NMR Analysis of Butyl Acrylate/Methyl Methacrylate/α-Methyl Styrene Terpolymers

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ABSTRACT: Composition analysis for butyl acrylate (BA)/methyl methacrylate (MMA)/α-methyl styrene terpolymers was carried out by NMR spectroscopy methods. ^{1}H-NMR was used primarily for this analysis, but because the method did not provide independent measurements for the BA and MMA fractions, the terpolymer composition analysis was open to higher than normal levels of uncertainty. Supplementary analyses were made with quantitative ^{13}C-NMR methods to confirm the results from ^{1}H-NMR (quantitative ^{13}C-NMR was used to provide corroboration of selected composition analyses). To confirm spectral assignments in the ^{1}H- and ^{13}C-NMR spectra, heteronuclear multiple quantum coherence and J Modulated Spin Echo (JMOD) pulse sequences were used. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2093–2098, 2007

Key words: NMR; copolymerization

INTRODUCTION

NMR spectroscopy of polymers can be used for a number of analytical purposes, the simplest possibly being the analysis of overall compositions with respect to the monomer fractions in multicomponent polymers. This is routinely done for copolymers, but the methods can also be extended to multicomponent polymers if there are well-defined signals for each type of monomer. ^{1}H-NMR has the advantage of the fast acquisition of spectra but the disadvantage that diagnostic signals for individual components may overlap, especially because the signals obtained for nominally chemically equivalent ^{1}H nuclei in polymers are relatively broad on account of the range of microenvironments for particular nuclei within the polymer chain. The uncertainties that can arise in analyses with ^{1}H-NMR because of signal overlap for different functionalities have been highlighted even for the most widely studied copolymer system, that is, styrene (STY)/methyl methacrylate (MMA).[1,2]

A kinetic investigation of the terpolymerization of butyl acrylate (BA)/MMA/α-methyl styrene (AMS) was carried out at elevated temperatures with a range of monomer feeds.[3] The study involved the analysis of a large number of samples to examine the effects of both the feed composition and conversion levels on the composition of the terpolymers (with respect to the proportions of the three monomers).

The products from terpolymerization were analyzed for the monomeric composition primarily by ^{1}H-NMR because it was the most convenient method for analysis in such a study. In this case, there was a higher than normal level of uncertainty because the typical diagnostic signals from the BA and MMA repeat units came in overlapping spectral areas.

^{13}C{^{1}H}-NMR is a powerful tool for diagnosis for very detailed polymer structural analysis. Unlike ^{1}H-NMR, it has a very large useful diagnostic region for typical organic materials (ca. 200 vs 12 ppm). There have been numerous studies that have used this fact to determine the microstructure of polymers.[4,5] The power of ^{13}C-NMR for microstructural analysis is such that it has been used in the past to confirm microstructures predicted by different types of copolymerization models.[6]

Therefore, to support the analysis of BA/MMA/AMS terpolymers made with ^{1}H-NMR, ^{13}C-NMR was used both to assign characteristic signals for the different monomers and to obtain quantitative data that confirmed the results from ^{1}H-NMR. In addition, selected samples were examined by J Modulated Spin Echo (JMOD) and two-dimensional (2D) heteronuclear multiple quantum coherence (HMQC) NMR to clarify some of the assignments made in the ^{1}H- and ^{13}C-NMR spectra. The details of the NMR analyses are described later.

EXPERIMENTAL

The experimental procedures and details for producing the terpolymers have been described previously.[3] The

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TABLE I
Feed and Terpolymer Composition

Reaction	Reaction temperature (°C)	BA/MMA/AMS feed composition (molar fraction)	Average terpolymer composition (molar fraction)		
			BA	MMA	AMS
1	115	0.085/0.495/0.419	0.117	0.556	0.326
2	115	0.085/0.495/0.419	0.140	0.541	0.319
3	115	0.107/0.618/0.274	0.102	0.648	0.249
4	115	0.264/0.450/0.286	0.231	0.473	0.296
5	140	0.085/0.495/0.419	0.130	0.640	0.232
6	140	0.125/0.694/0.181	0.101	0.747	0.155
7	140	0.107/0.618/0.274	0.127	0.687	0.186
8	140	0.264/0.450/0.286	0.272	0.462	0.265
9	140	0.085/0.495/0.419	0.129	0.641	0.230
10	115	0.107/0.618/0.274	0.118	0.626	0.256

feed compositions of the reaction mixtures, along with the average terpolymer compositions (obtained from ^{1}H-NMR analysis) for the products, are presented in Table I.

NMR spectroscopy

^{1}H-NMR spectra were recorded at room temperature for samples of the polymer (ca. 3%) dissolved in $CDCl_3$ (supplied by Cambridge Isotope Laboratories Inc., Andover, MA) with a Bruker 300-MHz spectrometer. The method used a 90° pulse with a 6-s pulse delay; 32 scans were collected. ^{13}C{^{1}H}-NMR spectra were obtained at room temperature for approximately 3–5% polymer solutions in $CDCl_3$ on a Bruker 500-MHz spectrometer with Avance software. The chemical shifts for both ^{1}H- and ^{13}C-NMR spectra were referenced to the respective solvent signals. Inverse-gated decoupling ^{13}C{^{1}H}-NMR was used with a 90° flip angle and a pulse delay of 10 s for the quantitative analysis of the terpolymer composition. The samples were scanned for approximately 16 h. A ^{13}C{^{1}H}-NMR attached proton test was also performed, with a JMOD pulse sequence, to produce spectra in which the positive signals were from CH_2 or quaternary C carbons and the negative signals were from CH and CH_3 centers. To refine the assignments of the signals in the ^{1}H- and ^{13}C-NMR spectra, a 2D HMQC experiment was used to establish correlations between the chemical shifts of the protons and their attached C nuclei. This technique produced a 2D plot in which one axis was designated by the ^{1}H-NMR spectrum and the other was designated by the ^{13}C-NMR spectrum. Signals arising at points of cross-reference between the two spectra showed the respective shifts for a particular proton center and its attached carbon.

RESULTS AND DISCUSSION

The fact that the compositions of copolymers and other multicomponent polymers can often be determined by simple ^{1}H-NMR analysis is well known. The technique works best when the individual monomers exhibit well-defined signals that are unique to the specific monomer so that the accuracy of the signal integration is reliable. Uncertainty arises when signals for an individual monomer do not come in a well-defined (isolated) region of the standard spectral range. This shortcoming has been highlighted for the NMR analysis of STY/MMA copolymers.[1] The simplest analysis of spectra from such copolymers assumes that the MMA fraction in these copolymers can be equated with the signals between 3.8 and 2.5 ppm. However, Kale et al.[1] showed this to be incorrect because signals for MMA extend below 2.5 ppm and in this region there is an overlap with signals from the STY CH units. Therefore, to analyze fractions accurately, an alternative manipulation of the spectral data has to be carried out.[2,7]

The BA/MMA/AMS terpolymer system comprises the convergence of three copolymer systems: BA/MMA, BA/AMS, and MMA/AMS (see Fig. 1 for representations of the monomer units). These copolymerizations have been studied over a range of temperatures and feed compositions. In these studies, the copolymer compositions were determined exclusively by ^{1}H-NMR.[8–10] This could be done with a high degree of confidence because the polymer bound units for each monomer have well-defined signals in spectral ranges that are unique, so the use of ^{1}H-NMR provides a reliable measure of the molar composition

For BA/MMA, the molar fraction of BA (F_{BA}) can be evaluated from ^{1}H-NMR-based integrated areas for the signals designated on the spectrum for $\mathrm{OC}H_2$ of BA (at ca. 4.1–3.8 ppm) and for $\mathrm{OC}H_3$ of MMA (at ca. 3.75–3.3 ppm).

The ^{1}H-NMR spectra for BA/AMS are slightly more complex because the $\mathrm{OC}H_2$ signals of BA extend over a fairly wide range of 4.2–2.5 ppm (see Fig. 2). Nevertheless, F_{BA} can be evaluated from the spectra as follows:

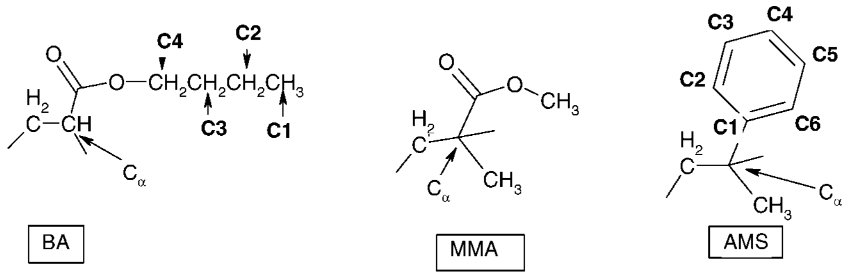

Figure 1 Representations of the monomeric units for BA, MMA, and AMS with designations for distinct carbon centers.

$$F_{\mathrm{BA}} = \frac{B/2}{[B/2 + A/5]} \tag{1}$$

where B and A are the integrated areas for the signals designated in the spectra for OCH_2 of BA and for aromatic H of AMS (7.5–6.7 ppm), respectively.

Finally, for MMA/AMS, the molar fraction of MMA (F_{MMA}) can be readily evaluated from ^{1}H-NMR because the styrenic signals are well defined, and although the signals for OCH_3 cover a wide range (3.8–2.5 ppm), they are distinct from signals for other structural subunits, as shown in Figure 3, so F_{MMA} can be evaluated as follows:

$$F_{\mathrm{MMA}} = \frac{M/3}{[M/3 + A/5]} \tag{2}$$

where M and A are the integrated areas for the signals designated in the spectra for OCH_3 of MMA and for aromatic H of AMS, respectively.

The analysis of the BA/MMA/AMS terpolymer is made more complex because the normal diagnostic signals for BA ($O—CH_2$) and MMA ($O—CH_3$) are found in the same spectral region (region Y in Fig. 4), so the proportions of the two monomers can not be measured independently. As noted previously, when BA and MMA are copolymerized with AMS, the chemical shifts for $O—CH_2$ and $O—CH_3$ protons in BA and MMA units, respectively, both extend from about 4 to 2.5 ppm. Therefore, to use the ^{1}H-NMR spectra for analysis, integrals from three spectral regions have to be considered. The spectrum can be split into three distinct regions (see Fig. 4). Region X, from approximately 7.5 to 6.5 ppm, arises from the aromatic protons on AMS. Region Y, from 4.1 to 2.4 ppm, arises from a combination of $O—CH_2$ signals from BA and OCH_3 signals from MMA. Region Z arises from $—CH_2^-$ and $—CH_3$ of the AMS and MMA units plus remaining $—CH$, $—CH_2$ and $—CH_3$ from BA.

With this breakdown of the spectra, the molar proportions of the three monomers can be estimated as follows:

$$[\mathrm{AMS}] = \frac{X}{5} \tag{3}$$

$$[\mathrm{MMA}] = \frac{X + 5Y - Z}{10} \tag{4}$$

$$[\mathrm{BA}] = \frac{Y - 3[\mathrm{MMA}]}{2} \tag{5}$$

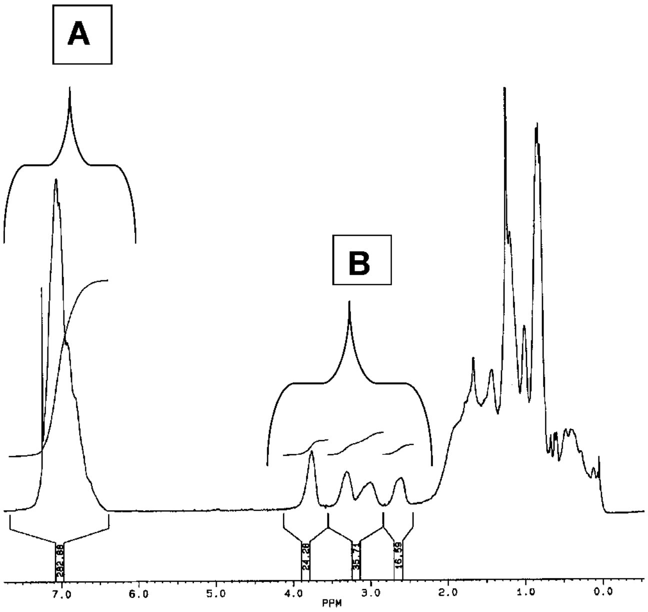

Figure 2 ^{1}H-NMR spectrum of the BA/AMS copolymer in $CDCl_3$.

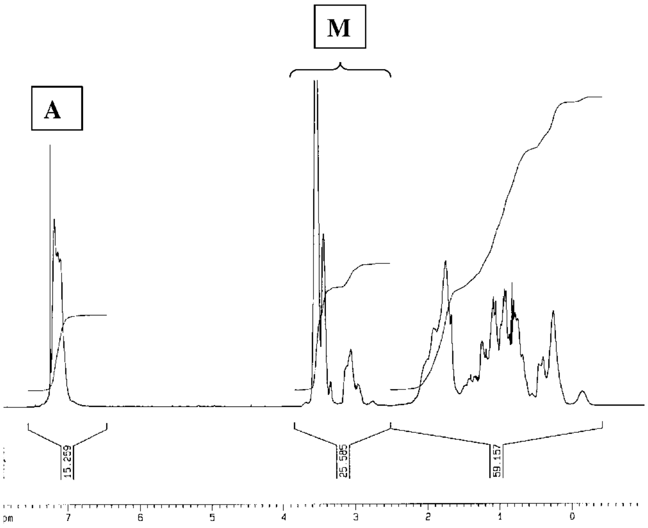

Figure 3 ^{1}H-NMR spectrum of the MMA/AMS copolymer in $CDCl_3$.

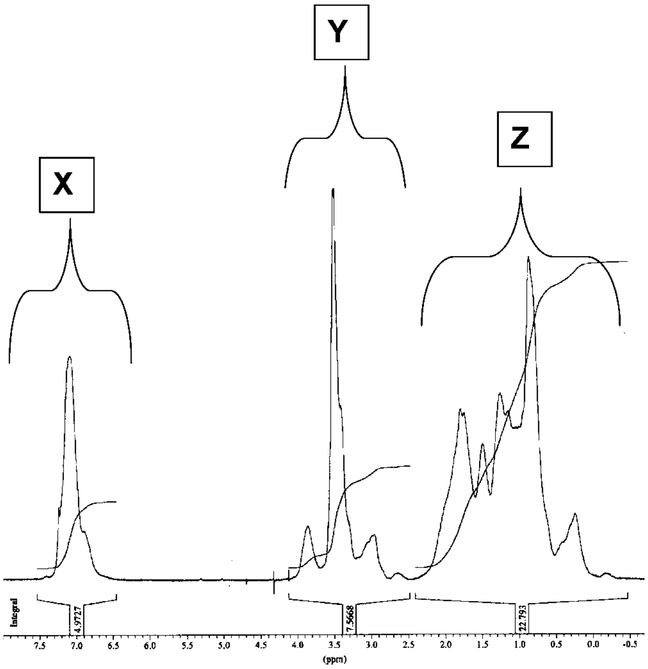

Figure 4 ^{1}H-NMR spectrum of the BA/MMA/AMS terpolymer in $CDCl_3$.

With this method, the terpolymer compositions were calculated for samples taken during kinetic studies. It was found, for all the feeds studied, that the trends in cumulative composition with respect to the conversion showed essentially no drift.[3] This behavior was also observed in the copolymerizations of AMS with MMA and BA. Because the composition was largely independent of the monomer conversion (i.e., no composition drift), the average terpolymer compositions could be calculated for the products of the reactions on the basis of the different feeds, and these results are presented in Table I. The feed compositions do not match the terpolymer compositions (the BA and MMA fractions in the terpolymer are always higher than those in the original feed), and this makes the system different from standard multicomponent polymerizations exhibiting azeotropic feed compositions. This is related to the fact that the polymerization is carried out above the ceiling temperature of AMS and to the resulting complexities in the polymerization kinetics.[11,12]

The method of analysis using ^{1}H-NMR spectra was convenient for the estimation of the terpolymer compositions for multiple samples. It is conceded that this method is not ideal because the expressions imply some correlation between the measured levels of BA and MMA, and this compounds any error normally associated with NMR analysis. In addition, spectral region Z also would have been associated with acetone, water, and occasionally hydrocarbon grease signals if the samples had not been carefully purified before NMR analysis. Despite these apparent shortcomings, the calculated relative standard deviations for the average molar fractions were generally less than 5%. The highest relative levels of uncertainty were noted in some terpolymers for BA fractions, which had F_{BA} values of about 0.1. In such cases, absolute standard deviations of 0.02 were obtained for F_{BA}, yielding relative errors of about 20% in the estimated F_{BA} value (cf. the average compositions for replicate experiments 1 and 2 in Table I).

To check the reliability of this analytical method, selected samples were also analyzed with $^{13}C\{^1H\}$-NMR. Figure 5 shows a typical $^{13}C\{^1H\}$-NMR spectrum obtained for a sample from a reaction at 140°C with a BA/MMA/AMS feed composition of 10/45/45 (w/w/w). Spectral assignments for the ^{13}C-NMR signals of the carbon centers in the terpolymers were primarily made on the basis of literature information reported for various polymers containing the three momomers.[4,5,13–17] Thus, spectral assignments for most of the carbon centers in all three monomers could be defined for the ^{13}C spectra of the terpolymer products (see Table II and Fig. 1).

The definitive assignment of some centers could not be made from the standard NMR spectra, and so JMOD (attached proton test) and HMQC were used to clarify the assignments. JMOD was used to confirm a number of assignments (see Fig. 6). In Figure 6(a), the positive signals denote CH_2 or quaternary C carbons. The negative signals define CH and CH_3 centers. The assignments for quaternary carbon centers for MMA and AMS were confirmed for multiple signals at about 45 and 42 ppm, respectively. There were small positive signals at approximately 48 ppm that may have been expected for branch points from quaternary carbons formed by H abstraction from C_α in

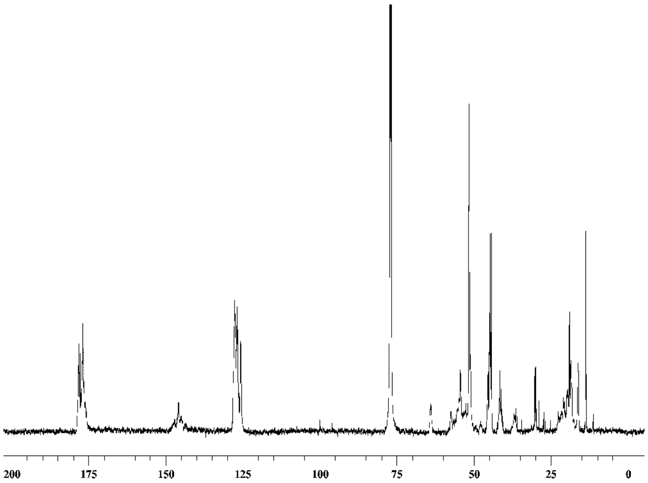

Figure 5 $^{13}C\{^1H\}$-NMR spectrum of the BA/MMA/AMS terpolymer in $CDCl_3$. The BA/MMA/AMS composition was 0.08/0.67/0.25 (molar fraction).

TABLE II
^{13}C-NMR Spectral Assignments for the BA/MMA/AMS Terpolymers

Carbon center	Chemical shift (ppm)
C1 for BA	13.6
CH_3 for MMA	16
CH_3 for AMS and MMA	17–22.2
C2 for BA	18.9–19.1
C3 for BA	29.5–31
CH_α for BA	36–40, poorly defined
C_α for AMS	41.2–42.5
C_α for MMA	44–46
$CH_{2\beta}$ for BA	48
$CH_{2\beta}$ for AMS and MMA	53–55
OCH_3 and $CH_{2\beta}$ for MMA	52
C4 for BA	63–65
C2–C6 for AMS	124–130
C1 for AMS	142–148
$C{=}O(OR)$ for BA and MMA	173–180

BA.[14] However, such species would probably have low concentrations, given that the levels of BA in the feed were low. A refined JMOD was run to definitively assign the quaternary carbons in the terpolymer: this confirmed the signals for CO_2R from BA and MMA, C1 from AMS, C_α from MMA, and C_α from AMS (see Table II for the assignments). This did not show any signal at 48 ppm, and this indicated that the signal at that chemical shift was possibly from $CH_{2\beta}$ for BA. In a sample with a higher level of BA, this signal became more significant and was also shown to not be from a quaternary carbon. This assignment to $CH_{2\beta}$ is tentative because it has been shown that the resonance for such a carbon center is very sensitive to the microenvironment of the polymer.[15]

The JMOD spectrum allowed the definitive assignment of C2 for BA (at ca. 19 ppm) from the range of signals between 17 and 22 ppm, which was mostly assigned to CH_3 carbon centers in both MMA and AMS. The signal at 16 ppm was assigned to CH_3 of MMA because it was close to that reported previously for poly(methyl methacrylate).[15] This signal was significant for the sample used to obtain the spectrum in Figure 6 because of the high MMA content in the terpolymer ($F_{MMA} = 0.64$). The signals over the range of 17–22 were not definitively assigned to CH_3 groups from either AMS or MMA because they were poorly resolved and previous studies have shown that signal positions for such centers are very sensitive to the sequence structure.[14,15,17]

HMQC provides an indication of which proton is attached to a particular carbon center by data from ^{1}H signal detection and ^{13}C-NMR spectra. Probably the most prominent signal in the HMQC spectrum (see Fig. 7) arises at the intercept of the signal at 52 ppm in the ^{13}C axis and about 4–2.5 in the ^{1}H spectrum axis, confirming the ^{13}C signal for the OCH_3 center and the range of signals expected in the ^{1}H spectrum. This experiment was also useful for confirming quaternary carbons because signals in the ^{13}C spectrum at about 42 and 45 ppm had no cross signals in the ^{1}H spectrum, confirming C_α of MMA and AMS. The postulate that the ^{1}H-NMR signal for the OCH_2 protons of BA covered a range of values was also confirmed by the fact that the signal at approximately 64 ppm in the ^{13}C spectrum cross-referenced with four well-defined regions in the ^{1}H-NMR spectrum from 4.1 to 2.5 ppm.

To perform quantitative NMR, an inverse-gated decoupling sequence was used. The integration of different diagnostic peaks was possible, but the ones chosen for the primary study were the signals at 62 ppm for BA (C4) and at 114–116 ppm for AMS (aromatic CH) and MMA (C_α). In the examined samples, these were clear signals with essentially no overlap

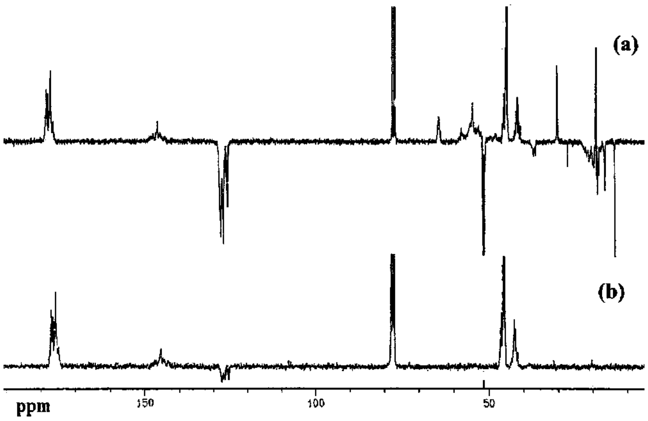

Figure 6 JMOD spectra for the 0.08/0.67/0.25 (molar fraction) BA/MMA/AMS terpolymer: (a) CH_2 and quaternary C as positive signals and CH and CH_3 as negative signals and (b) only quaternary C as positive signals.

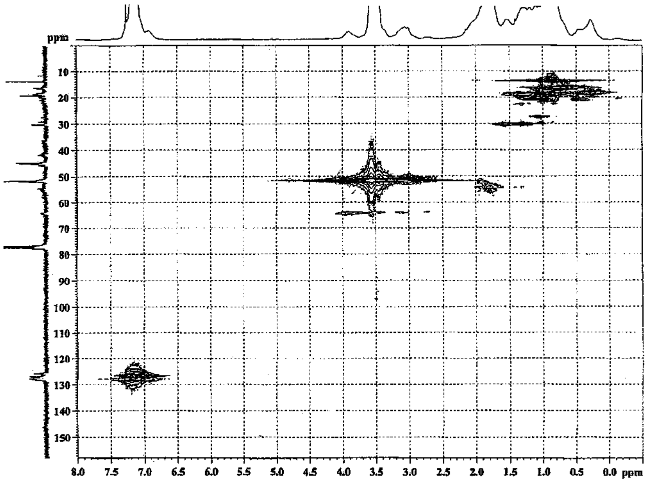

Figure 7 HMQC spectrum for the 0.08/0.67/0.25 (molar fraction) BA/MMA/AMS terpolymer.

TABLE III
Comparison of the Terpolymer Compositions Obtained from ^{1}H-NMR and ^{13}C{^{1}H}-NMR Spectra

BA/MMA/AMS feed (molar fraction)	Reaction temperature (°C)	^{1}H-NMR			^{13}C{H}-NMR		
		F_{BA}	F_{MMA}	F_{AMS}[a]	F_{BA}	F_{MMA}	F_{AMS}[a]
0.085/0.495/0.419	115	0.16	0.50	0.34	0.12	0.56	0.32
0.085/0.495/0.419	140	0.11	0.64	0.24	0.10	0.66	0.24
0.264/0.450/0.286	140	0.26	0.45	0.29	0.25	0.51	0.24

[a] Molar fraction of AMS.

with other resonances, and they had good signal-to-noise ratios. A comparison of composition analysis results from ^{1}H and ^{13}C{^{1}H} data is presented in Table III.

The determination of the terpolymer composition with ^{13}C-NMR is probably more reliable than that with ^{1}H-NMR because it offers a means of measuring each monomer independently as long as the signals have good signal-to-noise ratios. Nevertheless, the composition results obtained by the two methods were in fairly good agreement, giving some confidence that the ^{1}H-NMR method is reliable as a primary check of the terpolymer composition. The main deficiency of analysis by ^{13}C-NMR is the fact that an extended machine time (<16 h) is needed to obtain spectra that are suitable for quantitative analyses.

CONCLUSIONS

^{1}H- and ^{13}C-NMR spectroscopy has been used to characterize BA/MMA/AMS terpolymers. ^{1}H-NMR is reliable enough to provide fast screening of the terpolymer composition for large numbers of samples. In support of this, ^{13}C-NMR has largely confirmed the compositions obtained by the ^{1}H-NMR analysis. ^{13}C-NMR spectral assignments have been determined for the terpolymer and may be used to provide detailed, unambiguous characterization of the products.

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