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# Synthesis and Characterization of Water-Soluble Cellulose Derivatives with Thermo- and pH-Sensitive Functional Groups

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A series of water-soluble cellulose derivatives with thermo- and pH-sensitive properties were prepared in aqueous solutions by the graft copolymerization of *N*-isopropylacrylamide (NIPAAm) on carboxymethylcellulose (CMC). Ceric ammonium nitrate (CAN) was used in combination with nitric acid as the initiator system. The effects of various factors such as CAN concentration, NIPAAm and CMC amounts as well as reaction temperature on the grafting percentage and efficiency were studied. The resultant cellulose derivatives were characterized with respect to their structure and aqueous solution properties by IR spectra, thermogravimetric analyses and optical transmittance measurements.

**Keywords:** cellulose derivative; functionalization modification; stimuli-response polymer

## 1 Introduction

Among chemically modified polysaccharides, water-soluble cellulose derivatives are probably one of the most extensively studied during the last decades. As an important class of cellulosic functional materials, they have found very wide applications in the industries concerned with oil field treatments, food, biomedical products, protective colloids, coating, surfactants, hair conditioners, anti-static agents, dispersion agents, adhesives, textiles, etc. (1–7).

In recent years, much attention has been focused on water-soluble stimuli-response polymers, which are able to respond with dramatic property changes to small changes in their environment (8, 9). According to the stimuli, these polymers can be classified as temperature-, pH-, ionic strength-, electric- and magnetic field-sensitive. Some of them respond to a combination of two or more stimuli. For example, there is a coil-globule transition and phase separation at the lower critical solution temperature (LCST) in the case of temperature response (10). When pH-sensitive functional groups have been incorporated into thermosensitive polymers, the phase separation can also be triggered by a change in the pH at specific temperatures (11). Recent advances in the design of stimuli-responsive polymers have created opportunities for novel biomedical applications. Stimuli-responsive change in shape, surface characteristics, solubility, formation of an intricate molecular self-assembly and a sol-gel transition enabled several applications in the delivery of therapeutics, tissue engineering, cell culture, bio-separations and sensor or actuator systems (12–15).

In this work, a series of water-soluble cellulose derivatives with thermo- and pH-sensitive functional groups were prepared in aqueous solutions by the graft copolymerization of *N*-isopropylacrylamide (NIPAAm), which contains a thermosensitive *N*-isopropyl group, on carboxymethylcellulose (CMC), which contains pH-sensitive carboxymethyl groups, using ceric ammonium nitrate (CAN)/nitric acid as the initiator system. Described herein are their synthesis and characterization.

## 2 Experimental

### 2.1 *Material*

CMC was a product of Calbiochem-Behring Corp. (LaJolla, CA). Its molecular weight was of a nominal value

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$M_w = 500{,}000$. The content of the carboxyl groups was determined by titration of the acid form with 0.1 mol/L NaOH and was found to be 0.66 carboxyl groups per anhydroglycose unit. NIPAAm was purchased from Acros Chemical Company, purified by recrystallization in the mixture of benzene and hexane (1:10, v/v) and dried at 25°C in a vacuum desiccator. The ceric ammonium nitrate (CAN) and other chemicals were commercial grade products, and used without further purification.

### 2.2 *Grafting Procedure*

The grafting reactions were carried out under nitrogen in a three-necked round-bottom flask equipped with a stirrer, a reflux condenser and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, 0.1 g CMC was first dissolved in 20 ml distilled water at room temperature with constant stirring and bubbling of a slow stream of $N_2$ for about 15 min. The required quantity of NIPAAm monomer was dissolved in 3 ml distilled water and mixed with CMC solution. After nitrogen was purged through the mixed solution for 20 min, the determined quantity of freshly prepared initiator solution was added into the reaction system. The flask content was kept in a thermostatic water bath at different temperatures for the required time. After completion of the reaction, the products were precipitated in an excess of methanol, separated by filtration, and dried in a vacuum oven at 60°C. To obtain the pure graft copolymers, the resulting products were then extracted with an appropriate solvent to remove the produced homopolymer. It was found that extracting with methanol for 12 h was sufficient to remove the homopolymer (PNIPAAm). After complete removal of the homopolymer, the pure graft copolymer was dried at 60°C under vacuum to a constant weight.

### 2.3 *Structural Characterization*

The graft copolymers were characterized by the grafting parameters, infrared spectra (IR) and thermogravimetric analysis. The following grafting parameters were determined as follows:

$$\text{Grafting percentage} = (W_1 - W_0) \times 100/W_0$$
$$\text{Grafting efficiency} = (W_1 - W_0) \times 100/W_2$$

where $W_0$, $W_1$, and $W_2$ denote the weights of CMC, pure graft copolymer, and the monomer NIPAAm, respectively. The IR spectra were measured on a Nicolet Nexus 670 Fourier Transform Infrared Instrument using KBr pallets in the range of 400–4000 $cm^{-1}$. The thermogravimetric and differential thermogravimetric (TG/DTG) curves were recorded on a Perkin-Elmer TGS-2 derivatography at a heating rate of 20°C/min and nitrogen flow of 50 ml/min.

### 2.4 *Measurements of Optical Transmittance*

The optical transmittances of aqueous sample solutions in various temperatures and pH conditions were recorded at 500 nm with a 721 spectrophotometer made in the Shanghai Instrument Company of China. The temperature of the sample cell was thermostatically controlled using a circulator system. At each temperature, the sample solution was allowed to equilibrate for about 10 min before the measurement.

## 3 Results and Discussion

Although a number of methods are available for initiating the grafting sites on a polysaccharide backbone, ceric ion redox systems have gained considerable importance in the grafting reaction of cellulose or chemically modified cellulose due to its ease of application and minimized homopolymer formation (16, 17). This technique is based on the fact that when cellulose or chemically modified cellulose is oxidized by a ceric ion such as CAN, free radicals capable of initiating vinyl polymerization are formed on the chemically modified cellulose by a single electron transfer. Acid such as nitric acid is usually used as the reducing agent in the redox systems (18, 19). For this reason, a combination of CAN with nitric acid was used as the initiator system in this work.

Figure 1 gives the effect of CAN concentration on the grafting reaction when the concentration of nitric acid was kept to be $4.17 \times 10^{-2}$ mol/L. With the increase of CAN concentration from $5.20 \times 10^{-3}$ to $1.04 \times 10^{-1}$ mol/L, the grafting percentage increased from 13.3 to 232.5%, and the grafting efficiency increased from 2.0 to 34.3%. This shows that CAN has indeed an initiating ability for the graft copolymerization of CMC with NIPAAm in the presence of nitric acid.

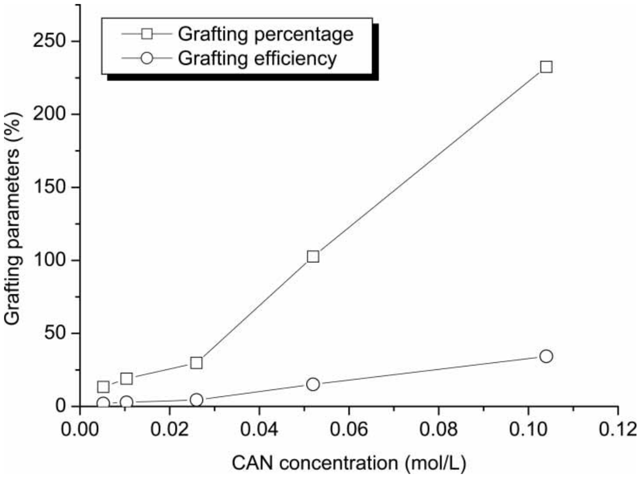

**Fig. 1.** Effect of CAN concentration on the grafting percentage and efficiency. Conditions: CMC, 0.5 g/dL; NIPAAm, 0.184 mol/L; Nitric acid, $4.17 \times 10^{-2}$ mol/L; 40°C; 6 h.

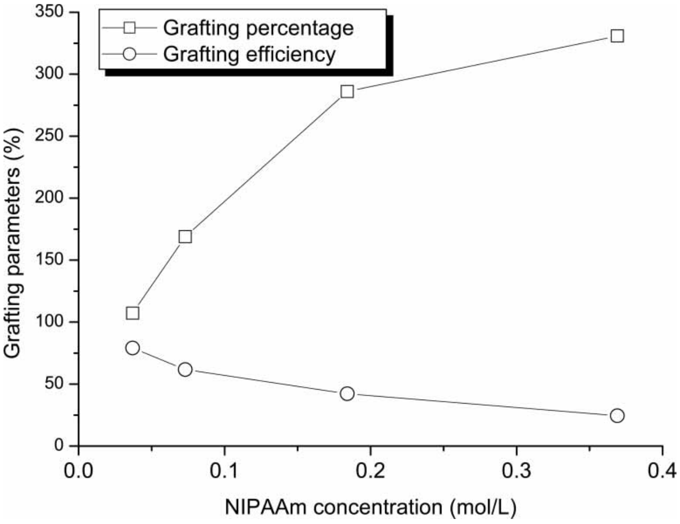

**Fig. 2.** Effect of NIPAAm concentration on the grafting percentage and efficiency. Conditions: CMC, 0.5 g/dL; CAN, 0.052 mol/L; Nitric acid, $4.17 \times 10^{-2}$ mol/L; 40°C; 6 h.

The effect of NIPAAm concentration on the grafting parameters was evaluated in a series of polymerizations in which the concentration of NIPAAm was varied from 0.037 to 0.369 mol/L. As shown in Figure 2, the grafting percentage increased while the grafting efficiency decreased with the increase of NIPAAm concentration. At higher NIPAAm concentrations, an increase of the grafting percentage could be interpreted in terms of the greater availability of NIPAAm molecules in the proximity of CMC, and a decrease of the grafting efficiency may be attributed to more homopolymer of NIPAAm monomer.

Figure 3 shows the effect of CMC amount on the grafting reaction. When the amount of CMC increased from 0.5 to 1.2 g/dL, the grafting percentage and grafting efficiency had both a decrease. This may be due to the fact that an increase of CMC amount increases the viscosity of the reaction medium, which in turn reduces the mobility of the macromolecules, thereby lowering the grafting extent.

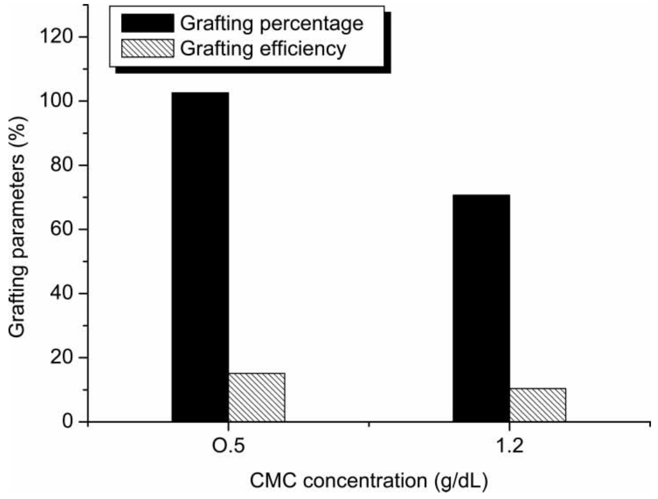

**Fig. 3.** Effect of CMC amount on the grafting percentage and efficiency. Conditions: NIPAAm, 0.184 mol/L; CAN, 0.052 mol/L; Nitric acid, $4.17 \times 10^{-2}$ mol/L; 40°C; 6 h.

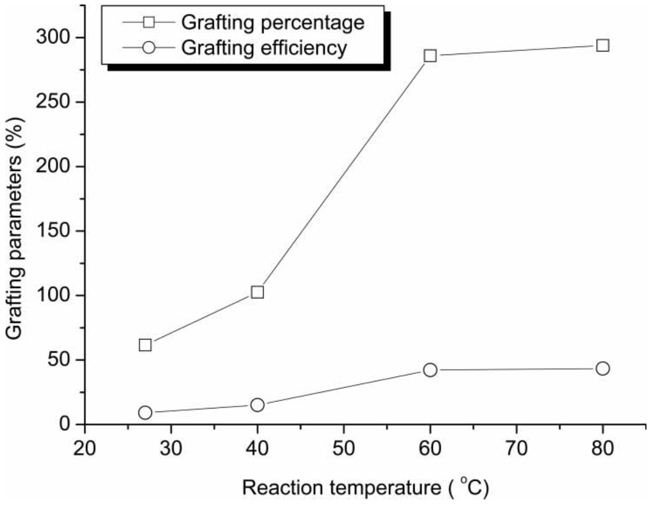

**Fig. 4.** Effect of reaction temperature on the grafting percentage and efficiency. Conditions: CMC, 0.5 g/dL; NIPAAm, 0.184 mol/L; CAN, 0.052 mol/L; Nitric acid, $4.17 \times 10^{-2}$ mol/L; 6 h.

The relationship between the grafting extent and the reaction temperature is illustrated in Figure 4. Within the temperature range investigated, increasing the temperature up to 60°C is accompanied by an increase in the grafting percentage and grafting efficiency, but beyond that point the polymerization temperature does not cause a significant change of the grafting percentage and grafting efficiency. This demonstrates that the appropriate increase of the temperature will favor the activation of backbone radicals and monomer radicals.

The FTIR spectra of pure CMC, NIPAAm homopolymer (PNIPAAm) and the grafted CMC were shown in Figure 5. Different from the spectrum of CMC or PNIPAAm, the spectrum of the grafted CMC shows not only the characteristic stretching vibrations of CMC, but also the additional characteristic absorption bands at 1648 $\text{cm}^{-1}$ and 1386 $\text{cm}^{-1}$ for NIPAAm units. Figure 6 gives the TG/DTG curves for the thermal degradation of pure CMC, PNIPAAm and the grafted CMC. Due to moisture, three samples all have a mass loss of 10 wt% below 100°C. CMC is characteristic of a single thermogravimetric step, and decomposes in the 200–310°C temperature range with a mass loss of 45 wt%. PNIPAAm exhibits a degradative step in the 300~460°C temperature range with a mass loss of 88 wt%, and has a peak decomposition temperature of 429°C. In contrast, the grafted CMC shows a two-stage degradation. The first TG stage occurred in the 210–390°C temperature range with a mass loss of 45 wt%, which could be ascribed to the degradation of the CMC backbone. The

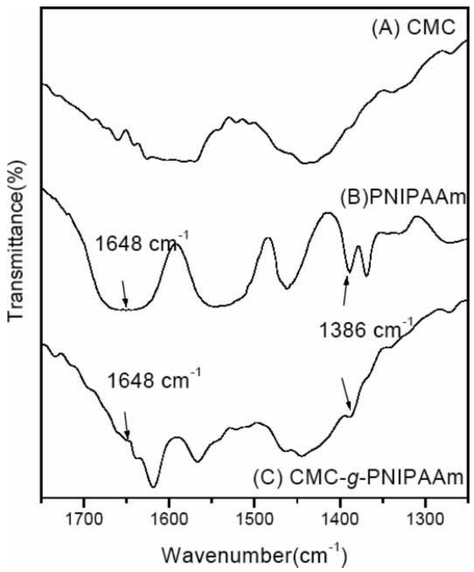

**Fig. 5.** The FTIR spectra of pure CMC (A), PNIPAAm (B), and the grafted CMC (C).

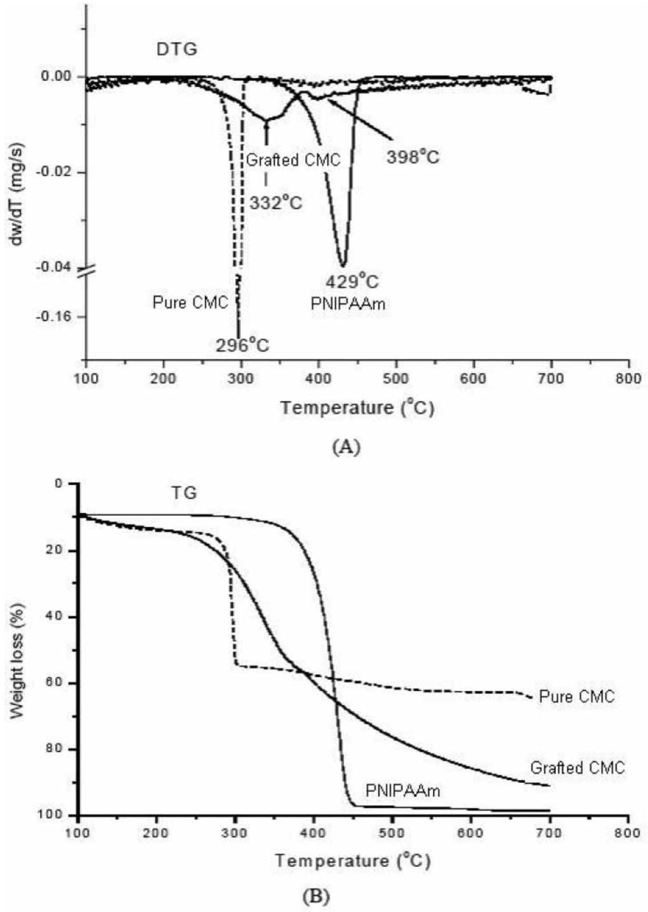

**Fig. 6.** TG/DTG curves for the thermal degradation of pure CMC, PNIPAAm and the grafted CMC at a heating rate of 20°C/min.

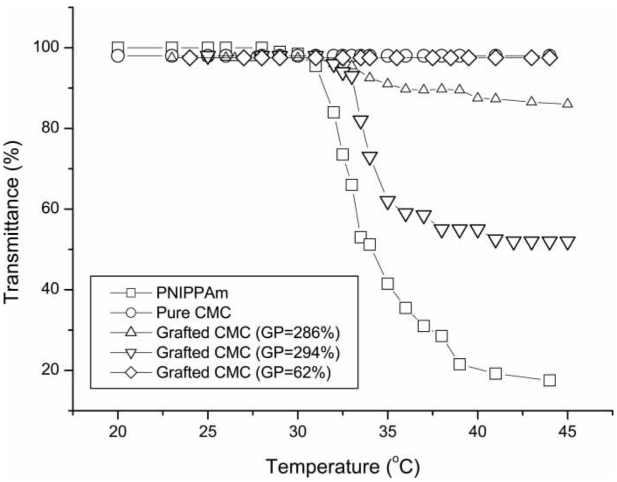

**Fig. 7.** The changes of optical transmittances with temperature for 0.5% aqueous solutions of pure CMC, PNIPAAm and the grafted CMC samples with different grafting percentages.

second TG stage occurred in 390–520°C with a mass loss of 25 wt%, which could be ascribed to the decomposition of the PNIPAAm side chains. Moreover, the first DTG peak of the grafted CMC is shifted to higher temperature when compared to that of CMC while its second DTG peak is shifted to lower temperature when compared to that of PNIPAAm. FTIR spectra and TG/DTG analyses confirmed the modification reaction of CMC by grafting PNIPAAm.

Figure 7 shows the changes of optical transmittances with temperature for 0.5% aqueous solutions of pure CMC, PNIPAAm and the grafted CMC samples with different grafting percentages. For unmodified CMC, its aqueous solution was observed to be completely transparent with the transmittance of almost 100% in the temperature range studied, which implied that no phase separation occurred in such polysaccharide solution when temperature was changed. Dependent on the grafting percentage (GP) of PNIPAAm on the CMC, however, the temperature-dependent transmittance changes of aqueous solutions containing the grafted CMC samples could be observed. With the increase of GP, the transmittance change becomes more obvious, showing the temperature-induced phase transition between hydrated and dehydrated states of the cellulose derivative (20). It is clear that the grafting of PNIPAAm side chains onto hydrophilic CMC backbone could provide the CMC with new, thermoresponsive property in aqueous solutions.

The effect of pH conditions on the temperature-dependent transmittance change for 0.5% aqueous solutions of the graft CMC (GP = 294%) is indicated in Figure 8. With the decrease of pH value, the temperature-dependent transmittance change is more remarkable. This pH-sensitive behavior could be ascribed to the dissociation and ionization of the carboxymethyl groups on the CMC backbone. The

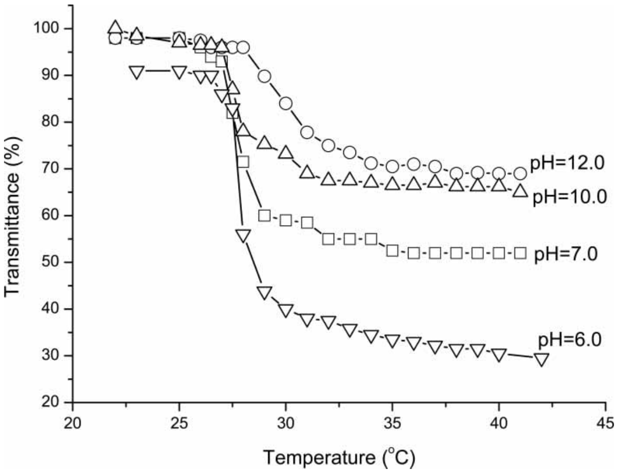

**Fig. 8.** The effect of pH conditions on the temperature-dependent transmittance change for 0.5% aqueous solutions of the graft CMC sample with the GP of 294%.

higher pH values of the solution prompt more ionic dissociation of the carboxymethyl groups, which may cause the formation of less hydrogen-bonded complexes between NIPAAm units and CMC backbone of the grafted CMC. The opposite holds true in the case of lower pH values of the solution. These results are in good agreement with the previous study (20), in which the graft copolymer of poly (acrylic acid) with poly(*N*,*N*-dimethylacrylamide) was investigated with respect to pH- and thermo-sensitive phase-separation behavior in aqueous solution.

## 4 Conclusions

In conclusion, water-soluble cellulose derivatives based on carboxymethylcellulose and poly(*N*-isopropylacrylamide) could be successfully prepared by a graft copolymerization method, in which the combination of ceric ammonium nitrate with nitric acid was used as the initiator system. Depending on the grafting extent of poly(*N*-isopropylacrylamide), such polysaccharide derivatives could be expected to have thermo- and pH-sensitive properties in aqueous solutions and function as intelligent polymeric materials for some industrial applications.

## 5 Acknowledgements

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## 6 References

1. Reveley, A.. In *Cellulose and Its Derivatives: Chemistry, Biochemistry and Applications*; Kennedy, J.E., Phillips, G.O., Wedlock, D.J. and Williams, P.A. (eds.); John Wiley and Sons: New York, 211, 1985.
2. Heinze, T. and Liebert, T. (2001) *Prog. Polym. Sci.*, **26**, 1689–1762.
3. Zhang, L.M. (2001) *Macromol. Mater. Eng.*, **286**, 267–275.
4. Zhang, L.M., Tan, Y.B. and Li, Z.M. (2001) *Carbohydr. Polym.*, **44**, 255–260.
5. Zhang, L.M. (1999) *Colloid Polym. Sci.*, **277**, 282–284.
6. Zhang, L.M. and Huang, S.J. (2000) *Polym. Int.*, **49**, 528–532.
7. Zhang, L.M., Tan, Y.B. and Li, Z.M. (2000) *J. Appl. Polym. Sci.*, **77**, 195–201.
8. Galaev, I.Y. and Mattiasson, B. (1999) *Trends Biotechnol.*, **17**, 335–340.
9. Dhara, D. and Chatterji, P.R. (2000) *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **40**, 51–68.
10. Schild, H.G. (1992) *Prog. Polym. Sci.*, **17**, 163–249.
11. Feil, H., Bae, Y.H., Feijen, J. and Kim, S.W. (1992) *Macromolecules*, **25**, 5528–5530.
12. Jeong, B. and Gutowska, A. (2002) *Trends Biotechnol.*, **20**, 305–311.
13. Jeong, B., Kim, S.W. and Bae, Y.H. (2002) *Adv. Drug Delivery Rev.*, **54**, 37–51.
14. Gil, E.S. and Hudson, S.M. (2004) *Prog. Polym. Sci.*, **29**, 1173–1222.
15. Shi, H.Y. and Zhang, L.M. (2006) *Carbohydrat. Res.*, **341**, 2414–2419.
16. Hebeish, A. and Guthrie, J.T. *The Chemistry and Technology of Cellulosic Copolymers*; Springer-Verlag: Berlin, 1981.
17. Zhang, L.M. and Chen, L.Q. (2002) *J. Appl. Polym. Sci.*, **83**, 2755–2761.
18. Ei-Din, N.M.S. (1991) *J. Appl. Polym. Sci.*, **43**, 1017–1024.
19. Gurdag, G., Yasar, M. and Gurkaynak, M.A. (1997) *J. Appl. Polym. Sci.*, **66**, 929–937.
20. Shibanuma, T., Aoki, T., Sanui, K., Ogata, N., Kikuchi, A., Sakurai, Y. and Okano, T. (2000) *Macromolecules*, **33**, 444–450.