were dissolved in 15 mL cyclohexane. 10 g 30 wt% acrylamide aqueous solution was dropped into the cyclohexane solution with high-speed stirring. The polymerization was initiated by 0.045 mmol potassium persulfate at 60°C in nitrogen atmosphere. After 4 h, 10 g 10 wt% sodium hydroxide was added into the emulsion and the hydrolysis of polyacrylamide proceeded at 80°C for 24 h, and then, the emulsion was precipitated by ethanol, and washed by ethanol six times and mixture of water and ethanol for three times to remove emulsifier, alkali and unreacted monomers. HPAM was dried in vacuum at 50°C for 48 h. The average molecular weight (M_w) of HPAM is 4.3×10^6 g/mol calculated using the experimentally determined $[\eta]$ and the Mark-Houwink equation $[\eta]$ (mL/g) = $8.2 \times 10^{-3} M_w^{0.85}$ (25). The intrinsic viscosity ($[\eta]$; mL/g) of HPAM in 0.5 mol/L NaCl was 3573 mL/g, which was achieved by capillary viscometry. The hydrolysis degree of HPAM was 44%, which was determined by elementary analysis. The molecule structure of HPAM is represented in Figure 1.

O-carboxymethyl chitosan (CMCH) [Molecular Weight $\sim 6.9 \times 10^4$, the degree of substitution of carboxymethyl group ~ 0.80 , the degree of deacetylation ~ 0.90] was purchased from Qingdao Bio-pharma Co. Ltd. in China, refined twice by dissolving it in aqueous solution, filtered, precipitated with ethanol and finally dried in vacuum at 50°C for 48 h. The molecule structure of CMCH is represented in Figure 1.

Other materials were analytical reagent and used as received.

2.2 Preparation of Sample Solutions

2 wt% HPAM, 1 wt% CMCH and HCl (from 0.005 to 0.1 mol/L) aqueous solutions were prepared. A series of sample solutions were then prepared by mixing different

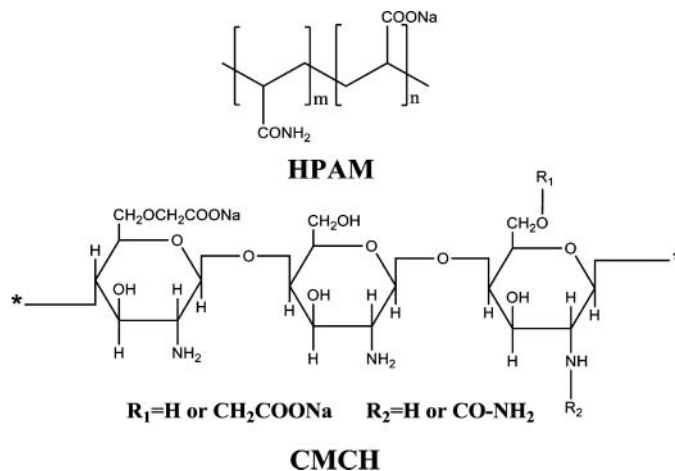


Fig. 1. Molecule structure of HPAM and CMCH.

amounts of the stock HPAM and CMCH solutions. These mixture systems were stirred for 12 h, and a HCl solution of desired amount and concentration was gently dropped into them. Sample solutions were then stirred for 24 h and left overnight to equilibrate before rheological measurements. In this paper, four systems with different concentrations of HPAM and CMCH at different pH values were investigated and named HPCMA, HPCMB, HPCMC, and HPCMD, respectively. Their components are presented in Table 1.

2.3 Rheological Measurements

The rheological measurements were carried out on a HAAKE RS6000 Rheometer (Germany) with a cone-plate sensor system (Ti; radius, 17.5 mm; cone angle, 1°). The temperature was maintained at $25.0 \pm 0.1^\circ\text{C}$. For the shear-dependent behavior, the viscosity measurements were carried out at shear rates ranging from 0.01 to 100 s^{-1} . After a proper stress was selected, the oscillatory rheological measurements of the dynamic shear moduli were carried out at a frequency of 10^{-1} – 10^2 rad/s.

Table 1. Components of four systems investigated*

Sample number	HPCMA		HPCMB		HPCMC		HPCMD	
	C_{HCl} (mol/L)	pH	C_{HCl} (mol/L)	pH	C_{HCl} (mol/L)	pH	C_{HCl} (mol/L)	pH
1	0	9.63	0	9.50	0	9.42	0	8.86
2	0.005	7.89	0.0025	8.10	0.00125	8.02	0.00125	7.64
3	0.0125	7.07	0.0075	6.72	0.005	7.16	0.005	6.82
4	0.025	5.72	0.0175	5.66	0.015	5.77	0.01	5.56

*Volume: 4 mL; Concentrations of two polymers (HPAM and CMCH, g/L): 10 and 1.25 (HPCMA); 5 and 1.25 (HPCMB); 5 and 0.375 (HPCMC); 2.5 and 0.625 (HPCMD).

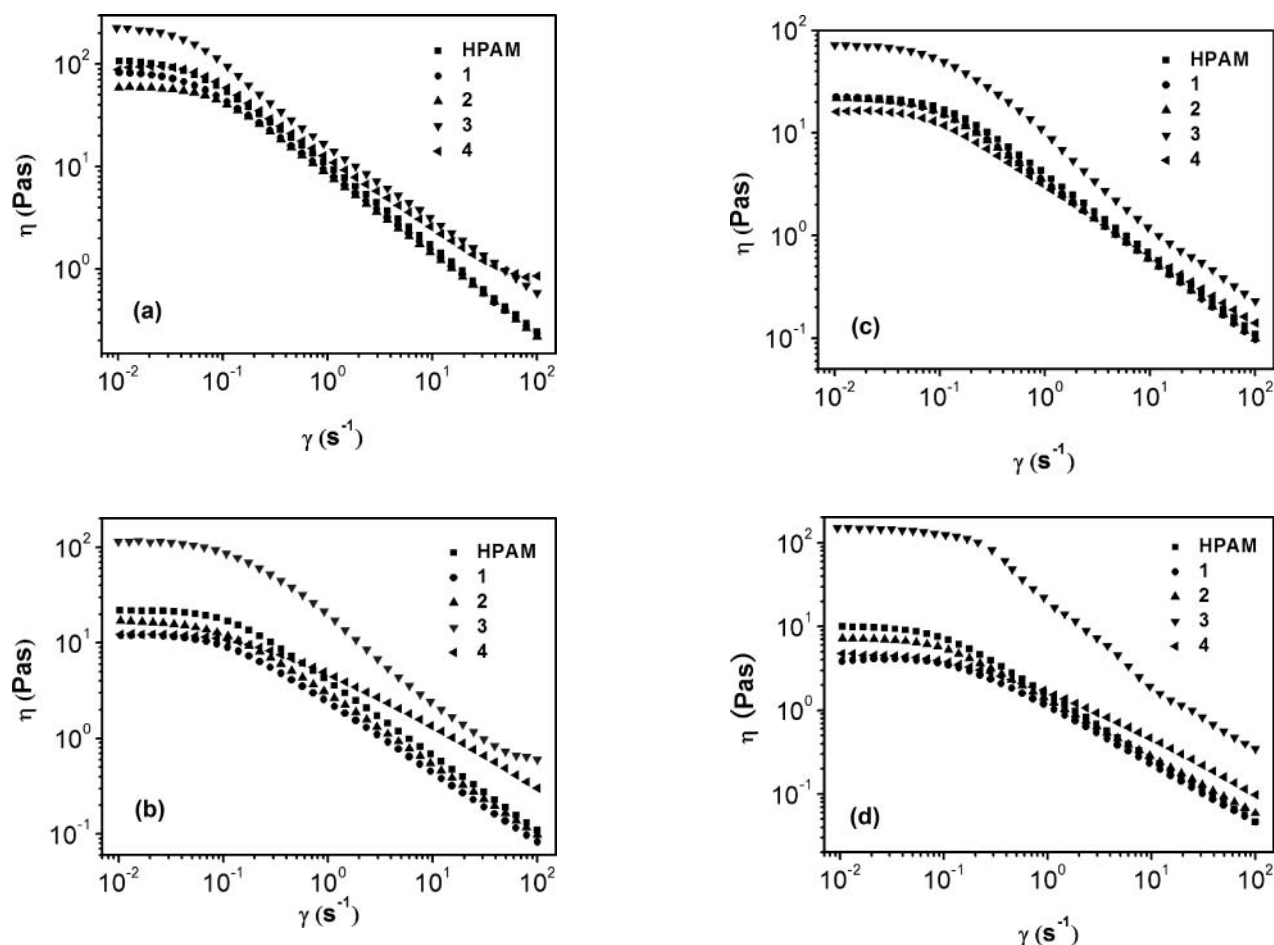


Fig. 2. Steady state shear flow curves of HPCM (a), HPCMB (b), HPCMC (c) and HPCMD (d) systems.

3 Results and Discussion

3.1 The Effect of pH on Apparent Viscosity of System

The steady state shear flow curves of four systems are shown in Figure 2. For all samples, as the shear rate is increased, the behavior of newtonian fluid is observed at a low shear rate, and the behavior of pseudoplastic fluid is observed at a higher shear rate. For all four systems, the apparent viscosity of HPAM solution is higher than that of HPAM and CMCH mixed solution in its original pH value. The apparent viscosity remarkably increases when pH approximates 7 and then decreases with the further decrease of pH value. This indicates that the strong interaction between HPAM and CMCH exists and is intensely affected by the pH value of solution. In alkaline environment, $-\text{COO}^-$ and $-\text{NH}_2$ are dominative conformations for carboxyl and amine groups (10). As a result, CMCH molecules could be regarded as “large anions” in solution, and an addition of electrolyte in the HPAM solution would compress the electrical double layer of molecular particles and screen the electric charges on the molecular chains, which causes the reduction in hydrodynamic volume of HPAM molecules and weakens the interaction between HPAM molecules,

as a result, the apparent viscosity decreases (3). With the decrease of pH value, many amine groups exist in the conformation of $-\text{NH}_3^+$, which could induce the aggregation of HPAM and CMCH based on the electrostatic attraction between $-\text{COO}^-$ of HPAM and $-\text{NH}_3^+$ of CMCH. As a result, the strong network structure between polymer chains forms and the apparent viscosity increases markedly. This kind of network has been represented in other paper (26), and is characterized by a hydrophilic microenvironment with a high water content and electrical charge density. The electrostatic attraction is stronger than most secondary binding interactions (27). In order to form such a network, both polymers have to be ionized and bear opposite charges. This strong network could only be formed at certain pH value, which is determined by the $\text{p}K_a$ of the two polymers (26). With the further decrease of pH value, many carboxyl groups tend to exist in the conformation of $-\text{COOH}$, which induces the reduction of the electrostatic attraction between HPAM and CMCH molecules. Additionally, the solubility of HPAM and CMCH decreases in acidic environment due to the deionization of charged functional groups. Therefore, the apparent viscosity decreases. The results from Figure 2 also show that CMCH is a good tackifier for HPAM solution in proper pH value. Moreover, the most proper pH

value is about 7. Take the HPCMD system for example, the apparent viscosity of sample numbered 3 (pH, 6.82) is nearly 11 times more than that of HPAM sample at the shear rate of 2.33 s^{-1} .

The Carreau-Yasuda model provides viscosity (η , Pas) as a function of shear strain rate ($\dot{\gamma}$, s^{-1}) for the non-Newtonian behavior of fluids at a specific temperature (28). The Carreau-Yasuda model is expressed by the following relationship (29):

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{[1 + (\lambda\dot{\gamma})^a]^{\frac{1-n}{a}}} \quad (1)$$

where η_0 is zero-shear-viscosity as $\dot{\gamma}$ decreases; η_{∞} is the constant value of η as $\dot{\gamma}$ increases; a is this exponent which affects the shape of the transition region between the zero-shear-rate plateau and the rapidly decreasing (power-law like) portion of the viscosity vs. shear rate curve, and increasing a sharpens the transition; λ is a time constant at which the transition occurs from the zero-shear-rate plateau to the power-law portion, n is a power-law-like parameter that describes the slope of the rapidly decreasing portion of the viscosity curve (30).

All samples show a good fit to the Carreau-Yasuda model in our experiment ($R^2 > 0.999$). Taking HPCMB system for example, the correlation coefficients of all samples exceed 0.9999 except the sample numbered 3 ($R^2 = 0.99975$). From Equation 1, the values of zero-shear-viscosity η_0 and flow behavior index n for all four systems are shown in Figure 3. It is obvious that all samples show a shear-thinning behavior. It can be observed that the η_0 and n of each system have the similar change tendency with the increase of HCl concentration. For all four systems, when pH is nearly 7, the sharp increase of η_0 is observed. It may be concluded that networks of molecules form at this pH value. For all four systems, the decrease of the value of n in neutral environment and the increase of it at acidic environment are observed. The variation of behavior index n could usually attribute to the increase or decrease in the number of network or entanglements of macromolecules (30). Moreover, the value of n of HPCMA system changes much less than that of HPCMD system during the process. The reason may be that in such HPAM concentration of HPCMA system, strong macromolecular network could form by intermolecular entanglement of HPAM, and the influence of CMCH on this system is much less than that on HPCMD system.

3.2 The Effect of pH on the Viscoelastic Properties

Before carrying out any oscillatory measurements, each sample should be checked to ensure that it is within the linear viscoelastic region where the complex modulus (G^*) is independent of the applied stress (31–32). The shear stress (τ) dependence of complex modulus (G^*) for the HPCMB system is shown in Figure 4 with various pH

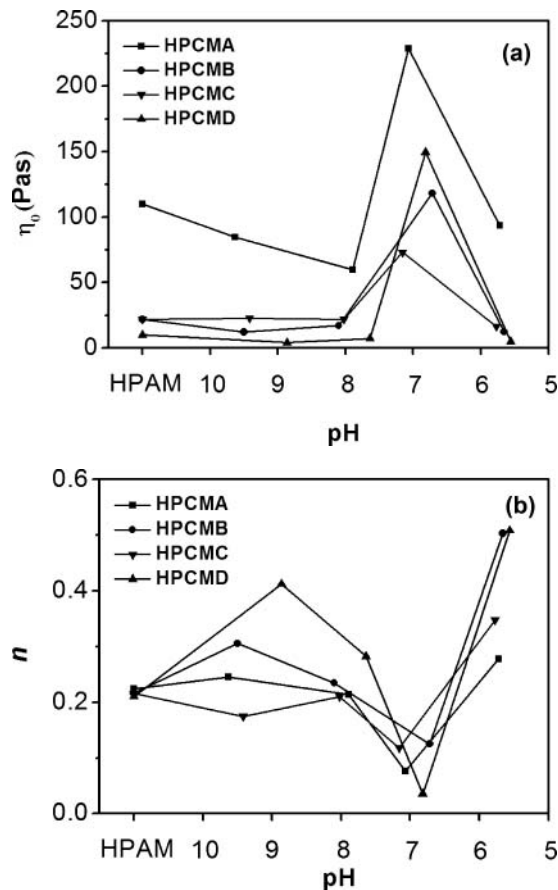


Fig. 3. Zero-shear-rate viscosity η_0 (a) and flow behavior index n (b) defined by the Carreau-Yasuda model for four systems.

values at 25°C as an example for confirming the linearity. The value of G^* remains nearly constant with increasing τ until the critical stress value (τ_c) is reached, then G^* begins to decrease. The values of G^* at a certain τ in the linear region at different pH values are in the same order

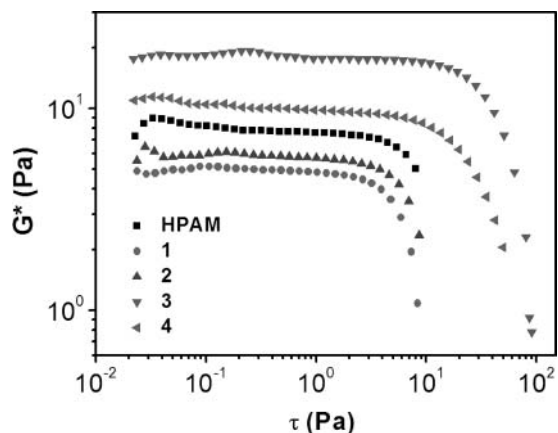


Fig. 4. Complex modulus (G^*) as a function of the applied stress at a constant frequency (6.283 rad/s) for HPCMB system at different pH values at 25°C .

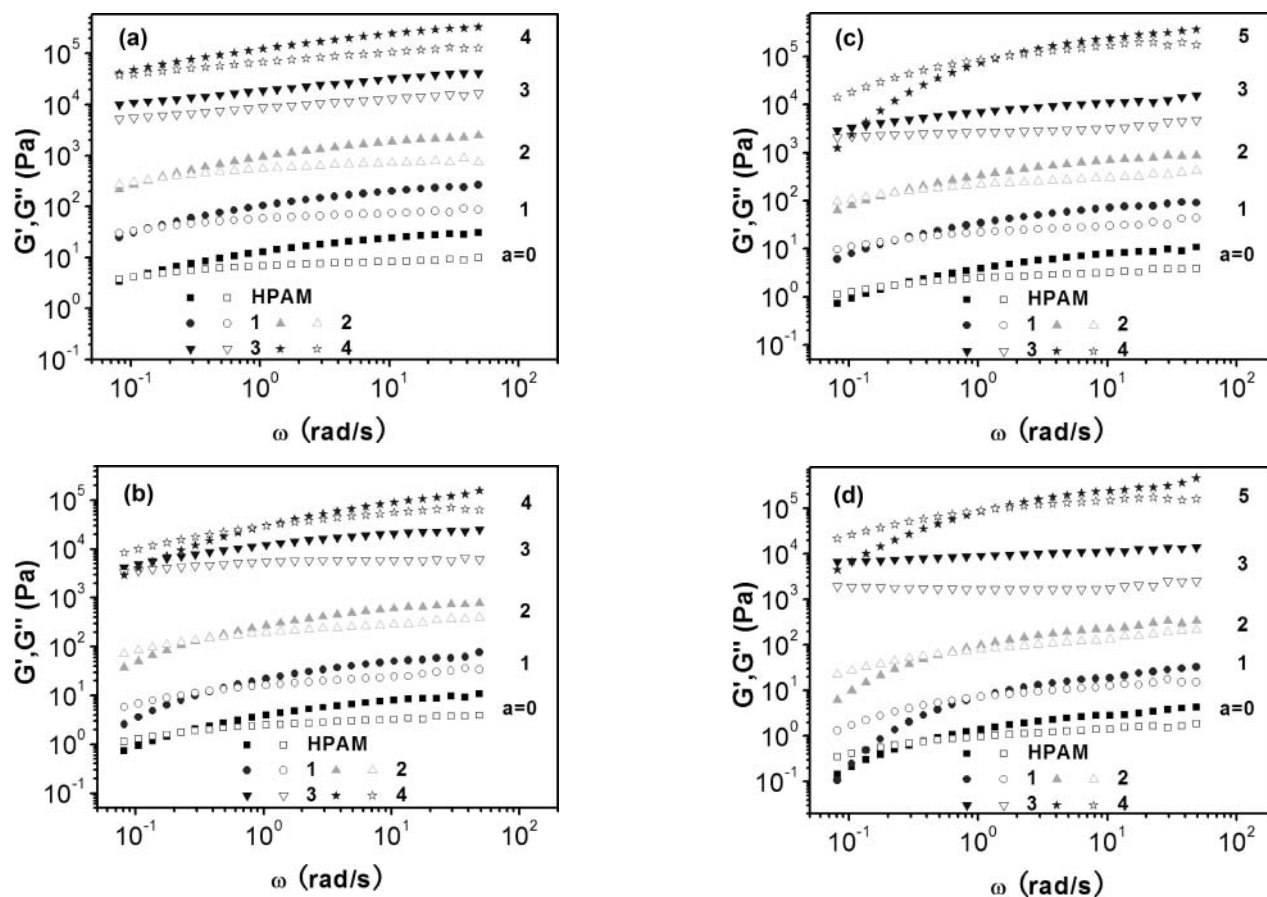


Fig. 5. Angular frequency ω dependence of storage modulus G' (solid symbol) and G'' (open symbol) for samples of HPCMA (a), HPCMB (b), HPCMC (c) and HPCMD (d) systems. The data have been vertically shifted by a factor of 10^a with given a to avoid overlapping.

as the values of τ_c at different pH values. The other systems also show the similar stress and pH values dependence for G^* during the process. All of the viscoelastic measurements were carried out at 1 Pa, which is within the linear region.

Figure 5 shows the angular frequency ω dependence of storage modulus G' (solid symbol) and G'' (open symbol) for all samples of four systems. The data are vertically shifted by a factor of 10^a to avoid overlapping. For all samples, both G' and G'' increase monotonously over the entire frequency range, which is in agreement with those reported in the literatures (33). For HPAM sample and HPAM/CMCH samples in alkaline and acidic environment of each system, G' is smaller than G'' at lower angular frequencies. With increasing frequency, G' and G'' show an intersection, after which G' becomes larger than G'' , indicating a more pronounced elastic behavior of the samples at higher frequencies. This is the characteristic of a viscoelastic fluid according to the Rouse-Zimm theory (34). For HPAM/CMCH sample in neutral environment of each system, G' becomes higher than G'' over the entire frequency range investigated, which indicates their elastic nature.

In addition, the difference in the value of these two moduli is less than one decade, indicating that the sample behaved as a weak gel (35).

Winter and Chambon found experimentally that the storage modulus G' and loss modulus G'' exhibit the power-law dependence on the angular frequency ω at the critical gel point (36–37):

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad (2)$$

Where n is the relaxation critical exponent. Therefore, from the results of Figure 5, it is indicated that pH value can markedly affect the viscoelastic property of the HPAM/CMCH mixture system. When pH is close to 7, there is a transition region from sol to gel, where the ω dependent curve of G' becomes parallel to G'' on the logarithmic coordinate over a wide frequency range.

It has been established that the viscoelastic properties of many associative polymer aqueous solutions can be described by Maxwell model (38–40). In the Maxwell model, G' increases monotonously and reaches the high frequency plateau modulus G_0 while G'' increases at first, reaches a maximum value and then decreases continuously. No

decrease of G' is observed at high frequency. As a result, G' and G'' do not show simple Maxwellian behavior characterized by a single relaxation time. These samples exhibited a distribution of relaxation times. This behavior is different from the telechelic polymers, which are characterized by a single relaxation time, attributed to the exit rate of the hydrophobe group from a micelle (41–42). In the case of this experiment, because of the chemical linkage between functional groups belonging to the same polymer chain, the disengagement of one junction from the complex will not lead to complete relaxation of the stress on the polymer chain; the chain is still linked to the complex through other junctions (40).

The intersection point of the curves of $G'(\omega)$ and $G''(\omega)$ gives the critical angular frequency (ω^*), and the relaxation time (λ_0) of the contribution of the longest relaxation process can be inferred from the following equation (36):

$$\lambda_0 = 1/\omega^* \quad (3)$$

According to the analysis of experiment data, the change in ω^* is observed as illustrated in Figure 6. The value of ω^* of sample numbered 3 in every system is not obtained in the range of the frequency investigated, however, high coefficients of correlation are obtained when these data of $G'(\omega)$ and $G''(\omega)$ are linearly fitted in log-log coordinate system. As a result, the intersection of two lines is defined as ω^* in such a case. After CMCH is added into HPAM solution, ω^* increases in three system, which indicates that CMCH induces the collapse of the HPAM molecular network. In HPCM/CMCH systems, with increasing pH value, ω^* decreases at first corresponding to an increase of relaxation time induced by formation of a stronger network. With a further increase of pH value, ω^* begins to increase, corresponding to a decrease of critical relaxation time due to the collapse of the network induced by the shrink of HPAM molecules. All of these variations are consistent with the observed variations of the flow behavior index n at corresponding pH value. It is obvious that the concentrations of HPAM and CMCH can remarkably affect the variation of ω^* in the process. Compared to the other three systems, ω^* of HPCMA system shows more insensitive to pH value, which might attribute to the high concentration of HPAM. However, in HPCMC system, there is no change in the value of ω^* after CMCH is added into HPAM solution, which indicates that the effect of CMCH of such a low concentration on HPAM molecular network might be insignificant. At the pH about 5.6, the values of ω^* of HPCMB, HPCMC and HPCMD systems are in the same order as the concentrations of CMCH in the three systems, which indicates that the molecule network of HPAM and CMCH aggregation with more CMCH component exhibits better performance of acid tolerance.

Winter and Chambon developed a constitutive equation based on the existence of an intermediate state of the material at which the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are congruent functions in the entire range $0 < \omega < \infty$ (43).

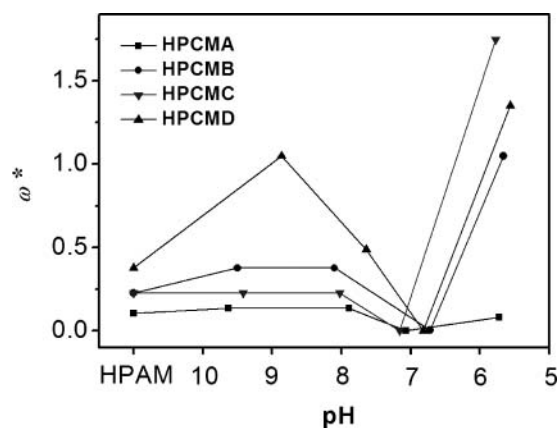


Fig. 6. Variation of ω^* as a function of pH value for four systems.

This work defined a new material property, the strength or stiffness (S), easily measures in a single oscillatory shear experiment during the crosslinking reaction. The parameter S can be obtained in the following equation (43–44):

$$G'(\omega) = S\omega^n \cos(n\pi/2)\Gamma(1-n) \quad (4)$$

Where n is a relaxation exponent and $\Gamma(1-n)$ is the Gamma function of $1-n$. Equation 4 is generally valid for viscoelastic liquids and solids. For $n \rightarrow 1$, the material is purely viscous; for $n \rightarrow 0$, the material is purely elastic. The case $n = 0.5$ was called an ideal gel (37).

In this paper, a non-linear regression procedure using Equation 4 enabled us to obtain gel stiffness (S) and the results are shown in Figure 7. The gel stiffness increases sharply when pH approximates 7. This can be due to the fact that strong three-dimensional networks formed in neutral environment. Compared HPCMB with HPCMC, the gel stiffness of HPCMB is lower than that of HPCMC in alkaline environment and is higher than that of HPCMC in a neutral environment. This indicates that CMCH

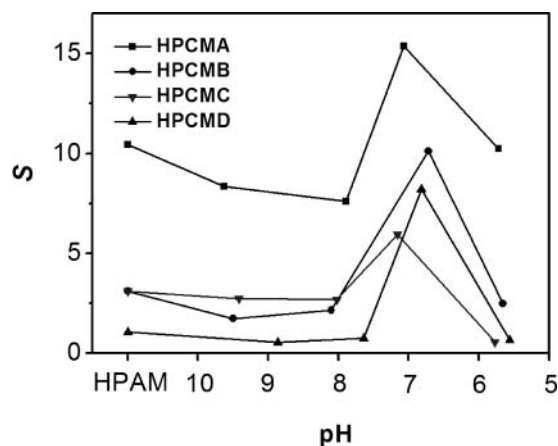


Fig. 7. Variation of gel stiffness (S) as a function of pH value for four systems.

component, which could be regarded as ionic crosslinking agent, plays an important role in the formation of strong networks. Moreover, compared HPCMC and HPCMD, it is interesting to note that the gel stiffness of HPCMC is lower than that of HPCMD in neutral environment. Considering that the concentrations of HPAM in HPCMC and HPCMD systems are 5 and 2.5 g/L and these of CMCH are 0.375 and 0.625 g/L, respectively, it could be concluded that proper concentrations of HPAM and CMCH are crucial for the formation of elastic molecular network.

4 Conclusions

The pH effects on the gelation behavior of HPAM and CMCH mixed system were investigated by rheological measurements. The viscosity measurement indicated that the interaction between HPAM and CMCH existed and could be significantly affected by pH value of the solution. Oscillation measurements showed that there was a sol-gel transition when pH was nearly 7, and the network structure of the system was firstly enhanced and then weakened due to the amphoteric property of CMCH with the decrease of pH value. Our results would probably be helpful for a better understanding of the gelation behavior of pH-responsive polymers.

Acknowledgments

The authors gratefully acknowledge the financial support from Major Research of the Ministry of Science and Technology, China (Grant No2008ZX05024-02-007) and National Basic Research Program of China (973 Program, 2009CB930103)

References

- Darwish, M.I.M., Van Der Maarel, J.R.C. and Zitha, P.L.J. (2004) *Macromolecules*, 37(6), 2307–2312.
- Caulfield, M.J., Qiao, G.G. and Solomon, D.H. (2002) *Chem. Rev.*, 102(9), 3067–3084.
- Xin, X., Xu, G., Wu, D., Li, Y. and Cao, X. (2007) *Colloids Surf., A*, 305(1–3), 138–144.
- Cummings, E.D., Brown, J.M., Sarva, S.T., Waldo, R.H. and Hilliard, G.M. (2007) *J. Proteome Res.*, 6(4), 1603–1608.
- Liu, X., Guan, Y., Yang, D., Li, Z. and Yao, K. (2001) *J. Appl. Polym. Sci.*, 79(7), 1324–1335.
- Nishimura, S., Nishi, N., Tokura, S., Nishimura, K. and Azuma, I. (1986) *Carbohydr. Res.*, 146(2), 251–258.
- Kennedy, R., Costain, D., McAlister, V. and Lee, T. (1996) *Surgery*, 120(5), 866–870.
- Muzzarelli, R., Ramos, V., Stanic, V., Dubini, B., Mattioli-Belmonte, M., Tosi, G. and Giardino, R. (1998) *Carbohydr. Polym.*, 36(4), 267–276.
- Sun, L., Du, Y., Fan, L., Chen, X. and Yang, J. (2006) *Polymer*, 47(6), 1796–1804.
- Wang, L., Chen, X., Liu, C., Li, P. and Zhou, Y. (2008) *J. Polym. Sci., Part B: Polym. Phys.*, 46(14), 1419–1429.
- Hoffman, A.S. (2002) *Adv. Drug Deliv. Rev.*, 54(1), 3–12.
- Lee, K. and Mooney, D. (2001) *Chem. Rev.*, 101(7), 1869–1880.
- Wang, Y., Tan, Y., Huang, X. and Xu, G. (2009) *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 46(4), 397–404.
- Mortensen, K. and Pedersen, J. (1993) *Macromolecules*, 26(4), 805–812.
- Dong, J., Chowdhry, B. and Leharne, S. (2006) *Colloids Surf., A*, 277(1–3), 249–254.
- Schild, H. (1992) *Prog. Polym. Sci.*, 17(2), 163–249.
- Hales, M., Barner-Kowollik, C., Davis, T. and Stenzel, M. (2004) *Langmuir*, 20(25), 10809–10817.
- Zhang, J., Cheng, S. and Zhuo, R. (2003) *Colloid Polym. Sci.*, 281(6), 580–583.
- Jeong, B., Bae, Y., Lee, D. and Kim, S. (1997) *Nature*, 388(6645), 860–862.
- Lee, J., Hua, F. and Lee, D. (2001) *J. Controlled Release*, 73(2–3), 315–327.
- Jeong, B., Bae, Y. and Kim, S. (1999) *Macromolecules*, 32(21), 7064–7069.
- Xu, P., Van Kirk, E., Zhan, Y., Murdoch, W., Radosz, M. and Shen, Y. (2007) *Angew. Chem.*, 119(26), 5087–5090.
- Liu, S., Weaver, J., Save, M. and Armes, S. (2002) *Langmuir*, 18(22), 8350–8357.
- Yang, Q., Wang, S., Fan, P., Wang, L., Di, Y., Lin, K. and Xiao, F. (2005) *Chem. Mater.*, 17(24), 5999–6003.
- Klein, J. and Conrad, K.D. (1978) *Makromol. Chem.*, 179, 1635–1638.
- Berger, J., Reist, M., Mayer, J., Felt, O., Peppas, N. and Gurny, R. (2004) *Eur. J. Pharm. Biopharm.*, 57(1), 19–34.
- Lee, J., Kim, S., Kim, S., Lee, Y., Lee, K. and Kim, S. (1999) *J. Appl. Polym. Sci.*, 73(1), 113–120.
- Harris, T. and Walczyk, D. (2009) *J. Appl. Polym. Sci.*, 111(3), 1286–1292.
- Yasuda, K., Armstrong, R. and Cohen, R. (1981) *Rheol. Acta*, 20(2), 163–178.
- Lewandowska, K. (2007) *J. Appl. Polym. Sci.*, 103(4), 2235–2241.
- Khatory, A., Lequeux, F., Kern, F. and Candau, S. (1993) *Langmuir*, 9(6), 1456–1464.
- Schulte, J., Enders, S. and Quitzsch, K. (1999) *Colloid Polym. Sci.*, 277(9), 827–836.
- Xin, X., Xu, G., Gong, H., Bai, Y. and Tan, Y. (2008) *Colloids Surf., A*, 326(1–2), 1–9.
- Lu, L., Liu, X., Dai, L. and Tong, Z. (2005) *Biomacromolecules*, 6(4), 2150–2156.
- Noisuwan, A., Hemar, Y., Wilkinson, B. and Bronlund, J. (2009) *Starch-Starke*, 61(3–4), 214–227.
- Winter, H. and Chambon, F. (1986) *J. Rheol.*, 30(2), 367–382.
- Chambon, F. and Winter, H. (1987) *J. Rheol.*, 31(8), 683–697.
- Tam, K., Jenkins, R., Winnik, M. and Bassett, D. (1998) *Macromolecules*, 31(13), 4149–4159.
- Tirtaatmadja, V., Tam, K. and Jenkins, R. (1997) *Macromolecules*, 30(11), 3271–3282.
- Zhuang, D., Cao, Y., Zhang, H., Yang, Y. and Zhang, Y. (2002) *Polymer*, 43(7), 2075–2084.
- Annable, T., Buscall, R., Ettelaie, R. and Whittlestone, D. (1993) *J. Rheol.*, 37(4), 695–726.
- Heitz, C., Prud'Homme, R. and Kohn, J. (1999) *Macromolecules*, 32(20), 6658–6667.
- Martinez-Ruvalcaba, A., Chornet, E. and Rodrigue, D. (2007) *Carbohydr. Polym.*, 67(4), 586–595.
- Winter, H. and Mours, M. (1997) *Adv. Polym. Sci.*, 134, 165–234.