Glycidyl Methacrylate and Vinylidene Chloride Copolymers. Nuclear Magnetic Resonance Characterisation

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ABSTRACT: The copolymers of glycidyl methacrylate/vinylidene chloride (G/C) were synthesized and the quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was used to determine the copolymer composition. The comonomer reactivity ratios as determined by Kelen–Tudos (KT) and non-linear least squares error in variable method (EVM) are $r_{\text{G}} = 2.55 \pm 0.56$, $r_{\text{C}} = 0.26 \pm 0.06$ and $r_{\text{G}} = 2.7$, $r_{\text{C}} = 0.27$, respectively. The Distortionless Enhancement by Polarization Transfer (DEPT), heteronuclear single quantum coherence (HSQC) and Total Correlation Spectroscopy (TOCSY) were used for the complete spectral assignments of $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra.

KEY WORDS Glycidyl Methacrylate/Vinylidene Chloride (G/C) Copolymers / Two-Dimensional NMR (2D-NMR) Studies / Sequence Distribution /

The vinylidene chloride polymers possess many unique characteristics in their structure and reactivity, but the homopolymer is difficult to mold.¹ The copolymers of vinylidene chloride with suitable monomers help to overcome this instability problem. Kamide *et al.*² have made the assignments of $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of vinylidene chloride/acrylonitrile copolymers and reported its sequence distribution. Cais *et al.*³ have investigated the microstructure of vinylidene/vinyl halide copolymers. The microstructure of vinylidene chloride/*trans*-4-methacryloyloxyazobenzene were investigated by Brar and Thiagarajan⁴ using one- and two-dimensional NMR spectroscopy.

In our earlier publications, the microstructure determination of glycidyl methacrylate with acrylonitrile, vinyl acetate, methacrylonitrile and styrene copolymers have been reported.^{5–8} In continuation of our earlier work, in this paper we report the complete compositional and configurational assignments of Glycidyl methacrylate/vinylidene chloride copolymers. The high-resolution 1D- and 2D-NMR spectroscopy has proved to be an informative technique for the investigation of microstructure of the polymers.^{9,10} Comonomers reactivity ratios were calculated using the Kelen–Tudos (KT)¹¹ and non-linear error in variable (EVM)¹² methods, using compositional data obtained from $^{13}\text{C}\{^1\text{H}\}$ NMR quantitative spectrum.

EXPERIMENTAL

Glycidyl methacrylate (Merck) and vinylidene chloride (Merck) were purified by distillation under reduced pressure and both the monomer were then stored be-

low 5 °C. A series of G/C copolymers containing different mol-fraction of G- in feed were prepared by solution polymerisation in benzene at 60 °C using benzoyl peroxide as an initiator. The conversion was kept below 10% by timely precipitating the copolymer in methanol. The copolymers were further purified using chloroform/methanol system. All the NMR spectra were recorded in CDCl_3 solvent at 25 °C as reported in our earlier publications.^{5–8}

RESULTS AND DISCUSSION

Copolymer Composition and Reactivity Ratios Determination

The composition of G/C copolymers was determined from quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The mol fractions of monomers in feed and in copolymer and their molecular weight distribution data are given in Table I. The copolymer composition data was used to determine the terminal model reactivity ratio (KT method). These initial estimates of reactivity ratios, along with the copolymer composition data were used for the calculation of the reactivity ratios by non-linear error in variable method. The value of reactivity ratios as obtained from Kelen–Tudos (KT)¹¹ and non linear error in variable method (EVM)¹² $r_{\text{G}} = 2.55 \pm 0.56$, $r_{\text{C}} = 0.26 \pm 0.06$ and $r_{\text{G}} = 2.7$, $r_{\text{C}} = 0.27$, respectively.

$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra Studies

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of G/C copolymer ($F_{\text{G}} = 0.54$) in CDCl_3 is shown in Figure 1 along with the complete signal assignments. The α -methyl group of G-unit is assigned around δ 16.0–22.0 ppm. The spectral region around δ 43.0–66.0 ppm is very com-

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Table I. The mol fraction in feed and in copolymer and molecular weight distribution data of G/C copolymers

Sample	Feed in mol fraction	Copolymer composition	$\overline{M}_n^c \times 10^{-5}$ g mol ⁻¹	$\overline{M}_w^c \times 10^{-5}$ g mol ⁻¹	Polydispersity
	f_G^a	F_G^b			
GC1	0.10	0.28	1.76	2.38	1.35
GC2	0.20	0.45	1.43	2.15	1.50
GC3	0.30	0.54	1.35	2.02	1.50
GC4	0.45	0.70	1.28	2.02	1.58
GC5	0.50	0.75	1.04	1.75	1.75

^a f_G is the mol fractions of G-comonomer in feed. ^b F_G is the mol fractions of G-comonomer in the copolymer. ^c $\overline{M}_n$ and $\overline{M}_w$ are number average and weight average molecular weight of copolymers calculated using Gel permeation chromatography technique.

Figure 1. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of G/C copolymer ($F_G = 0.54$) in CDCl_3 .

plex and overlapped and can be assigned to aliphatic carbons in the main and side chain of copolymer. The DEPT-135 spectrum (Figure 2) was used to assign the spectral region. The epoxy methylene, epoxy methine and $-\text{OCH}_2$ carbon signals are assigned at δ 44.5, δ 48.8, and δ 66.3 ppm respectively. The β -methylene carbon of both G- and C-units resonate around δ 52.0–67.0 ppm. The quaternary carbon of G- and C-units in the copolymer are assigned around δ 49.0 and δ 83.8–88.2 ppm, respectively. The carbonyl carbon resonance of G-centered units is assigned around δ 175.5–177.8 ppm.

The $^{13}\text{C}\{^1\text{H}\}$ resonances of the α -methyl groups for poly(glycidyl methacrylate) and copolymer samples of different feed composition are shown in Figure 3a–d. The assignments to various signals are done by comparing with the assignments done in poly(glycidyl methacrylate) spectrum¹³ and by observing change in signal intensity with change in the copolymer compo-

sition. The signals at δ 16.7 ppm and δ 18.9 ppm are assigned to GrGrG, GrGmG respectively, by comparing with the assignments done in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of poly(glycidyl methacrylate).¹³ The signals around δ 18.4 and δ 20.3 ppm, which first shows increase and then decrease in intensity with decrease in G-content in copolymer is assigned to GrGrC and GrGmC respectively. The signal around δ 20.7 ppm, which shows increase in intensity with increase in C-content (decrease in G-content) in copolymer, is assigned to CGC triad sequence. The various α -CH₃ assignments done in $^{13}\text{C}\{^1\text{H}\}$ NMR are further confirmed by 2D-HSQC NMR assignments.

The expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the quaternary carbon resonances of C-unit in the G/C copolymers of different compositions are shown in Figure 4. In this region, the signals around δ 83.8–84.5 ppm which show decrease in intensity with decrease in the C-content is assigned to CCC triad sequence, while the

Figure 2. The DEPT-135 spectrum of G/C copolymer ($F_G = 0.54$) in CDCl_3 .

Figure 3. The Expanded $^{13}\text{C}\{^1\text{H}\}$ spectra showing α -methyl carbon signal in (a) poly(glycidyl methacrylate), copolymers with composition F_G : (b) 0.75, (c) 0.54, and (d) 0.28.

Figure 4. The Expanded $^{13}\text{C}\{^1\text{H}\}$ spectra showing quaternary carbon signal of C-unit in G/C copolymers with composition F_G : (a) 0.28, (b) 0.54, and (c) 0.75.

signal around $\delta 87.4$ – 89.0 ppm which show increase in intensity with decrease in the C-content (increase in G-

Figure 5. The Expanded $^{13}\text{C}\{^1\text{H}\}$ spectra showing carbonyl carbon signal of G-unit in (a) poly(glycidyl methacrylate) copolymers with composition F_G : (b) 0.75, (c) 0.54, and (d) 0.28.

content) is assigned to GCG triad sequence. The resonance signal around $\delta 86.5$ ppm is assigned to GCC triad sequence.

The expanded carbonyl region in $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in G/C copolymers of different composition are shown in Figure 5. The three broad signals around $\delta 174.8$ – 175.75 , $\delta 175.7$ – 176.6 , and $\delta 176.6$ – 177.7 ppm are assigned to mm, rm, and rr configurational sequences by comparing them with $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of poly(glycidyl methacrylate). The three broad signals show variation in intensity with copolymer composition, which shows that these are not pure configurational rather overlapped with compositional sequences. The signals around $\delta 174.8$ – 175.7 ppm shows increase in intensity with decrease in G-content in copolymer, while signals around $\delta 176.7$ – 178.0 ppm

Figure 6. The 2D-HSQC NMR spectra of G/C copolymers showing α -methyl group of G-unit, in copolymers with composition F_G : (a) 0.28, (b) 0.54, and (c) 0.75.

shows decrease in intensity with decrease in G-content in G/C copolymer. This shows that signals around δ 174.8–175.7 ppm have predominant concentration of CGC copolymer compositional sequences in copolymer, while signals around δ 175.7–176.6 ppm are due to GCC triad sequence overlapped with GrGmG configurational sequence.

2D-HSQC NMR Studies

The expanded 2D-HSQC NMR spectra of α -methyl group of G-unit are shown in Figure 6a, b, and c ($F_G = 0.28, 0.54$, and 0.75 in copolymer). The α -methyl group shows both compositional and configurational sensitivity. The cross peaks at δ 16.9/0.98 and 18.9/1.12 ppm are assigned to GrGrG and GrGmG respectively, on basis of the assignments done in HSQC NMR spectrum of poly(glycidyl methacrylate). The other cross-peaks in the α -methyl region are assigned on the basis of change in intensity with the change in copolymer composition. The cross-peaks at δ 18.5/1.5 and δ 20.5/1.69 ppm which does not show

relative change in intensity with respect to each other are assigned to GrGrC and GrGmC configurational sequences respectively, while the cross peak around δ 21.0/1.9 ppm which increases in intensity with decrease in G-content (increase in C-content) is assigned to CGC configurational sequence respectively.

The expanded 2D-HSQC NMR spectra of epoxy methine, epoxy methylene, oxy methylene groups in G-units and β -methylene group in both G- and C-units are shown in Figure 7a, b, and c ($F_G = 0.28, 0.54$ and 0.75). The β -CH₂ region, due to its symmetry is sensitive to dyad, tetrad etc. This region is divided into GG, GC, and CC dyads on the basis of change in intensity of signals with the change in the copolymer composition. The three dyads are assigned around δ 53.4/1.99, δ 56.0–59.0/2.25–3.4, and δ 62.0–67.0/3.25–3.85 ppm respectively. The GC and CC dyad show further splitting along carbon axis which shows change in intensity with the change in the copolymer composition and hence are assigned to higher order compositional sequences. In GC dyad, the two

Figure 7. The 2D-HSQC NMR spectra of G/C copolymers showing β -methylene group in both G- and C-units, epoxy and oxy-methylene groups of G-unit in copolymer with compositions F_G : (a) 0.28, (b) 0.54, and (c) 0.75.

cross peaks at δ 55.5/2.6–2.9 and 55.5/3.3 ppm are assigned to CGCC tetrad, while the cross peaks around δ 57.5/2.5 and 57.5/3.0 ppm are assigned to GGCC tetrad sequence. The cross peaks at δ 59.5/2.28 and 59.5/2.9 ppm are assigned to GCGG tetrad sequence. In CC dyad, the three crosspeaks at δ 62.5/3.8, 64.5/3.6, and 66.5/3.3 ppm are assigned to CCCC, CCCG, and GCCG tetrad sequence respectively, by observing the change in intensity of cross peaks with the change in the copolymer composition. In the Figure 7, the cross peak at δ 49.0/3.28 ppm is assigned to epoxy methine group of copolymer. The $-\text{OCH}_2$ methylene protons that are adjacent to the chiral center in G/C copolymer show diastereomerism and give two crosspeaks at δ 66.4/3.82 and δ 66.4/4.32 ppm. Similarly, the epoxy methylene proton signals give two cross peaks at δ 44.5/2.68 and 44.5/2.87 ppm respectively.

2D-TOCSY NMR Spectra Studies

The 2D-HSQC NMR spectrum was used to assign the broad and overlapped ^1H NMR spectrum. The

proton spectrum along with complete assignments is shown in Figure 8 ($F_G = 0.54$). The TOCSY spectra of low mixing time (4 ms) of G/C copolymer of different composition ($F_G = 0.28, 0.54$, and 0.75) was recorded to observe the three bond coupling between the protons of different directly coupled groups in G/C copolymer Figure 9a, b, and c, respectively. The crosspeak at δ 1.55/2.0 ppm is assigned due to geminal coupling between inequivalent α -methyl protons. The cross peaks around δ 2.2–2.3/2.85 ppm (1), (2) and δ 2.4/ 3.3 ppm (3) are assigned due to geminal coupling between inequivalent β -methylene protons in GCGG and GCGC tetrad sequences respectively, while the cross peaks at δ 2.5/3.3 (4) and δ 2.8/3.3 (5) ppm are assigned to geminal coupling between inequivalent β -methylene protons in CCGC tetrad sequence. These assignments are done by observing the change in intensity of cross peaks with the change in the copolymer composition. The vicinal coupling between side chain group of G-unit can also be clearly seen (cross peak no. 6–11). These are assigned as reported in our earlier publications.^{5–8}

Figure 8. The ^1H NMR spectrum of G/C copolymer ($F_G = 0.54$) in CDCl_3 .

Figure 9. The 2D-TOCSY NMR spectra of G/C copolymers with composition F_G : (a) 0.28, (b) 0.54, and (c) 0.75.

CONCLUSIONS

The reactivity ratios of G/C copolymer system are found to be $r_G = 2.7$, $r_C = 0.27$. The various 1D-

(DEPT) and 2D-(HSQC, TOCSY) NMR spectroscopic techniques are used to resolve the broad and overlapped signals in ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The carbonyl carbon and α -methyl group carbon of G-unit and quaternary carbon of C-unit assigned to triad com-

positional sequence in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The β -methylene carbon resonances is very well resolved and assigned to tetrad compositional sequences using 2D-HSQC NMR spectral technique. The 2D-TOCSY NMR spectrum is used to confirm the assignments done for β -methylene protons in 2D-HSQC NMR spectrum.

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