Water-Soluble Grafted Polysaccharides Containing Sulfobetaine Groups: Synthesis and Characterization of Graft Copolymers of Hydroxyethyl Cellulose with 3-Dimethyl(methacryloyloxyethyl)ammonium Propane Sulfonate

LI-MING ZHANG,[1,2,3] **LI-QIONG CHEN**[1]

[1] Institute of Polymer Science, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, People's Republic of China

[2] Key Laboratory for Polymeric Composite and Functional Materials of the Ministry of Education, Zhongshan University, Guangzhou 510275, People's Republic of China

[3] Laboratory of Cellulose & Lignocellulosics Chemistry, Chinese Academy of Science, Guangzhou 510650, People's Republic of China

ABSTRACT: New water-soluble grafted polysaccharides containing sulfobetaine groups were synthesized by the grafting of the sulfobetaine-type zwitterionic monomer 3-dimethyl-(methacryloyloxyethyl)ammonium propane sulfonate (DMAPS) onto hydroxyethyl cellulose (HEC) in the presence of a ceric ammonium nitrate (CAN)/ethylenediaminetetraacetic acid (EDTA) initiation system. The effects of the concentrations of CAN, EDTA, DMAPS, and HEC, as well as the polymerization time and temperature, on the grafting reactions were investigated in terms of the grafting percentage (%GP) and grafting conversion (%GC) of the monomer. The %GP and %GC increased and then decreased with increasing concentrations of CAN, EDTA, and HEC. The %GP and %GC increased with increasing DMAPS concentration up to a certain value, beyond which the %GP did not significantly increase and the %GC decreased. The appropriate polymerization time and temperature were favorable for the grafting reactions. With infrared, thermogravimetric analysis, and viscosity measurements, the resulting grafted polysaccharides were characterized. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2755–2761, 2002; DOI 10.1002/app.10191

Key words: graft copolymerization; ampholytic polysaccharides; sulfobetaine monomers; hydroxyethyl cellulose; functionalization of polymers

INTRODUCTION

Considerable research is now being carried out on the grafting of vinyl monomers onto polysaccha-rides and related substrates. The wide range of available monomers suggests that graft copolymerization is one of the most efficient methods for modifying their properties and preparing new materials. For example, the grafting of hydrophobic monomers such as methyl methacrylate, styrene, acrylonitrile, butadiene, and vinyl acetate can greatly enhance the processability and fabricating properties of polysaccharide substrates as well as their adhesion onto hydrophobic fibers, which has led to their widespread use in the textile and paper industries; the grafting of hydrophilic monomers such as acrylamide, acrylic acid, sodium styrene sulfonate, *N*-vinylpyrrolidone, and 2-hydroxy-3-methacryloyloxypropyltrimethyl

ammonium chloride can obviously improve the solubility of polysaccharides in aqueous media and their functions, which has led to their widespread use as various flocculants, thickening agents, and turbulent drag reducers for industrial applications.[1–3] This field of research has considerable academic and industrial interest.

Among the various grafted polysaccharides that have been investigated, water-soluble cellulosic graft copolymers are probably among the most extensively studied during the last few decades. There have been many investigations dealing with the grafting of a neutral monomer or an anionic monomer onto water-soluble cellulose derivatives such as carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC).[2,4–7] Recently, the grafting of a cationic monomer such as dimethyldiallylammonium chloride, trimethylallylammonium chloride, or dimethylaminoethyl methacrylate or a cationic monomer coupled with a neutral/anionic monomer onto nonionic HEC or anionic CMC has also been investigated in our laboratory, and the resulting water-soluble cationic or amphoteric cellulosic graft copolymers have been found to have potential applications as effective clay-hydration inhibitors, shale suppressants, and multifunctional drilling-fluid additives for the oil-field industry.[8–13] To our knowledge, however, there is no information available on the graft copolymerization of cellulose or its chemically modified analogues with the sulfobetaine-type zwitterionic monomers derived from dimethylaminoalkyl acrylate and dimethylaminoalkyl acrylamides, which recently have been widely considered as functional monomers to be used as minor components for synthetic copolymers in industries concerned with textiles, medical products, charged dispersing agents, protective colloids, and other related materials.[14–16]

In this study, we attempted to prepare new water-soluble grafted polysaccharides containing such sulfobetaine groups by grafting the zwitterionic monomer 3-dimethyl-(methacryloyloxyethyl)-ammonium propane sulfonate (DMAPS) onto HEC in the presence of an ethylenediaminetetraacetic acid (EDTA)/ceric ammonium nitrate (CAN) initiation system. For this purpose, the effects of various factors, such as the initiator concentration, monomer concentration, HEC amount, reaction time, and temperature, on the grafting of DMAPS onto HEC were studied, and the resulting grafted polysaccharides were characterized with infrared (IR), thermogravimetric analysis (TGA), and viscosity measurements.

EXPERIMENTAL

Materials

Commercial HEC obtained from Hoechst Co. (Dusseldorf, Germany) was used. Its molecular weight was 4.56×10^5 (H_2O, 25°C), as determined by a viscosity method.[17] The sulfobetaine monomer DMAPS was obtained from Aldrich Chemical Co. (Milwaukee, WI). CAN, EDTA, acetone, acetic acid, and 1,2-ethandiol were analytical-grade.

Graft Copolymerization

The graft copolymerization reaction was carried out in a 250-mL, four-necked, round flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a gas inlet, which was immersed in a thermostat water bath. The N_2 gas was purged into the flask for removal of the oxygen during the reaction. First, a definite amount of HEC (2.0–4.0 g/dL) was dissolved in distilled water at 35°C with stirring for 30 min. Then, the required concentrations of CAN solution (2.5–10.0 mmol/L) and EDTA solution (2.5–7.5 mmol/L) were added successively to the reaction system. After 10 min, the required amount of the zwitterionic monomer DMAPS was introduced. The reaction mixture was continuously stirred at 35°C for 4 h. For the polymerization versus time and temperature, separate polymerizations were stopped under various reaction periods. After the completion of the reactions, the rough products were first precipitated in an excess of acetone and then separated by filtration. To obtain the pure graft copolymer, we used a mixture of acetic acid and 1,2-ethandiol (60:40 v/v) to extract the homopolymer that might be produced during the polymerization. Extracting with this solvent system for 6 h was sufficient to remove the poly(DMAPS) homopolymer. Then, the resulting graft copolymer was dried under reduced pressure to a constant weight. On the basis of gravimetric measurements, the grafting parameters were determined as follows:

$$\%GP = (W_p - W_0)/W_0 \times 100$$

$$\%GC = (W_p - W_0)/W_m \times 100$$

where %GP is the grafting percentage and %GC is the grafting conversion of the monomer and W_0, W_p, and W_m are the weights of the HEC, purified graft copolymer, and zwitterionic monomer DMAPS, respectively. In a similar fashion, the
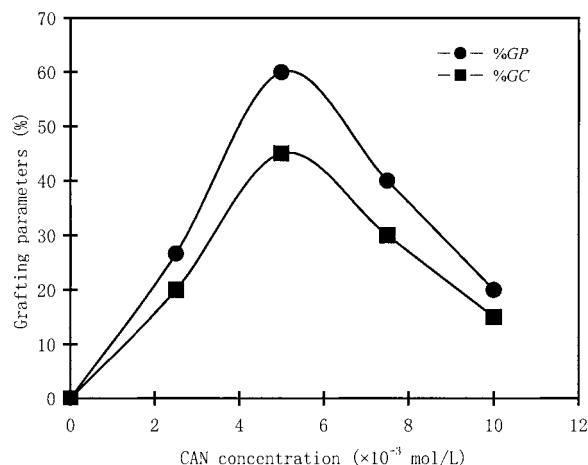
Figure 1 Effect of the CAN concentration on grafting: HEC, 3.0 g/dL; DMAPS, 0.1432 mol/L; EDTA, 5.0×10^{-3} mol/L; pH, 7.0; time, 4 h; and temperature, 35°C.

control experiments were carried out in the absence of CAN or HEC, respectively.

Characterization Methods

First, the IR spectra were obtained with a Bruker Equinox-55 spectrophotometer (Billerica, MA). KBr pellets were prepared for the measurements of pure HEC and its graft copolymer.

Second, TGAs of pure HEC and its graft copolymer were carried out with a Netzsch TG-209 analyzer (NETZSCH-Geratebau GmbH, Germany). The heating rate was 20°C/min in an air atmosphere.

Third, viscosity measurements of two graft copolymers with various %GP values in distilled water and aqueous salt solutions were carried out with an Ubbelohde viscometer at 30 ± 0.05°C. For each sample solution, the flow time was measured at five different concentrations. The intrinsic viscosity was then obtained (from the point of intersection) after the extrapolation of two plots, η_{sp}/C versus C and ln η_{rel}/C versus C, to zero concentration.[18] Here, C is the polymer concentration (g/dL), and η_{sp}/C is the reduced viscosity calculated from the relation $\eta_{sp}/C = \eta_{rel} - 1$, where $\eta_{sp} = \eta/\eta_0 \approx t/t_0$, with t being the flow time of the sample solution and t_0 being the flow time of the solvent at the measurement temperature; ln η_{rel}/C is the inherent viscosity.

RESULTS AND DISCUSSION

Synthesis of the Graft Copolymers

Effect of the CAN Concentration

Figure 1 shows the effect of the CAN concentration on grafting. Increasing the concentration of

CAN up to 5.0×10^{-3} mol/L is accompanied by an increase in the %GP and %GC, whereas a further increase causes a decrease in the %GP and %GC. In particular, the graft copolymerization of HEC with DMAPS did not occur in the absence of CAN.

CAN has gained considerable importance in the grafting reactions of vinyl monomers onto cellulosic substrates.[2] This technique is based on the fact that when cellulose or chemically modified cellulose is oxidized by CAN, free radicals capable of initiating vinyl polymerization are formed on the cellulose or chemically modified cellulose by a single electron transfer. For the grafting of DMAPS onto HEC, therefore, an increase in the grafting parameters with an increase in the CAN concentration may result from the production of more radical sites, which is favorable for grafting. However, a decrease of in grafting parameters at a higher CAN concentration may be due to the efficiency of Ce(IV) taking part in the termination of growing grafted chains and homopolymerization.

Effect of the EDTA Concentration

Figure 2 gives the effect of the EDTA concentration on grafting. The change in the grafting parameters with the EDTA concentration is similar to the effect of the CAN concentration on grafting. In Figures 1 and 2, we can observe that the maximum values of %GP and %GC are reached at the same concentration of CAN and EDTA, 5.0×10^{-3} mol/L. Previously, Hsu et al.[19,20] studied the interaction of EDTA with CAN used as a new redox initiator in the aqueous polymerization of
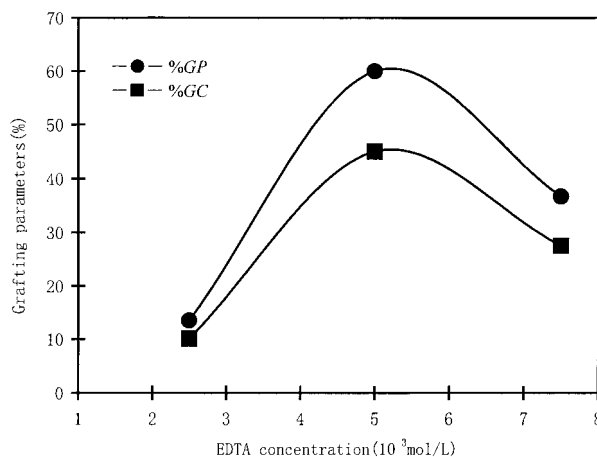

Figure 2 Effect of the EDTA concentration on grafting: HEC, 3.0 g/dL; DMAPS, 0.1432 mol/L; CAN, 5.0×10^{-3} mol/L; pH, 7.0; time, 4 h; and temperature, 35°C.
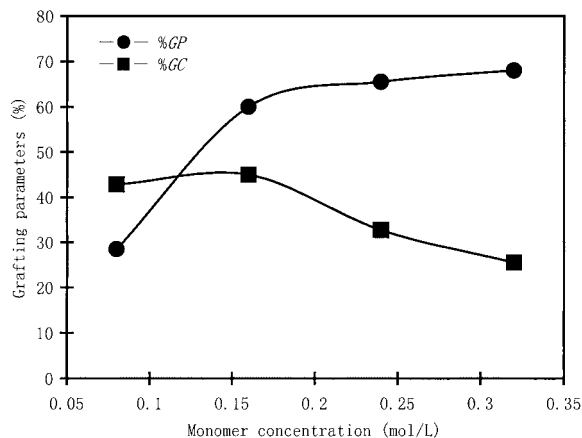
Figure 3 Effect of the DMAPS concentration on grafting: HEC, 3.0 g/dL; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; pH, 7.0; time, 4 h; and temperature, 35°C.

acrylamide, and they found that a 1:1 complex of charge transfer could be formed that easily produced free radicals. Thus, it seems that CAN and EDTA under the same concentration could better form a 1:1 complex of charge transfer, leading to higher efficiency of initiation.

Effect of the Monomer Concentration

Figure 3 demonstrates the effect of the DMAPS concentration on grafting. The %GP and %GC increase with the DMAPS concentration increasing up to 0.16 mol/L; beyond this, the %GP gradually levels off in the concentration regions studied, whereas the %MC decreases. As the monomer concentration increases, the diffusion of DMAPS molecules into the HEC backbone increases; consequently, there is an increase in the grafting parameters. The leveling off of the %GP could be associated with the depletion of the initiator and the reduction of the active sites on the HEC molecules as the graft copolymerization proceeds. Meanwhile, the depletion of the initiator and the reduction of the active sites on the HEC backbone lead to a decrease in the %GC. Moreover, the homopolymerization may occur at high DMAPS concentrations. Therefore, there is a reasonable DMAPS concentration for synthesizing graft copolymers.

Effect of the HEC Amount

The effect of the HEC amount on grafting initiated by CAN/EDTA is depicted in Figure 4. Increasing the amount of HEC up to 3.0 g/dL causes an obvious increase in the %GP and %GC,

whereas a further increase causes a decrease in the %GP and %MC. On the one hand, an increase in HEC results in more grafting sites, which is favorable for grafting. On the other hand, an increase in HEC increases the viscosity of the reaction medium, which in turn reduces the mobility of the macromolecules, thereby lowering the %GP and %GC. No homopolymer was formed in a control experiment carried out under all the reaction conditions, except that HEC was deliberately not added to the reaction mixture. This indicates that the presence of HEC is essential for the creation of free-radical sites, which further initiate the process of graft copolymerization. In other words, the redox process that resulted from the CAN/EDTA system in this case initiates free radicals exclusively on the polysaccharide backbone, thereby providing little chance for homopolymer formation. Similar results were also obtained for the grafting of acrylamide onto starch or guargum with CAN/nitric acid as the initiator.[21,22]

Effects of the Temperature and Time

The effects of the reaction time and temperature on the grafting of DMAPS onto HEC were examined, as shown in Figure 5. The polymerization reaction is characterized by a fast initial rate, which is followed by a much slower rate during the later stage of the reaction.

Meanwhile, the maximum graft extent was observed at 35°C, and a relatively high %GP could also be observed even at the low temperature of 24°C. According to Hsu et al.,[19,20] the CAN/EDTA initiating system can lower the activation energy of the polymerization reaction via the formation
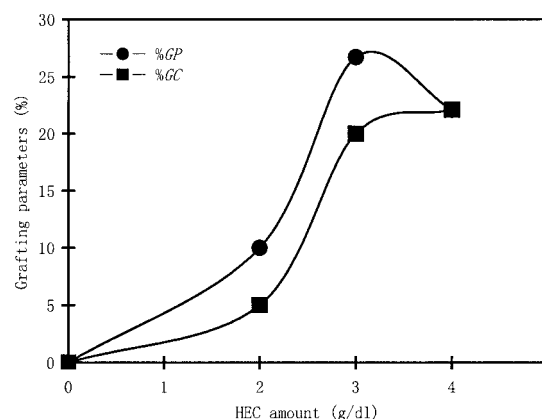

Figure 4 Effect of the HEC amount on grafting: DMAPS, 0.1432 mol/L; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; pH, 7.0; time, 4 h; and temperature, 35°C.
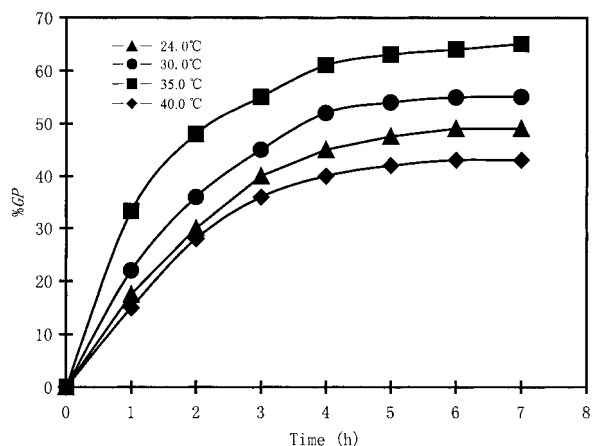
Figure 5 Dependence of the CAN/EDTA-initiated graft copolymerization of DMAPS onto HEC on the time of grafting at various reaction temperatures: HEC, 3.0 g/dL; DMAPS, 0.1432 mol/L; CAN, 5.0×10^{-3} mol/L; EDTA, 5.0×10^{-3} mol/L; and pH, 7.0.

of a charge-transfer complex, which is more effective than the common CAN/HNO$_3$ system or the individual CAN initiator. Beyond 35°C, the %GP and %GC decrease. This may be because the termination rate of free radicals on the grafted chains and the homopolymerization rate of the monomer increase with the temperature increasing further.

Characterization of the Graft Copolymers

IR Spectra

The IR spectra of purified HEC and its graft copolymer with DMAPS (%GP = 40.0) are given in Figure 6. For ungrafted HEC, there is a broad absorption band around 3437 cm^{-1} due to the stretching of the hydroxyl groups, in addition to bands occurring at 2875 and 1124 cm^{-1} that belong to C—H stretching vibration in methylene groups and C—O—C antisymmetric stretching vibrations, respectively. In contrast, the IR spectrum of the graft copolymer shows not only the characteristic absorption bands of HEC but also additional characteristic absorption bands of the carboxylic ester carbonyl group at 1725 cm^{-1}, the sulfonyl group at 1062 cm^{-1}, and the quaternary groups at 938 cm^{-1}. This indicates that the sulfobetaine monomer DMAPS has been grafted onto HEC.

Thermogravimetry (TG) Curves

Figure 7 gives the TG and derivative thermogravimetry (DTG) curves for the thermal degradation of HEC and its graft copolymer (%GP = 40.0) at a heating rate of 20°C/min under an air atmosphere. The TG curve of ungrafted HEC has three distinct stages, and the corresponding DTG
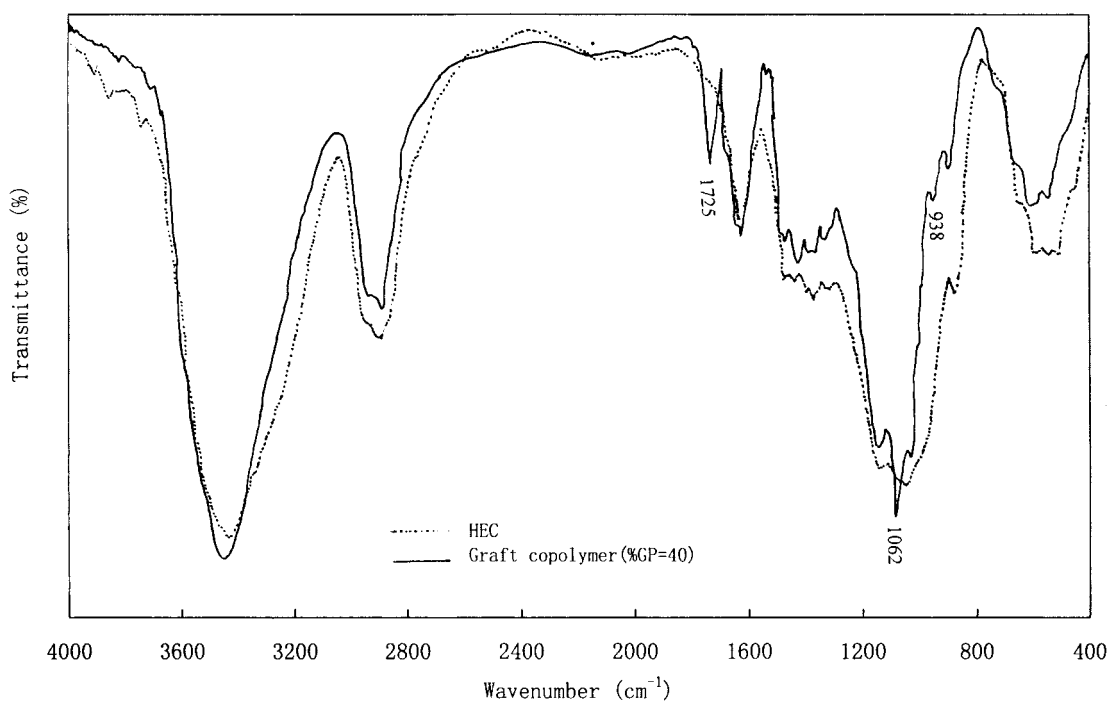

Figure 6 IR spectra of HEC and its graft copolymer with DMAPS (%GP = 40.0).
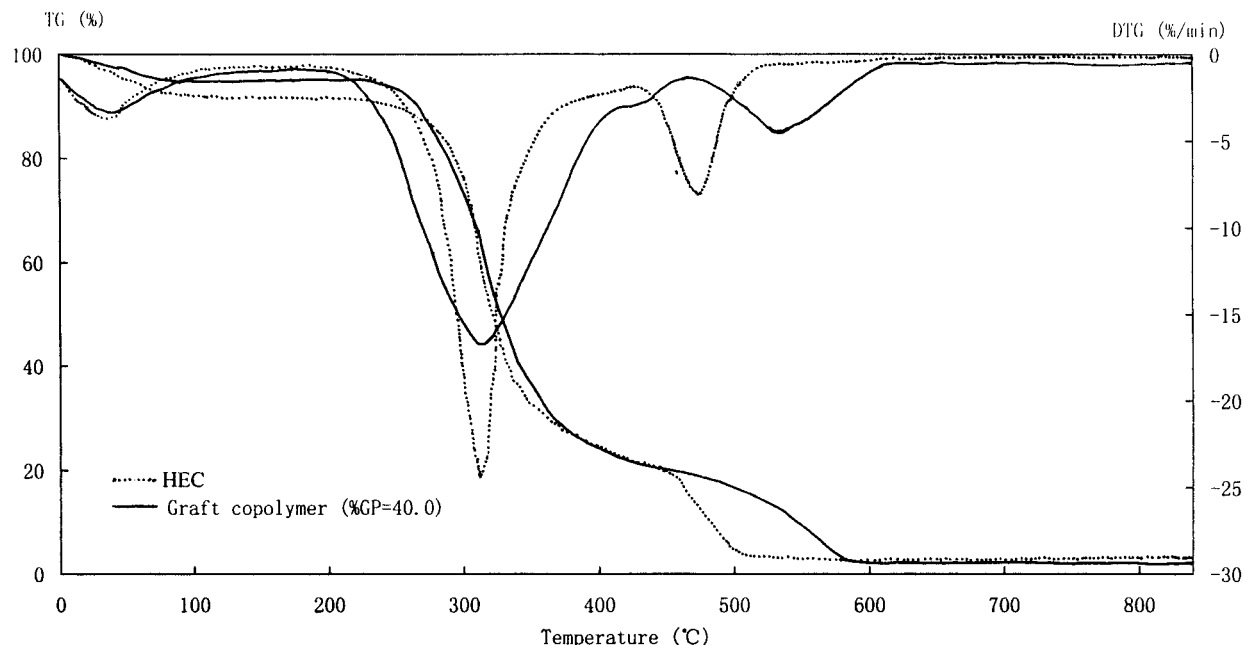
Figure 7 TG and DTG curves for the thermal degradation of HEC and its graft copolymer (%GP = 40.0) at a heating rate of 20°C/min under an air atmosphere.

curve shows three maximum peaks at 58.7, 317, and 484°C. The slight weight loss of HEC in the first stage is due to the loss of water. In the second stage, the weight loss starts at 159°C and continues to 438°C with a 71% weight loss; it has a maximum rate at 317°C. The third stage is completed with a 16% weight loss by 525°C and shows a maximum rate of weight loss at 482°C. In contrast, the TG curve of the graft copolymer also shows three distinct stages, but the temperature corresponding to the maximum rate of weight loss for the third stage is 547.6°C. Besides, the degradation in the second stage starts at 155°C and proceeds up to 467°C, at which temperature the graft copolymer loses 76% of its original weight. The third degradation stage of the graft copoly-
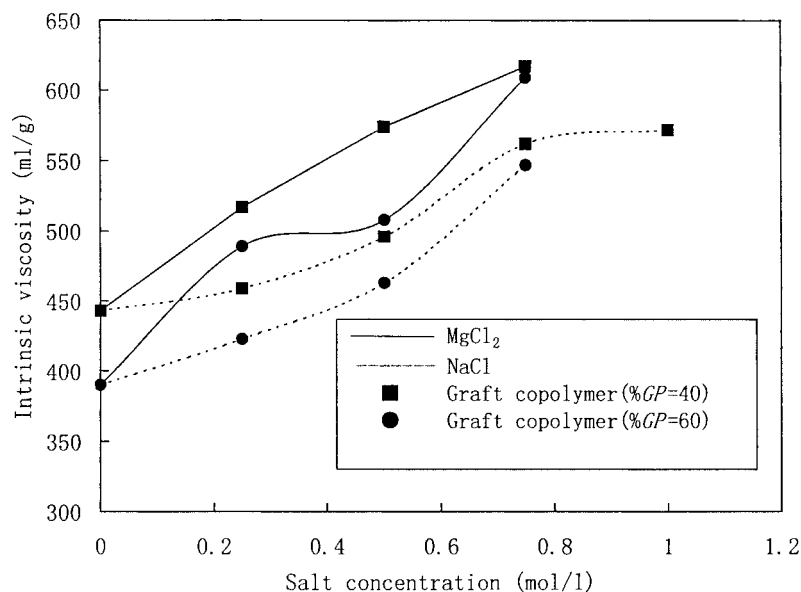

Figure 8 Intrinsic viscosity changes of two graft copolymers in aqueous salt solutions.

mer involves a 17% weight loss from 467 to 637°C. These differences in the thermal decomposition characteristics confirm that the graft copolymer contains the chain structure of the DMAPS unit.

Viscosity Behavior

Figure 8 gives the intrinsic viscosity changes of two graft copolymers in aqueous salt solutions. These solutions of the graft copolymers show increasing intrinsic viscosity as the amount of salt in the solutions is increased, especially in the presence of $MgCl_2$. Moreover, the higher the %GP of the graft copolymer is and the higher the salt concentration is, the higher the intrinsic viscosity is, showing an interesting antipolyelectrolyte effect that is different from the solution behavior of common nonionic, anionic, or cationic grafted polysaccharides.[23] These results are due to the fact that the addition of salt disrupts the intermolecular and intramolecular associations derived from zwitterionic sulfobetaine groups of the graft copolymer, which agree well with similar observations for poly(sulfobetaine)s[24] and polyampholytes incorporating sulfobetaine-type amphoteric monomer.[14–16]

CONCLUSIONS

Novel water-soluble grafted polysaccharides containing sulfobetaine groups were synthesized by the grafting of the zwitterionic monomer DMAPS onto HEC. The main factors affecting the grafting, including the initiator type, initiator concentration, monomer concentration, HEC amount, reaction time, and temperature, were studied, and the rate of grafting corresponding to each initiating system and the overall activation energy were determined. With this study, the optimum reaction conditions for obtaining the maximum grafting degree were found. Moreover, IR, TGA, and viscosity measurements provided evidence of grafting.

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