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Reaction of Glycidyl Methacrylate at the Hydroxyl and Carboxylic Groups of Poly(vinyl alcohol) and Poly(acrylic acid): Is This Reaction Mechanism Still Unclear?

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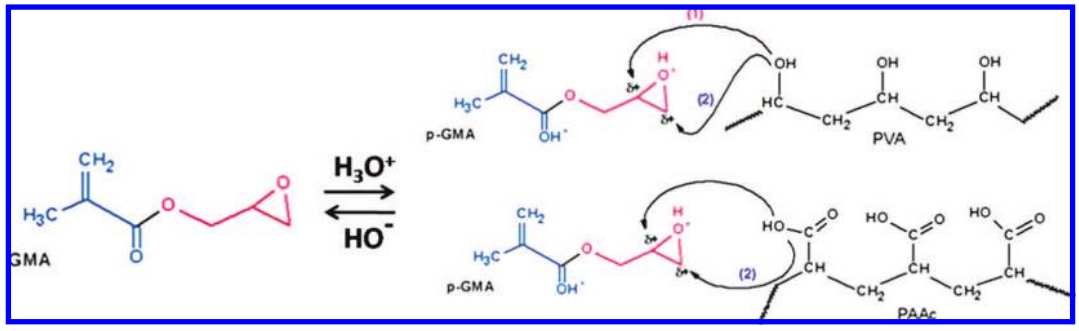
Received January 14, 2009



Transesterification and epoxide ring-opening reactions are two mechanism routes that explain chemical modifications of macromolecules by glycidyl methacrylate (GMA). Although the coupling reaction of the GMA with macromolecules has widely been investigated, there are still mechanisms that remain to be explained when GMA is processed in an aqueous solution at different pH conditions. To this end, reaction mechanisms of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) by GMA in water in acidic and basic conditions were investigated thoroughly. The presence of hydroxyl groups in PVA and carboxyl groups in PAAc allowed for a better evaluation of the reaction mechanisms. The analysis of the ^{1}H and ^{13}C NMR spectra clearly demonstrated that the chemical reactions of GMA with carboxyl groups and alcohols of the macromolecules in an aqueous solution are dependent on pH conditions. At pH 3.5, the GMA reacts with both the carboxylic and the hydroxyl groups through an epoxide ring-opening mechanism. At pH 10.5, the GMA undergoes a hydrolysis process and reacts with hydroxyl groups by way of both the transesterification and the epoxide ring-opening mechanisms, whereas the ring-opening reaction is the preferential pathway.

Introduction

Although natural and synthetic polymers are reactive toward many cross-linking agents, such as di-*n*-methyol compounds, divinyl sulfones, and diepoxides, the chemical reaction of polymers with the use of glycidyl methacrylate (GMA) as a modifier has been a suitable strategy for producing vinyl macromolecules. From a chemical point of view, this methodology consists of incorporating carbon−carbon π-bonds coming from the GMA onto the structure of the macromolecule, which enables it to undergo a gelling process through a radical cross-linking polymerization reaction.[1−7] The synthesis of hydrogels from chemically modified polymers is a motivating way for developing biodegradable polymer networks, which are strongly

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10.1021/jo900033c CCC: $40.75
Published on Web 04/10/2009

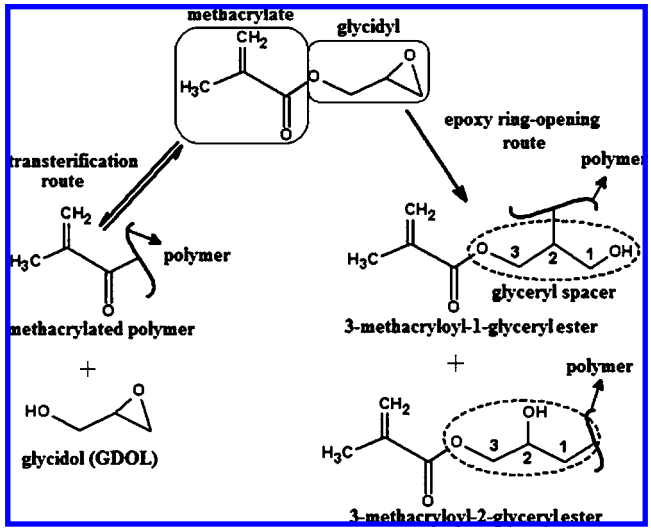

FIGURE 1. Schema of the chemical reaction of GMA with a macromolecule by way of transesterification and epoxide ring-opening mechanisms.

recommended for uses in the development of new modified drug-delivery devices and vitro-retinal replacement surgery.[8−14] Furthermore, superabsorbent hydrogels for applications in which the efficient use of water is required, for example, soil conditioning in agriculture, can be synthesized through a polymerization cross-linking reaction at the vinyl moiety of the modified polymer with acrylic monomers.[5]

There are two reaction routes that explain chemical modifications of natural and synthetic polymers through the use of the GMA: transesterification and epoxide ring-opening mechanisms.[14−18] The reaction mechanism of GMA with dextran (Dex), by using dimethyl sulfoxide (DMSO) as a solvent and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as a catalytic agent, has been reported by van Dijk-Wolthuis et al.[1,2] It has been found that transesterification is the predominant route for the GMA−Dex system when a polar aprotic solvent, such as the DMSO, is used as a reaction medium. Methacrylated Dex was found as a main product and glycidol (GDOL) as a byproduct. Equivalent results were verified when inulin was treated with GMA in an aprotic solvent. Li et al.[19] discussed the reaction mechanisms between the chondroitin sulfate and the GMA in a protic solvent at pH 7.6. Both of the reaction mechanisms may take place simultaneously, depending on pH and the chemical nature of the solvent. It has been also described that the transesterification mechanism is a rapid and reversible reaction route and that the epoxide ring-opening mechanism is a slow and irreversible reaction route. Over the initial stage of the reaction, there is a predominant formation of the resultant products of the transesterification. With the evolution of the reaction, there is a decrease in pH of the reaction medium that limits the transesterification and makes the epoxide ring-opening mechanism more favorable. By this logic, for a long period of reaction, the formation of the resultant products of the epoxide ring-opening mechanism would be predominant over that of the transesterification mechanism. However, the reaction of chondroitin sulfate by GMA at pH 3 indeed occurs via epoxide ring opening.[13] In this case, there is an attachment of a whole GMA molecule onto the sulfate and carboxylic groups of the chondroitin sulfate. When the reaction is processed via transesterification, only hydroxyl groups of the polysaccharide are directly attached to the methacryloyl groups from the GMA. Although the reaction mechanism of the GMA with chondroitin sulfate in an aqueous medium has been described, there is still an interesting question that remains to be answered: could the hydroxyl groups of the chondroitin sulfate also react with the GMA by way of an epoxide ring-opening route in a protic solvent? With the purpose of responding to this question and also complementing the studies performed by both van Dijk-Wolthuis et al.[1] and Li et al.,[19] a detailed examination of the reaction mechanisms of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) by GMA in water was performed. The idea of using these polymers as model compounds may be based on their chemical structures: the presence of the hydroxyl groups of PVA and the carboxyl groups of PAAc allowed for a better evaluation of the reaction mechanisms. The use of polymers with different functional groups enabled us to better understand and describe the resultant products and mechanisms of reactions by GMA. Functionalization of macromolecules by way of either the ring opening of epoxides[20] or transesterification[21] is an important issue on laboratorial and industrial scales. There have been no reports describing a thorough investigation on the reaction mechanisms of GMA with macromolecules in water. This work aims to be a contribution for a better comprehension of the reaction mechanisms of macromolecules by GMA.

Results and Discussion

Spectroscopic Characterization of GMA and Modified Polymers in pH 3.5 and pH 10.5. GMA Molecule. For a better evaluation of the GMA reaction with the polymers, a more detailed schema of both the transesterification and the epoxide ring-opening mechanisms is shown in Figure 1. The reaction products that result in an epoxide ring opening pathway are two isomers: 3-methacryloyl-1-glyceryl and 3-methacryloyl-2-glyceryl esters. Methacrylated polymer, as the main product, and GDOL as the byproduct are the results of a transesterification pathway. Figure 2a,b shows the ^{1}H and ^{13}C NMR reference spectra of GMA. The resonance lines in both of the NMR

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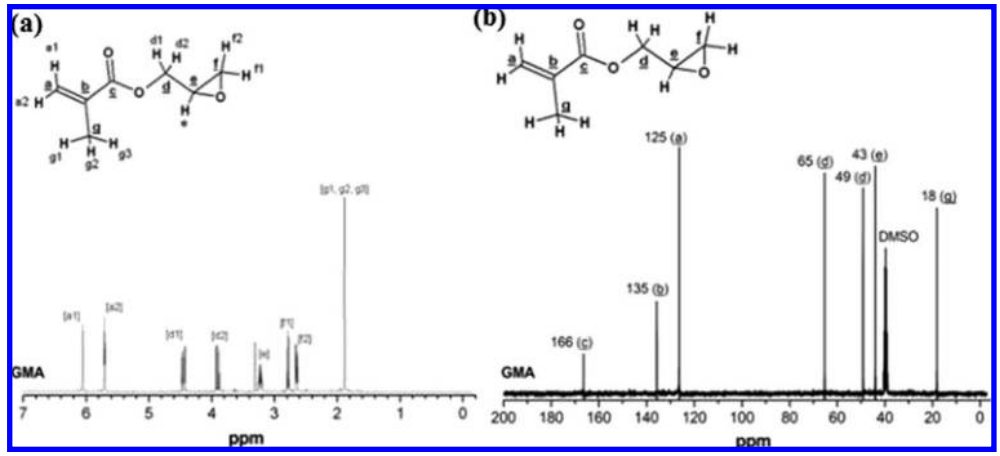

FIGURE 2. ^{1}H (a) and ^{13}C (b) NMR spectra of the pure GMA (DMSO-d_6).

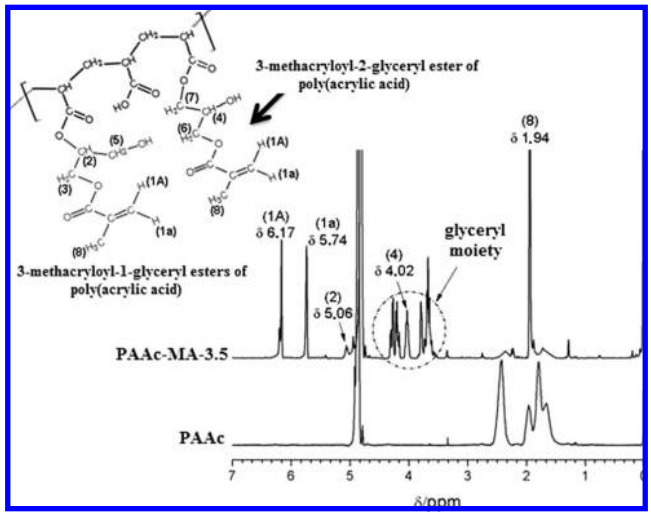

FIGURE 3. ^{1}H NMR spectra of PAAc and PAAc−MA-3.5 for a coupling reaction at pH 3.5 (300 MHz, D_2O).

spectra were indentified and associated with the corresponding ^{1}H and ^{13}C nuclei at the GMA molecule, drawn in the inset.

PAAc−MA-3.5. Figure 3 shows ^{1}H NMR spectra of PAAc and PAAc−MA-3.5. The signals at δ 6.17 and δ 5.74, in the PAAc−MA-3.5 spectrum, were assigned to vinyl carbon-linked hydrogen. The signal at δ 1.94 corresponded to methyl carbon-linked hydrogen at the vinyl carbons, and the signals at δ 5.06 and δ 4.02 were attributed to a glyceryl spacer coming from GMA. The appearance of these signals indicates the formation of the 3-methacryloyl-1-glyceryl ester of PAAc and the 3-methacryloyl-2-glyceryl ester of PAAc, which are reaction products resultant of the epoxide ring-opening mechanism pathway. In the view that two products can be formed by way of an epoxide ring-opening reaction, a more detailed examination in the spectral region of δ 5−3 was carried out to determine the proportion of the methacryloyl-1-glyceryl ester and methacryloyl-2-glyceryl ester products.

Figure 4 shows expanded ^{1}H NMR spectra of PAAc and PAAc−MA-3.5 in the spectral region of δ 5−3. The signals at δ 5.06 and δ 4.02 were attributed to the hydrogen of the methacryloyl-1-glyceryl and methacryloyl-2-glyceryl esters, respectively, as indicated in the spectrum. The ratio of the integrals of these two signals corresponded to 1:8. This means that approximately 12.5% of the GMA were attached to the PAAc structure as the 3-methacryloyl-1-glyceryl ester and 87.5% as the 3-methacryloyl-2-glyceryl ester, in a reaction medium at pH 3.5.

^{13}C NMR spectra of PAAc and PAAc−MA-3.5, shown in Figure 5, were also recorded to confirm the ^{1}H NMR data. The corresponding signals of the vinyl carbon were clearly observed at δ 138.77 and δ 129.86 in the PAAc−MA-3.5 spectrum, methyl carbon at δ 23.43, and carbonyl carbon at δ 172.40. The signal in the spectral region of δ 80−60 reveals the presence of the glyceryl spacer. In addition, the corresponding signals of the four- and five-numbered carbons in the inset were detected at δ 78.68 (4) for the 3-methacryloyl-1-glyceryl ester of PAAc and at 72.66 (5) for the 3-methacryloyl-2-glyceryl ester of PAAc. Both the ^{1}H and the ^{13}C NMR data demonstrated that the acidic reaction in which the GMA molecule is attached onto the PAAc structure occurs by way of an epoxide ring-opening mechanism. The proportion of the ring-opening products consisted of 12.5% as the 3-methacryloyl-1-glyceryl ester of PAAc and 87.5% as the 3-methacryloyl-2-glyceryl ester of PAAc.

A drawing of coupling reactions of GMA with PAAc in an aqueous solution at pH 3.5 is shown in Figure 6. The whole process starts off with the transfer of a proton from an acidic liquid onto the epoxide-linked hydroxyl group of the GMA molecule (*p*-GMA). When the *p*-GMA reacts with PAAc, the epoxide ring-opening reaction of the GMA should occur through two mechanism pathways, yielding two isomers as the reaction product: the 3-methacryloyl-1-glyceryl ester of PAAc (pathway 1) and the 3-methacryloyl-2-glyceryl ester of PAAc (pathway 2).

PAAc−MA-10.5. Neither ^{1}H NMR nor ^{13}C NMR spectra demonstrated any evidence for the reaction of GMA with PAAc in an aqueous solution at pH 10.5 (spectra not shown here), compared with the corresponding reference spectra of GMA and PAAc. The lack of spectroscopic evidence for the reaction products of GMA with PAAc was very likely caused by the basic conditions of the reaction medium.

According to the literature,[18] the GMA undergoes a hydrolysis reaction at the basified media, yielding deprotonated methacrylic acid (up-AcMet) and GDOL, which can also acquire a deprotonated form at the strongly basic conditions, as shown in Figure 7. The deprotonation of the GDOL occurs because the negative charge that exists on the molecule is stabilized by a resonance mechanism that delocalizes the charge over both oxygen atoms. With the increasing pH of the medium, the reaction equilibrium is delocalized towards nucleophiles, such as dp-AcMet, dp-

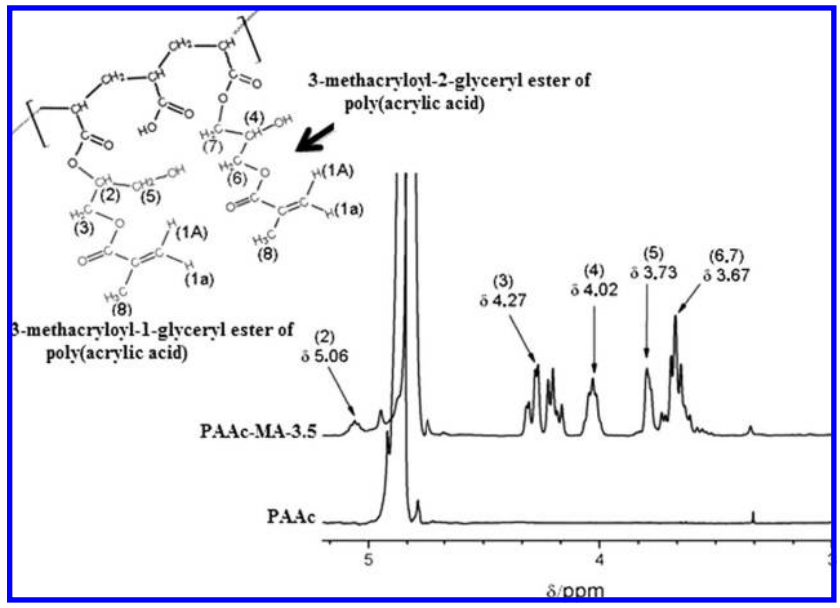

FIGURE 4. Expanded ^{1}H NMR spectra of PAAc and PAAc−MA-3.5 in the spectral region of δ 5−3, for a coupling reaction at pH 3.5 (300 MHz, D_2O).

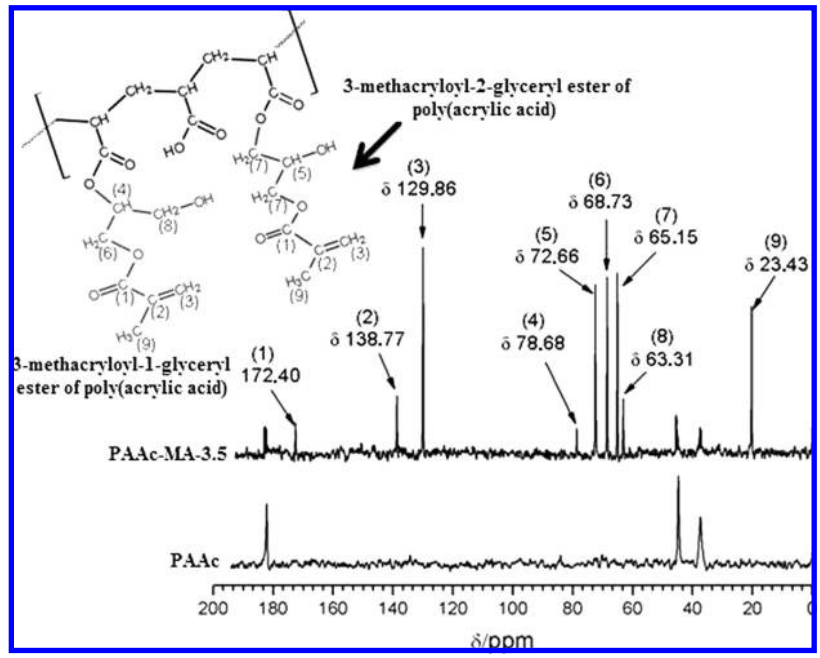

FIGURE 5. ^{13}C NMR spectra of PAAc and PAAc−MA-3.5 for a coupling reaction at pH 3.5 (75.5 MHz, D_2O).

GDOL, and dp-PAAc, and this appears to be an unsuitable condition for reaction processing.

Reactions of GMA with chondroitin sulfate at slightly basic conditions (pH 8.5) have already been investigated.[18] It has been reported that the GDOL couples onto both the carboxylate ($-COO^-$) and the sulfate ($-SO_3^-$) groups of chondroitin sulfate. As discussed in the prior part of this paper, the coupling reaction of GMA with the carboxylate groups at PAAc was not verified. There may be a dependence of the reaction conditions on pH. With changing pH, there should be a variation of concentration of protonated and deprotonated molecules that hinders the coupling reaction of the GMA with the polymer. By considering that the reaction kinetics is dependent on the concentration of the molecules, the pH would then have a significant effect on the coupling velocity of the molecules onto PAAc. At low pH conditions, the GMA molecule recovers to its original structure, and thereby, the reaction indeed occurs by way of an epoxide ring-opening mechanism.

PVA−MA-3.5. Figure 8 shows ^{1}H NMR spectra of PVA and PVA−MA-3.5. The signals observed in the PVA−MA-3.5 spectrum, which evidence the resultant product of the GMA−PVA reaction at pH 3.5, were associated with their corresponding ^{1}H as follows: vinyl carbon-linked hydrogen at δ 6.21 and 5.74 and methyl carbon-linked hydrogen at the vinyl carbon at δ 1.98. The corresponding signal of the glyceryl spacer was observed in the spectral region of δ 4.5−3.5. This means that the coupling reaction of GMA onto PVA is processed through an epoxide ring-opening pathway. In view of the overlap at the spectral region of δ 4.5−3.5, the proportion of the isomers, the

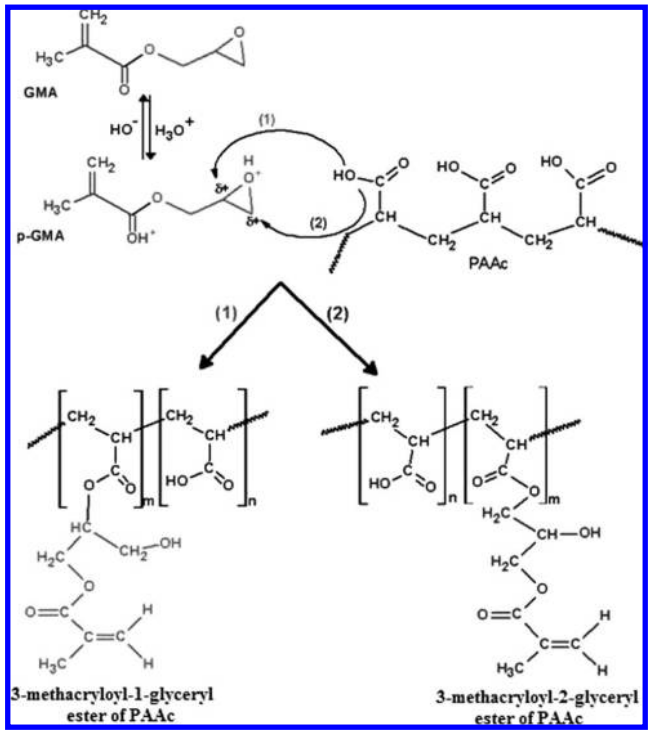

FIGURE 6. Schema of the coupling reaction of GMA with PAAc in an aqueous solution at pH 3.5 via an epoxide ring-opening mechanism.

3-methacryloyl-1-glyceryl ether of PVA and the 3-methacryloyl-2-glyceryl ether of PVA, cannot be determined.

Figure 9 shows the ^{13}C NMR spectra of PVA and PVA−MA-3.5. The corresponding ^{13}C-resonance signals of the vinyl carbon in the PVA−MA-3.5 spectrum were observed at δ 138.4 and δ 130.21, carbonyl carbon at δ 178.00, and methyl carbons at δ 20.08. The corresponding ^{13}C chemical shifts of the glyceryl spacer, amplified and shown in the inset, were observed in the spectral region of δ 80−60. The signals observed at δ 77.33 and 72.43 were attributed respectively to the carbon resonances of the 3-methacryloyl-1-glyceryl ether of PVA (carbon 4) and of the 3-methacryloyl-2-glyceryl ether (carbon 5) of PVA−MA-3.5. The ^{13}C NMR data, which corroborate the ^{1}H NMR data, demonstrate that GMA reacts with alcohol groups at the PVA structure at pH 3.5 through an epoxide ring-opening mechanism.

In response to the question proposed in the introductory part of this paper, it can be said that the GMA indeed reacts with the hydroxyl groups of the macromolecules in an aqueous solution at pH 3.5 through an epoxide ring-opening mechanism. A proposed schema of such a reaction is shown in Figure 10. In an acidified aqueous medium, the *p*-GMA reacts with the PVA through an epoxide ring-opening mechanism, thus yielding the two isomers: the 3-methacryloyl-1-glyceryl ether of PVA and the 3-methacryloyl-2-glyceryl ether of PVA.

PVA−MA-10.5. Figure 11 shows ^{1}H NMR spectra of PVA and PVA−MA-0.5. The appearance of the signals at δ 6.18 and δ 5.74 in the PVA−MA-10.5 spectrum was attributed to the vinyl carbon-linked hydrogen, and the signal at δ 1.94 was associated with the carbon methyl-linked hydrogen at the vinyl carbon. The corresponding ^{1}H signal of the glyceryl spacer was observed at the spectral region of δ 4.5−3.5, as evidence of the occurrence of the epoxide ring-opening reaction.

The proportion of 3-methacryloyl-1-glyceryl ether and 3-methacryloyl-2-glyceryl ether of PVA−MA-10.5 was not determined

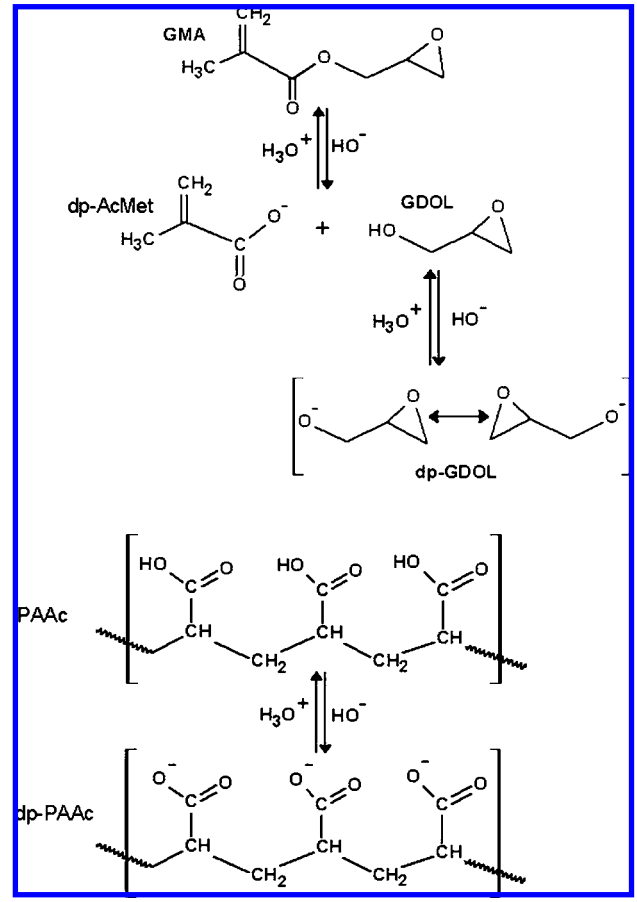

FIGURE 7. Schema of a hydrolysis reaction of GMA and the ionization of PAAc. With the increasing pH of the medium, the reaction equilibrium is delocalized toward three nucleophiles, such as dp-AcMet, dp-GDOL, and dp-PAAc.

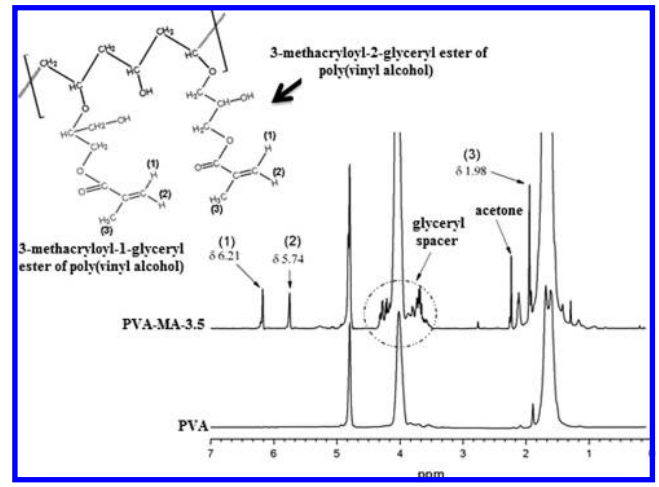

FIGURE 8. ^{1}H NMR spectra of PVA and PVA−MA-3.5 for a coupling reaction at pH 3.5 (300 MHz, D_2O).

because of the overlap of signals at the region of δ 4.5−3.5. The appearance of three new signals at δ 5.67, 5.36 (vinyl carbon-linked hydrogen), and 1.86 (methyl carbon-linked hydrogen at the vinyl groups) is most likely caused by the formation of transesterification products: vinyl methacrylate of PVA−MA-10.5 and GDOL. The proportion of the reaction products of transesterification and epoxide ring-opening were calculated by the ratio between the area of the signals at δ 5.67

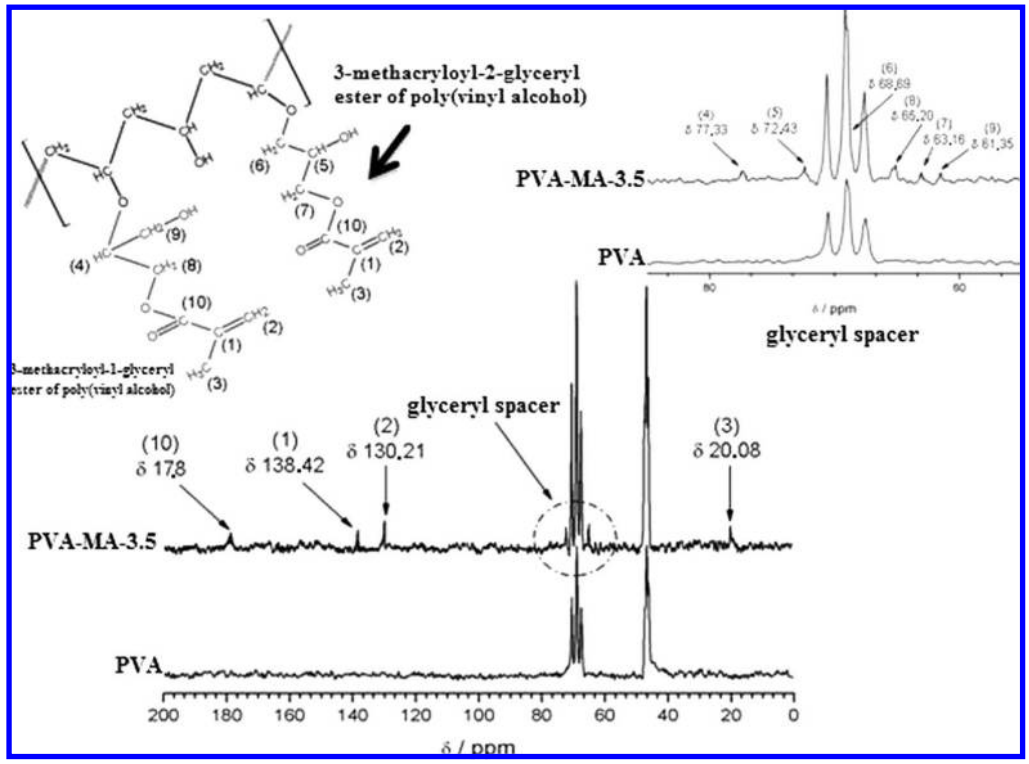

FIGURE 9. ^{13}C NMR spectra of PVA and PVA−MA-3.5 for a coupling reaction at pH 3.5 (75.5 MHz, D_2O).

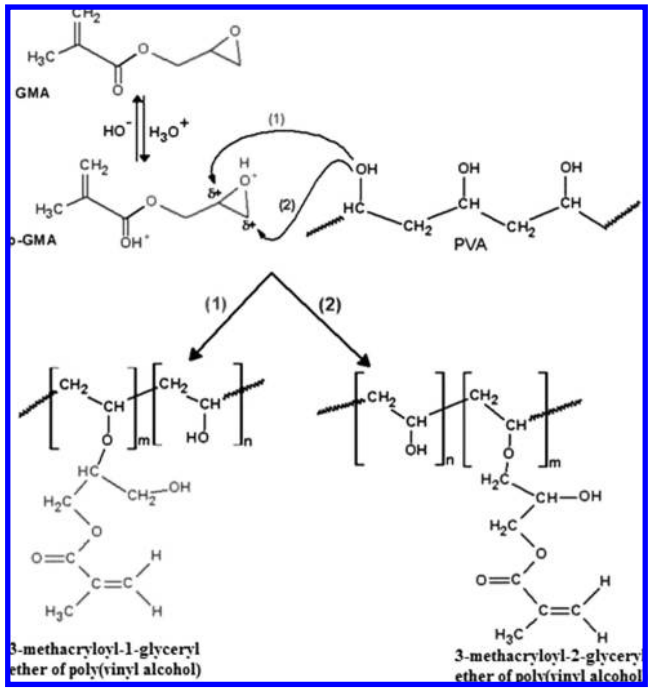

FIGURE 10. Schema of the coupling reaction with PVA in an aqueous solution at pH 3.5. The *p*-GMA reacts with hydroxyl groups of PVA through an epoxide ring-opening mechanism, yielding two isomers: the 3-methacryloyl-1-glyceryl ether of PVA and the 3-methacryloyl-2-glyceryl ether of PVA.

and δ 5.36 and the area of the signals at δ 6.18 and δ 5.74, respectively.

With a ratio of [transesterification product]/[epoxide ring − opening product] of 1/7, the total amount of attached GMA in the PVA at pH 10.5 was obtained as follows: 14.3% via the transesterification reaction and 85.7% via the epoxide ring-opening reaction.

Figure 12 shows ^{13}C NMR spectra of PVA and PVA−MA-10.5. The corresponding ^{13}C signals of the carbons at the 3-methacryloyl-1-glyceryl ether (carbon 6) and 3-methacryloyl-2-glyceryl ether (carbon 7), both of PVA−MA-10.5, were observed at δ 77.35 and at δ 72.24, respectively. These signals are additional evidence of the epoxide ring-opening reaction. Nevertheless, the signal at δ 18.51, corresponding to methyl carbon at the PVA−MA-10.5, indicated the occurrence of the transesterification reaction. From the ^1H and ^{13}C NMR data, it would then be concluded that the coupling reaction of GMA with PVA at pH 10.5 occurred through both the transesterification and the epoxide ring-opening pathways, with an integral ratio of 1:7.

Figure 13 shows a proposed schema of coupling mechanism routes of GMA with PVA. In an aqueous solution with pH 10.5, a given number of hydroxyl groups from the PVA are converted to a deprotonated form that generates ethoxide molecules. It follows that the ethoxides could react with the GMA through three mechanism routes: (1) with the epoxide ring at GMA resulting in the 3-methacryloyl-1-glyceryl ether of PVA, (2) with GMA in the same way of route 1 but resulting in the 3-methacryloyl-1-glyceryl ether of PVA, and (3) with carbonyl groups at GMA resulting in both vinyl methacrylate of PVA and GDOL, as products.

Conclusion

The chemical reactions of the GMA with acid groups (−COOH) and alcohols (−OH) of the macromolecules in an aqueous solution are dependent on pH conditions. At pH 3.5, the GMA reacts with both the carboxylic and the hydroxyl groups through an epoxide ring-opening mechanism. At pH 10.5, the GMA undergoes a hydrolysis process and reacts with

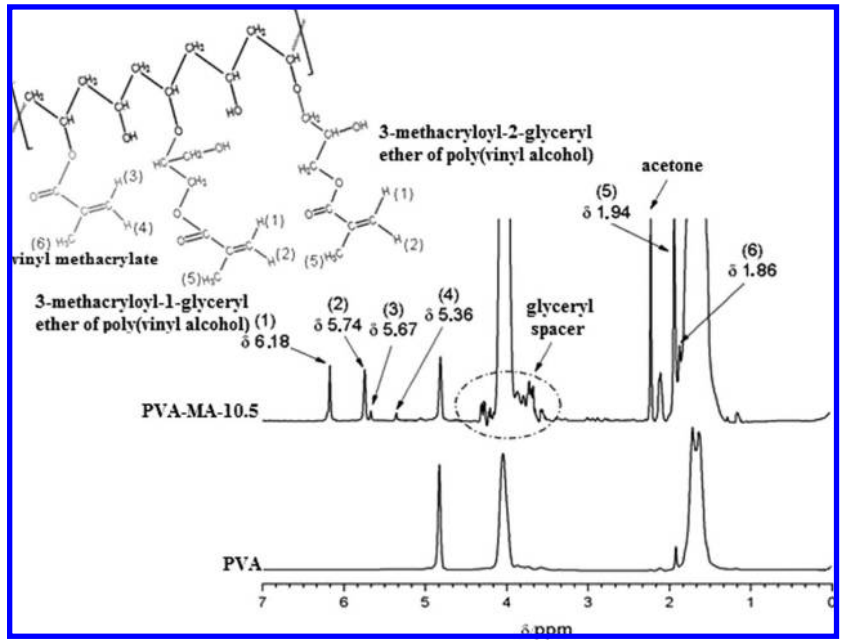

FIGURE 11. ^{1}H NMR spectra of PVA and PVA−MA-10.5 for a coupling reaction at pH 10.5 (300 MHz, D_2O).

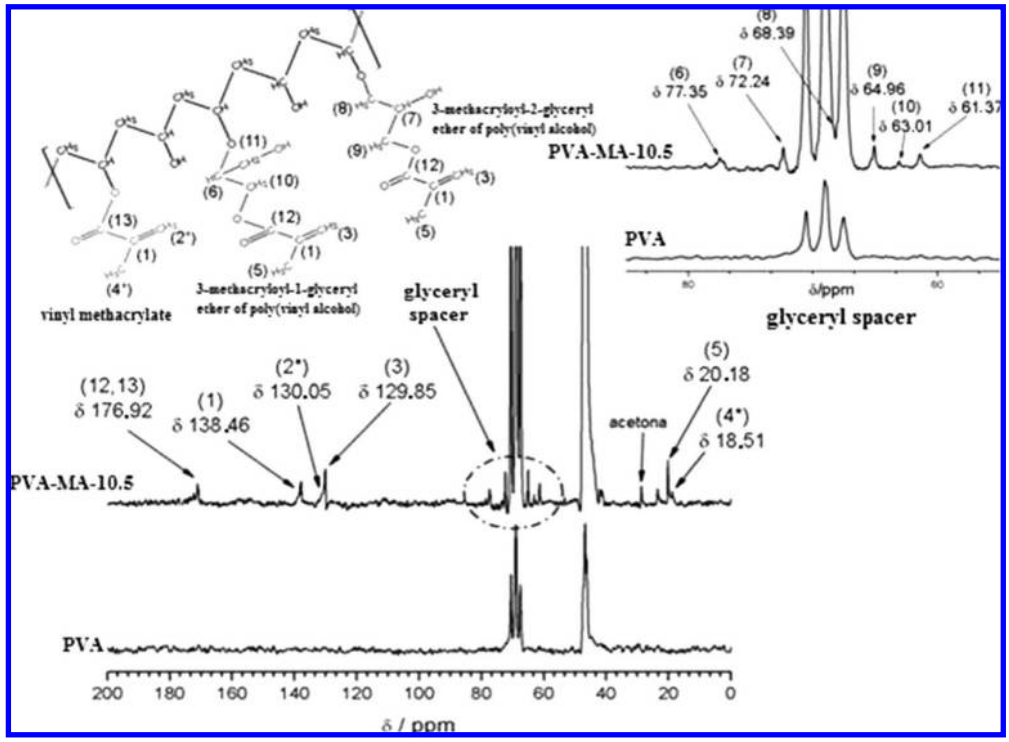

FIGURE 12. ^{13}C NMR spectra of PVA and PVA−MA-10.5 for a coupling reaction at pH 10.5 (75.5 MHz, D_2O).

hydroxyl groups by way of both the transesterification and the epoxide ring-opening mechanisms, whereas the ring-opening reaction is the preferential pathway.

Experimental Section

Materials. Starting reagents were used without further purification: GMA PVA >99% hydrolyzed (average M_w 124 000−186 000); PAAc (99% average M_w 750 000); sodium hydroxide (NaOH, 95%); chloridric acid (HCl, 36.5−38%); acetone (99.5%).

Chemical Modification of PAAc by GMA (PAAc−MA). PAAc-modifying solutions of either pH 3.5 or pH 10.5 were prepared according to the following methodologies: 1.5 g of PAAc was dissolved into 150 mL of distilled−deionized water under a stirring speed of 300 rpm at room temperature. After the mixture was completely homogenized, 200 μL of a 2 mol L^{-1} HCl solution was dropped into the mixture to adjust the pH to 3.5, and 6 mL of a 2 mol L^{-1} NaOH solution was used to obtain pH 10.5. After that, 0.98 mL of GMA was mixed into either solution by a constant and vigorous stirring at 50 °C for 24 h. Then, 10 mL of acetone were introduced to precipitate the reaction product, which was separated by a centrifugation process at room temperature. The as-prepared products were then lyophilized to record ^{1}H and ^{13}C NMR spectra.

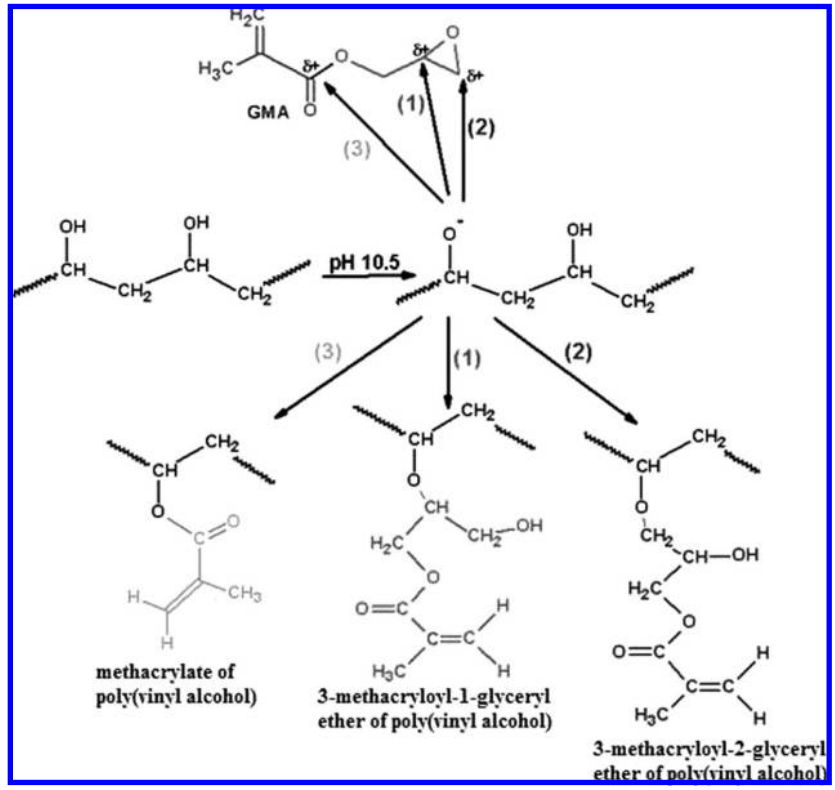

FIGURE 13. Schema of the reaction of GMA with PVA in an aqueous solution at pH 10.5 through three mechanism routes.

Chemical Modification of PVA by GMA (PVA−MA). PVA-modifying solution was prepared by using the analogous methodology to that of the PAAc, except for adjusting the pH of the acidic and basic solutions. Here, 440 μL of 2 mol L^{-1} HCl solution was used for pH 3.5 and 520 μL of 2 mol L^{-1} NaOH solution for pH 10.5. By considering the different pH conditions used to modify both the polymers, the following labels were used to identify them: PAAc−MA-3.5 for pH 3.5, PAAc−MA-10.5 for pH 10.5, PVA−MA-3.5 for pH 3.5, and PVA−MA-10.5 for pH 10.5.

NMR Measurements. NMR spectra were performed on a Varian Mercury plus BB 300 MHz spectrometer, operating at 300.059 MHz for ^{1}H and 75.457 MHz for ^{13}C. D_2O solutions consisting of 150 mg L^{-1} of polymer (raw or modified one) and 0.05% 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP-d_4), as the internal standard (0 ppm), were prepared in NMR tubes of 5 mm diameter to acquire the spectra. The angle pulse of 90° with a relaxation delay of 30 s was used for ^{1}H NMR spectra. For the ^{13}C NMR, a pulse angle of 30° was used with a relaxation delay of 1 s. DMSO-d_6, as the solvent, and tetramethylsilane (TMS), as the internal standard, were used for recording the GMA spectra. DEPT, HMQC, and COSY spectra were also performed for help on the attribution of the chemical shifts of both the ^{1}H and the ^{13}C.

Acknowledgment. E.C.M. acknowledges the Conselho Nacional de Desenvolvimento Tecnológico (CNPq-Brazil) for financial support, Proc. 308611/2006-3. A.V.R. and A.R.F. thank the CNPq Brazil for their undergraduate and doctorate fellowships, respectively. M.R.G. is grateful to Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP, Proc. 06/50952-4) for his postdoctoral fellowship.

JO900033C