Glycidyl methacrylate and *N*-vinylpyrrolidinone copolymers: synthesis and nuclear magnetic resonance characterization

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Poly(glycidyl methacrylate) and water-soluble copolymers of glycidyl methacrylate with *N*-vinylpyrrolidinone were prepared by free-radical-initiated solution polymerization in chloroform. Polymer microstructure was investigated by high-field ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.), ^{1}H decoupled ^{13}C n.m.r., ^{1}H–^{13}C correlation n.m.r. and 135 DEPT (distortionless enhancement by polarization transfer) n.m.r. The combined use of these techniques allowed unequivocal ^{13}C and ^{1}H n.m.r. assignments of carbons and protons to be established. Copolymer composition was thus determined from ^{1}H n.m.r.

(Keywords: poly(glycidyl methacrylate); vinylpyrrolidinone copolymers; n.m.r. characterization)

INTRODUCTION

In recent years, copolymers based on glycidyl methacrylate have received increasing attention. The interest in these copolymers is largely due to the ability of pendent epoxide groups to enter into a large number of chemical reactions[1–3], thus offering the opportunity for chemical modification of the parent copolymer for various applications. For instance, copolymers based on glycidyl methacrylate have been used for binding enzymes and other biologically active species[4,5], and in electronic applications as negative electron-beam resists[6]. The high reactivity of the epoxide group is primarily due to the considerable strain in the three-membered ring. The reactivity of the ring is also affected by its position, by the presence of other polar groups and bulky substituents in the molecule, by the type of solvent used for preparation, and by temperature[7]. The other factors that become operative in the case of high-molecular-weight polymers are the mobility of sequences and molecular weight.

In connection with another project, we needed to develop water-soluble epoxide-containing high-molecular-weight polymers. The monomer and homopolymer of glycidyl methacrylate are both highly hydrophobic, and the nature of poly(glycidyl methacrylate) is markedly affected by the mode of polymerization. For example, bulk polymerization of glycidyl methacrylate leads to a crosslinked homopolymer that is not soluble in ordinary solvents, while solution polymerization will lead to linear, solvent-soluble polymers with no apparent crosslinking[8]. Crosslinking is considered to be due to the involvement of the epoxide function. Glycidyl methacrylate has been homopolymerized in solution by several workers[9–13], while other workers have prepared potentially water-soluble copolymers based on glycidyl methacrylate and *N*-vinylpyrrolidone[12,13].

The microstructure of polymers, which involves the distribution of monomers in the copolymers (number-average sequence length) and the stereochemical arrangement of various groups pendent to the polymer backbone (tacticity), fundamentally influences their physical and chemical properties[14]. High-resolution n.m.r., particularly the proton-noise-decoupled ^{13}C technique, has proved effective in the elucidation of the microstructure of synthetic polymers[15,16]. Of the currently available literature, there seems to be some confusion regarding ^{13}C assignments in poly(glycidyl methacrylate) and related copolymers[13,17–19]. For instance, Babu *et al.*[17,18] suggest that the backbone methylene and quaternary carbons in glycidyl methacrylate repeat units have ^{13}C chemical shifts situated at 48–49 ppm and 44.7–45.4 ppm respectively, while Reddy *et al.*[13] suggest the contrary. Moyhan *et al.*[19] make no mention of the backbone methylene or quaternary carbons. In view of renewed interest in these systems, we felt it worth while to re-examine this problem.

In this paper, the microstructural elucidation of poly(glycidyl methacrylate) and poly(glycidyl methacrylate-*co*-vinylpyrrolidinone) copolymers prepared by solution polymerization in chloroform is detailed. By the combined use of high-field proton-decoupled ^{13}C, ^{1}H–^{13}C correlation and 135 DEPT n.m.r., unequivocal assignments of carbon and proton signals have been established.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA) and *N*-vinylpyrrolidinone (VPD) (Aldrich Chemical Co.) were de-inhibited by

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distillation under reduced pressure. Both monomers were stored under refrigeration overnight prior to polymerization. Poly(*N*-vinylpyrrolidinone) (molecular mass 360 000) was obtained from the Aldrich Chemical Co. 2,2′-Azobisisobutyronitrile (Merck (BDH) Ltd) was recrystallized from a chloroform/petroleum ether mixture. H.p.l.c.-grade methanol, chloroform, cyclohexane and 97% t-butyl methyl ether were obtained from the Aldrich Chemical Co. and used as received.

Glycidyl methacrylate polymerization

First, 5 g de-inhibited glycidyl methacrylate and 0.3 g 2,2′-azobisisobutyronitrile in 25 ml chloroform were placed in a septum sealed, 100 ml conical flask and deoxygenated by flushing with nitrogen for 1 h. The flask was then immersed in a water bath at 60 ± 0.1°C and the polymerization allowed to proceed for 1 h before being terminated by rapid cooling in ice. The polymer was precipitated from solution by dropwise addition to t-butyl methyl ether, filtered and washed repeatedly with t-butyl methyl ether and dried. The recovery procedure was repeated twice before the polymer was dried under vacuum at 40°C for 48 h.

Glycidyl methacrylate-N-vinylpyrrolidinone copolymerization

First, 1.9 g de-inhibited glycidyl methacrylate, 18.0 g de-inhibited *N*-vinylpyrrolidinone and 1.2 g 2,2′-azobisisobutyronitrile in 40 ml chloroform were deoxygenated and copolymerized for 30 min as above. The copolymer (A) was precipitated from solution by dropwise addition to cyclohexane, filtered, washed repeatedly with cyclohexane and dried. The recovery was repeated twice using a methanol/t-butyl methyl ether mixture before the polymer was dried under vacuum at 40°C for 48 h. A second copolymer (B) containing a higher glycidyl methacrylate residue was prepared using the same procedure but using 2.7 g glycidyl methacrylate, 9.0 g *N*-vinylpyrrolidinone and 0.7 g 2,2′-azobisisobutyronitrile in 23 ml chloroform.

N.m.r. characterization

High-field ^{13}C (100 MHz) and ^{1}H (400 MHz) n.m.r. spectra were recorded on 13–16% w/w solutions in $CDCl_3$ on a JEOL GX400 spectrometer. Chemical shifts were recorded in ppm downfield from tetramethylsilane (TMS). Typical recording conditions for the ^{13}C and 135 DEPT n.m.r. spectra were: temperature, 30°C; spectral width, 30.1 kHz; pulse width, 5 μs; acquisition time, 0.54 s; number of scans, 1000; repetition delay, 2.5 s. Typical recording conditions for the ^{1}H n.m.r. spectra were: temperature, 30°C; spectral width, 4.0 kHz; pulse width, 3.9 μs; acquisition time, 4.1 s; number of scans, 32; repetition delay, 0.7 s. Typical recording conditions for ^{1}H–^{13}C correlation n.m.r. were: temperature, 30°C; spectral width, 19.0 kHz; pulse width, 9.5, 19.0, 18.6 μs; repetition delay, 1.0 s; acquisition time, 0.05 s; number of scans, 104; number of stacks 256. Typical recording conditions for the proton-decoupled ^{13}C n.m.r. spectra were: temperature, 30°C; spectral width, 5.9 kHz; pulse width, 5.0 μs; repetition delay, 2.5 s; acquisition time, 0.5 s; number of scans, 1000.

G.p.c. characterization

The g.p.c. system was calibrated with poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) in

Table 1 Assignment of peaks in ^{13}C n.m.r. spectra of poly(glycidyl methacrylate), poly(*N*-vinylpyrrolidinone) and poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)

Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13
GMA			17.8	166.5	64.8	48.9	44.1						
VPD										172.9	30.9	16.9	44.1
PGMA	52.0	44.7	16.8	176.0	65.7	48.6	44.4						
	54.0	45.0	18.8	177.1		48.8							
PVPD								32.0	43.5	175.3	31.3	18.2	41.0
								38.0	45.0				43.5
P(GMA-*co*-VPD)	52.0	44.7	17.0	176.0	65.7	48.6	44.5	32.0	43.5	174.0	31.5	17.0	41.0
	54.0	45.0	19.0	177.0	66.0	49.0		38.0	45.0	176.0	32.0	19.0	43.5

Table 2 Assignment of peaks in ^{1}H n.m.r. spectra of poly(glycidyl methacrylate), poly(*N*-vinylpyrrolidinone) and poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)

Sample	H1	H3	H5	H6	H7	H8	H9	H11	H12	H13
GMA	5.62	1.96	4.00	3.26	2.68					
	6.16		4.47		2.85					
VPD						4.42	7.06	2.49	2.12	3.52
PGMA	1.5	0.9	3.8	3.2	2.65					
	2.0	1.1	4.4		2.85					
PVPD						1.4	3.7	2.0	1.8	3.2
						1.7	3.9	2.4	2.3	
P(GMA-*co*-VPD)	1.5	0.9	3.8	3.2	2.65	1.4	3.8	2.1	1.8	3.2
	2.0	1.1	4.4		2.85	1.8		2.5	2.5	

dimethylformamide (DMF) and the results expressed as 'PEO/PEG equivalent' weight-average molecular masses. The weight-average molecular mass of the poly(glycidyl methacrylate) was determined as 31 700 (polydispersity 2.9), while the weight-average molecular masses of the copolymers A and B were determined as 22 300 (polydispersity 7.3) and 91 250 (polydispersity 3.4) respectively.

Copolymer composition

Copolymer composition was determined by elemental analysis (EMASyst 1106 elemental analyser data system). The percentage of glycidyl methacrylate in copolymers A and B was determined as 43.0 and 63.5 mol% respectively.

RESULTS AND DISCUSSION

^1H and ^{13}C n.m.r. spectra of monomers

The ^{13}C and ^{1}H n.m.r. spectra of the monomers were recorded to aid signal assignments in the polymers. The assignments are shown in *Tables 1* and *2* according to the key in *Figure 1*. For glycidyl methacrylate, the absence of the backbone methylene and quaternary carbons allows assignment of the resonances at 44.1 ppm (2.68 and 2.85 ppm) and 48.9 ppm (3.26 ppm) to epoxide methylene (7) and methine (6) carbons (and protons) respectively. Assignments for the other carbons and protons are listed in *Tables 1* and *2*. Assignments in *N*-vinylpyrrolidinone were aided by published data reported for *N*-vinylpyrrolidinone and methylpyrrolidinone[20]. The assignments are summarized in *Tables 1* and *2*.

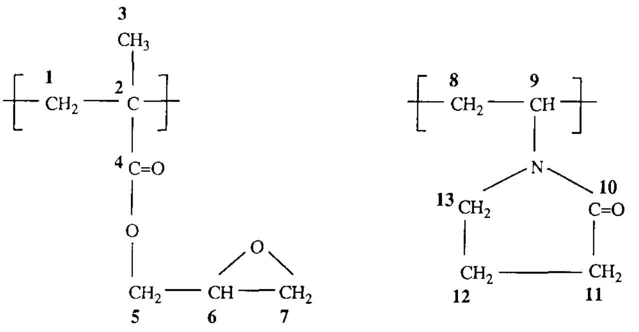

Figure 1 Key to position numbering in tables (the corresponding atoms in the polymer carry the same numbers)

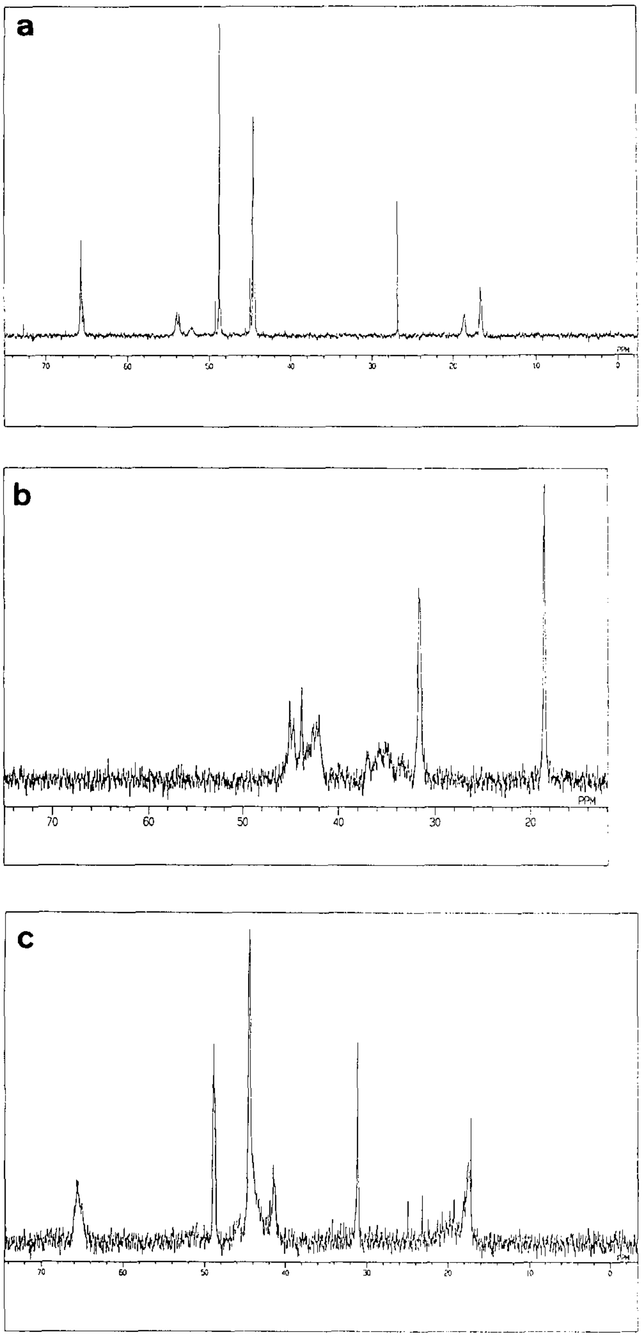

Figure 2 ^{13}C n.m.r. spectra of (a) poly(glycidyl methacrylate), (b) poly(*N*-vinylpyrrolidinone) and (c) poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)

Table 3 ^{13}C n.m.r. assignments for poly(glycidyl methacrylate)

Chemical shift (ppm)	Off-resonance decoupled[a]	135 DEPT[b]	Assignment[c]
16.8	d or q	Positive	Methyl (3)
18.8	Unresolved	Positive	Methyl (3)
44.4	t	Negative	Epoxide methylene (7)
44.7, 45.0	s	None	Quaternary (2)
48.6, 48.8	d	Positive	Epoxide methine (6)
52, 54	Unresolved	Negative	Backbone methylene (1)
65.3	t	Negative	Methylene (5)
65.7	t	Negative	Methylene (5)
176.0–177.1	s	None	Carbonyl (4)

[a] s = singlet, d = doublet, t = triplet, q = quartet

[b] Positive = CH or CH_3; negative = CH_2; none = quaternary or carbonyl

[c] Carbon numbers refer to *Figure 1*

Table 4 ^{13}C n.m.r. assignments for poly(*N*-vinylpyrrolidinone)

Chemical shift (ppm)	Off-resonance decoupled[a]	135 DEPT[b]	Assignment[c]
18.2	t	Negative	Methylene (12)
31.3	Unresolved	Negative	Methylene (11)
41.0–43.5	Unresolved	Negative	Methylenes (8, 13)
43.5–45.0	Unresolved	Positive	Backbone methine (9)
175.3	Unresolved	None	Carbonyl (10)

[a] t = triplet
[b] Positive = CH or CH_3; negative = CH_2; none = quaternary or carbonyl
[c] Carbon numbers refer to *Figure 1*

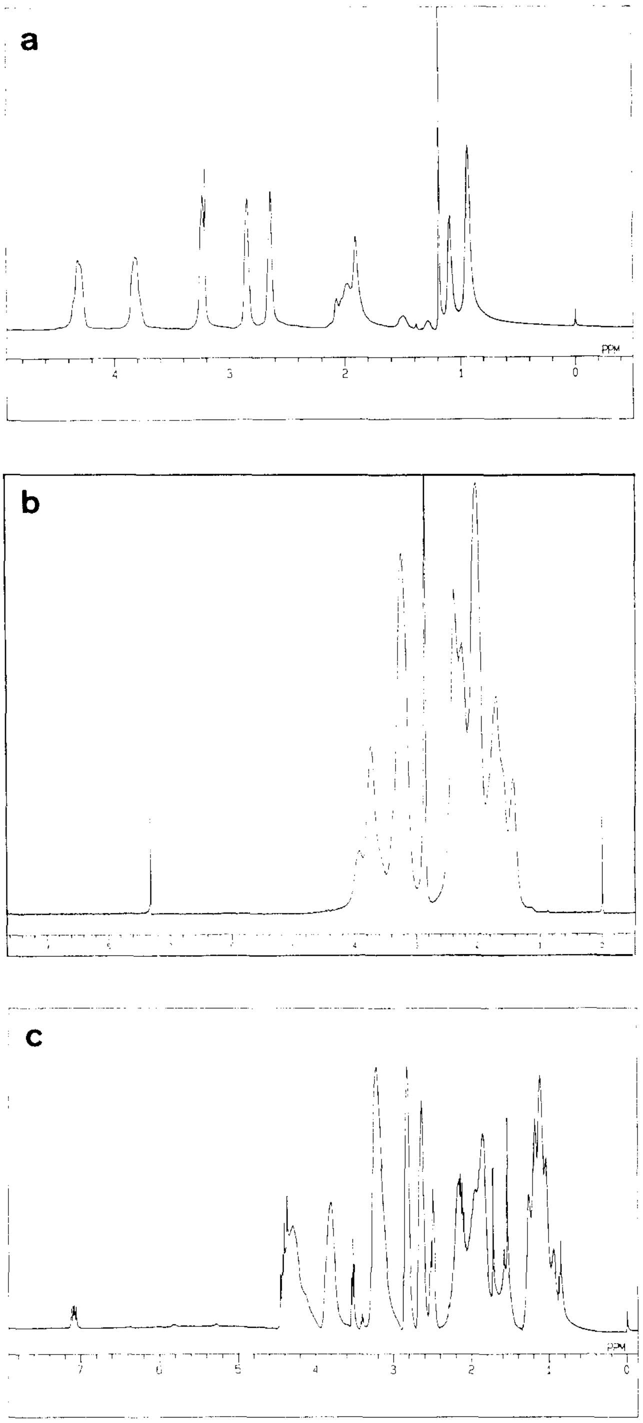

Figure 3 ^1H n.m.r. spectra of (a) poly(glycidyl methacrylate), (b) poly(*N*-vinylpyrrolidinone) and (c) poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)

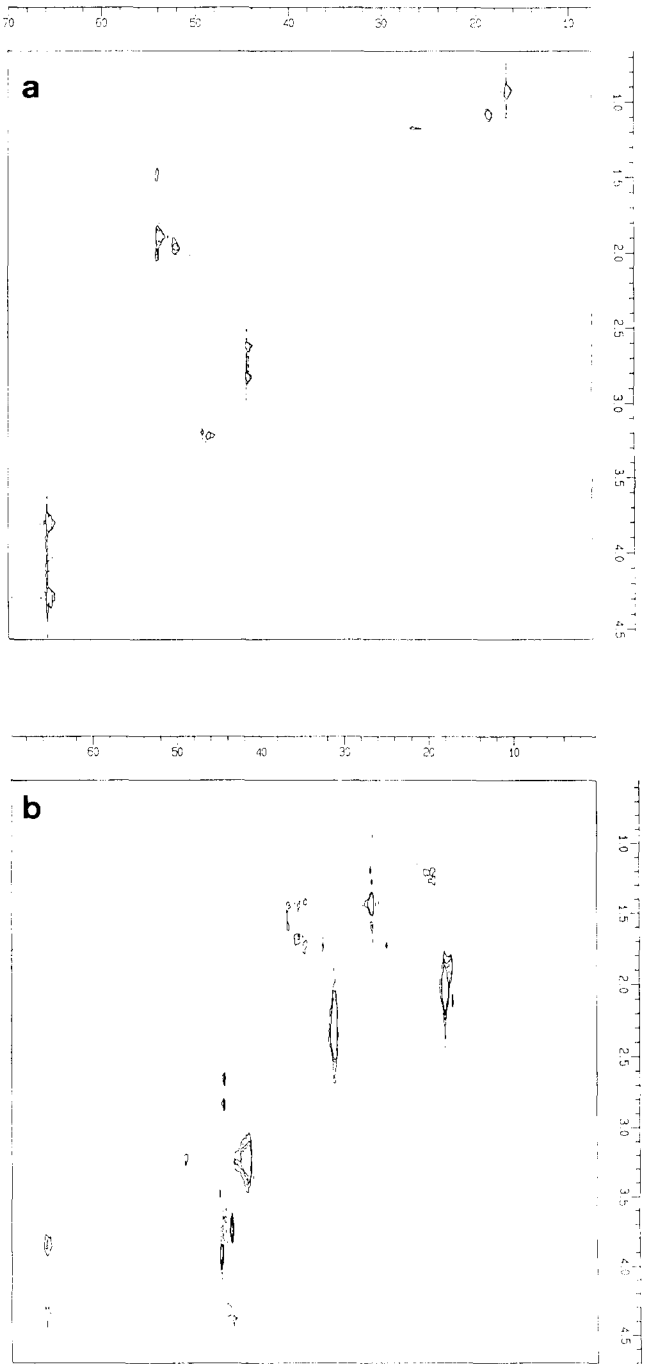

Figure 4 ^1H–^{13}C correlation n.m.r. spectra of (a) poly(glycidyl methacrylate) and (b) poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)

N.m.r. spectra of poly(glycidyl methacrylate)

Spectral assignments were aided by published spectra of analogous acrylic polymers[21] and ^{1}H n.m.r. peak integrals, and the spectra are shown in *Figures 2a* and *3a*. In addition, proton-decoupled and off-resonance spectra were recorded along with 135 DEPT to identify unambiguously the origin of the signals. In DEPT n.m.r., the signal amplitude is strongly influenced by the running parameters being correct for each proton type. Proton-decoupled off-resonance ^{13}C n.m.r., however, is more reliable by providing absolute information regarding the proton type. A summary of the reasoning behind the ^{13}C signal assignments is given in *Table 3*. In many cases, the small differences in chemical shifts of closely adjacent peaks are due to tacticity effects. The weak signal at 49.2 ppm was assigned to a solvent impurity. Having established the ^{13}C chemical shifts, ^{1}H–^{13}C correlation n.m.r. was used to identify the proton resonances, the spectrum being shown in *Figure 4a*. Resonances at 16.8–18.8 ppm and 48.6–48.8 ppm appear with opposite intensity to other resonances in the spectrum, and are thus assigned to methyl (3) and methine (6) groups respectively. Similar reasoning led to assignment of all other signals, and these are summarized in *Tables 1* and *2*.

*N.m.r. spectra of poly(*N*-vinylpyrrolidinone)*

The ^{13}C and ^{1}H n.m.r. spectra of poly(*N*-vinylpyrrolidinone) are shown in *Figures 2b* and *3b*. *Table 4* summarizes the reasoning behind the assignments detailed in *Table 2*. The assignments are summarized in *Tables 1* and *2*.

*Poly(glycidyl methacrylate-*co*-vinylpyrrolidinone)*

Spectral assignments were aided by comparison with homopolymer spectra and a 135 DEPT spectrum of copolymer A. Spectra of the copolymer can be considered (*Figures 2c* and *3c*) as superpositions of the homopolymer spectra. *Figure 4b* shows the ^{1}H–^{13}C correlation n.m.r. spectrum of copolymer A. Since this contains a greater proportion of *N*-vinylpyrrolidinone, those resonances dominate the spectra. By observing the couplings, assignments were made and are shown in *Tables 1* and *2*. The spectra from copolymer B, which contained more glycidyl methacrylate, were used to confirm these assignments.

Having established the assignments, ^{1}H n.m.r. was used to determine copolymer composition. The area corresponding to one proton on the glycidyl methacrylate residue (A) was determined from the integrals of the peaks at 2.65 and 2.85 ppm belonging to the methylene protons (7). The area corresponding to one proton on the vinylpyrrolidinone residue (B) was determined from the peak at 3.2 ppm corresponding to two vinylpyrrolidinone protons (13) and one glycidyl methacrylate proton (6). The percentage of glycidyl methacrylate (mol% GMA) was then determined using the equation:

$$\text{mol\% GMA} = \frac{100A}{A+B}$$

The percentage of glycidyl methacrylate for copolymers A and B was determined as 38.2 and 63.8 mol% respectively, which agreed closely with the values given by elemental analysis.

CONCLUSION

Application of high-field proton-decoupled ^{13}C, ^{1}H–^{13}C correlation and 135 DEPT n.m.r. has allowed unequivocal assignments of protons and carbons in poly(glycidyl methacrylate) and poly(glycidyl methacrylate-*co*-vinylpyrrolidinone) copolymer to be established. Furthermore, copolymer composition could then be determined using the established ^{1}H n.m.r. data.

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