Investigation of microstructure of glycidyl methacrylate/a-methyl styrene copolymers by 1D- and 2D-NMR spectroscopy

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Abstract

The copolymers of glycidyl methacrylate/a-methyl styrene were synthesized. The quantitative $^{13}\text{C}^{1\text{H}}$-NMR spectroscopy was used to determine the copolymer compositions. The distortionless enhancement by polarization transfer, $^{13}\text{C}^{1\text{H}}$ heteronuclear single quantum coherence and total correlation spectroscopy were used for the complete spectral assignment of $^{13}\text{C}^{1\text{H}}$- and $^{1}\text{H}$-NMR spectra.

Keywords: Glycidyl methacrylate/a-methyl styrene copolymers; 2D-NMR studies; Sequence distribution

1. Introduction

The high-resolution 1D- and 2D-NMR spectroscopy has proved to be one of most informative technique for the investigation of microstructure of the polymers [1]. $^{13}\text{C}^{1\text{H}}$ heteronuclear single quantum coherence (HSQC) NMR techniques have been used for the compositional [2-4] and configurational [5-7] assignments of the polymers.

In our earlier publications, the microstructure determination of glycidyl methacrylate/acylonitrile, glycidyl methacrylate/vinyl acetate, glycidyl methacrylate/methacrylonitrile and glycidyl methacrylate/styrene copolymers have been reported [8-11]. In continuation of our earlier work, in this paper we report the complete compositional and configurational assignments of glycidyl methacrylate/a-methyl styrene (G/M) copolymers using the $^{13}\text{C}^{1\text{H}}$, distortionless enhancement of polarization transfer (DEPT) and 2D-NMR (HSQC and total correlation coherence spectroscopy (TOCSY)).

2. Experimental

Glycidyl methacrylate (G) (Merck) and a-methyl styrene (M) (Merck) were purified by distillation under reduced pressure and both the monomers were then stored below 5 °C. A series of G/M copolymers containing different mole fraction of G in feed were prepared by bulk polymerization 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 [8-11].

3. Results and discussion

3.1. 1D studies

The quantitative $^{13}\text{C}^{1\text{H}}$-NMR spectroscopic technique was used to determine copolymer composition. The $^{13}\text{C}^{1\text{H}}$-NMR spectrum of G/M copolymer ($FG= 0.50$) in CDCl$_3$ is shown in Fig. 1 along with the
complete signal assignments. The α-methyl group of G-
and M-unit is assigned around δ17.0-25.0 ppm. The
spectral region around δ42.0-66.0 ppm is very complex
and overlapped and can be assigned to aliphatic car-
bons in the main and side chain of the copolymer. The
extent of overlap of epoxy methylene, β-methylene and
epoxy methine carbon signals cannot be ascertained
from $^{13}\text{C}[^1\text{H}]$-NMR spectrum alone and so the DEPT-
135 spectrum (Fig. 2) was used to assign the spectral
region. The epoxy methylene, epoxy methine and
-\text{OCH}_2 carbon signals are assigned at δ44.5, δ48.8 and
δ66.0 ppm respectively, by comparing with the assign-
ments in $^{13}\text{C}[^1\text{H}]$-NMR spectrum of poly(glycidyl
methacrylate) [12]. The quaternary carbon of glycidyl
methacrylate in the copolymer is assigned around δ49.0
ppm. The aliphatic quaternary carbon of M-unit ap-
pears around δ43.5 ppm. The β-methylene carbon of
both G- and M-unit resonate around δ52.0-61.0 ppm.
The carbonyl carbon resonances of the G- and the aro-
matic quaternary carbon of M-centered units are as-
signed around δ175.2-179.5 and δ142.0-151.0 ppm
respectively.

3.2. 2D-NMR studies

3.2.1. Heteronuclear single quantum coherent studies

The 1D-α-methyl group spectrum is quite complex
and difficult to resolve. However, the 1D-NMR spectra
of poly(glycidyl methacrylate) [12] and poly(α-methyl
styrene) [13] well indicates that addition of α-methyl
styrene in G/M copolymer causes slight downfield shift
in the α-methyl region along carbon axis and upfield
shift along proton axis. The assignments in α-methyl
group in the copolymer are done using the above ob-
servation and by observing the change in intensity of the
crosspeaks with change in the copolymer composition.
The expanded complete 2D-HSQC NMR spectra is as
shown in Fig. 3(a) and (b) ($G_{G} = 0.70$ and 0.23). The α-
methy l group carbon resonance is assigned to G- and M-
centered triad compositional sequences on the basis of
change in intensity with change in the copolymer com-
position. The crosspeaks at δ16.8/0.95 and δ18.8/1.1
ppm are assigned to GrGrG and GrGmG respectively,
on basis of the assignments done in poly(glycidyl
methacrylate) HSQC NMR spectrum. The crosspeak at
\[ \text{Fig. 2. The DEPT-135 spectrum of G/M copolymer (} F_G = 0.5) \text{ in CDCl}_3. \]

\[ \text{Fig. 3. The complete 2D-HSQC NMR spectra of G/M copolymers of composition} \quad F_G: (a) 0.70 \text{ and (b) 0.23.} \]

18.5/0.3 ppm which almost disappears in Fig. 3(b) \((F_G = 0.23)\) is assigned to GGM triad sequence, while the crosspeak around 21.5/0.5 ppm which increases in intensity with increase in M-content is assigned to MGM triad sequence. In M-centered triad sequence, the crosspeak at 21.4/0.8 and 20.5/1.05 are assigned to MMG and GMG triad sequence, again by observing the change in intensity of the crosspeaks with change in the copolymer composition.

The \(b\)-CH2 region, due to its symmetry is sensitive to dyad, tetrad etc. This region is divided into GG(d51.5-56.0 ppm), GM(d56.0-59.5 ppm) and MM(d59.5-61.5 ppm) dyads on the basis of change in intensity of signals with the change in the copolymer composition and by comparing with the poly(glycidyl methacrylate) 2D-HSQC NMR spectrum. The MG dyad shows further splitting into three crosspeaks along proton axis due to configurational sequences. The two crosspeaks at
d57.8/1.5 and d57.5/1.9 (H_b) ppm are due to two in equivalent proton in meso-configuration and assigned to MmG and that at d57.5/1.7 ppm is due to racemic and assigned to MrG configurational sequence. All these assignment are shown in 2D-HSQC NMR spectrum (F_G = 0.70 and 0.23), Fig. 3(a) and (b).

In Fig. 3(a) and (b), the -OCH_2 methylene protons in the G/M copolymer show both compositional sensitivity and diastereomerism. The -OCH2 methylene proton signals can be divided into three broad envelopes. The three envelope are assigned to GGG, GGM and MGM triad compositional sequences, on the basis of change in intensity of signals with change in copolymer composition and by comparing with oxy-methylene region in HSQC NMR spectrum of poly(glycidyl methacrylate). Further each triad sequences shows two peaks for diastereomeric protons. The two diastereomeric protons of GGG triad sequence occur at d4.2 and d3.65 ppm, and of GGM occur at d4.0 and d3.5 ppm and that of MGM triad sequence at d3.6 and d3.2 ppm. The epoxy methylene proton region is assigned around d44.7/2.4-2.8 ppm These methylene protons show both compositional sensitivity and diastereomerism. The peak positions of triad compositional sequence and diastereomic protons in various compositional sequences are overlapped and cannot be resolved and hence are difficult to assign. The epoxymethine group is assigned at d48.0/3.1 ppm.

3.2.2 2D-TOCSY spectra studies

Once 13C{^1}H-NMR spectrum is assigned completely, the various overlapped resonance signals in {^1}H-NMR spectrum are assigned by one-to-one correlation between carbon and proton with the help of 2D-HSQC NMR spectra. The proton spectrum along with complete assignments is shown in Fig. 4 (F_G = 0.50). In order to understand the connectivity and confirm the various couplings in the polymer chain, the TOCSY spectrum was recorded. Three and more than three bond coupling between the protons of different directly coupled groups in G/M copolymer can be clearly seen in TOCSY experiments in high mixing time (80 ms) as shown in Fig. 5 (F_G = 0.50).

The two non-equivalent protons MmG centered b-methylene group is coupled, giving crosspeak around d1.3/1.82 ppm (1). The vicinal coupling (crosspeak no.
2-11) between side chain group of G- unit can also be clearly seen and are assigned as reported in our earlier publication [11].

4. Conclusions

The various 1D (DEPT) and 2D(HSQC, TOCSY) NMR spectroscopic techniques are used to resolve the broad and overlapped signals in $^1$H- and $^{13}$C{$^1$H}-NMR spectra. The a-methyl carbon resonances are assigned to triad compositional and configurational sequences and the b-methylene carbon resonances are assigned to dyad compositional sequences with the help of 2D-HSQC NMR spectrum.

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References