Use of Solution-State Deuterium NMR To Investigate Cross-Linking and Branching Acrylate Polymer Systems

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ABSTRACT: Solution-state deuterium NMR experiments indicate that only about 30% of a partially deuterated allyl methacrylate (ALMA-d_5), a divinyl cross-linking agent, actually cross-linked in certain control polymers. In addition, these experiments provided insight into the mechanism of the cross-linking reaction. In a separate set of experiments on a polymer of poly(butyl acrylate) (pBA) in which 10% of BA monomers had fully deuterated side chains, the lack of additional resonances in the solution-state deuterium NMR spectrum indicated that little or no side chain branching occurs. Based on signal-to-noise calculations, an upper limit of 0.2% was calculated for the level of side chain branching. These experiments demonstrate the utility of deuterium isotopic substitution combined with solution-state deuterium NMR as a viable method of studying low-frequency events in synthetic polymer systems.

Introduction

Questions concerning cross-linking and branching in acrylic and other polymer systems have historically been difficult to address spectroscopically due to the relatively low frequency of these events. Some success has been achieved using ^{13}C NMR to analyze poly(butyl acrylate).[1] An alternate approach is to use NMR spectroscopy in combination with isotopic substitution. In NMR spectroscopy, the unique resonant frequencies of isotopes can be taken advantage of to afford a form of "spectral editing". In general, synthetic substitution of deuterium for hydrogen at sites of interest in combination with solution-state deuterium NMR can allow one to observe chemistry at these sites without overlap from the remaining protons in the system. This approach has been successfully applied to study local dynamics in proteins such as subtilisin inhibitor[2] and myoglobin[3] and in DNA.[4] Deuterium exchange has also been applied to structural studies in small molecules.[5,6] Recently, work has been done in which the rate of transesterification of the methoxy groups of methyl methacrylate with CD_3ONa in styrene/methyl methacrylate copolymers has been measured using $\{^2H\}^{13}C$ INEPT experiments.[7]

In this study, two problems were addressed. The first concerns the double incorporation efficiency of allyl methacrylate (ALMA), a divinyl monomer that is used at low levels in acrylic polymers to generate cross-links. This question is difficult to answer by proton or carbon NMR because the cross-linked ALMA resonances overlap with other acrylate monomer backbone resonances. In addition, because ALMA is used at levels of 1% or less, the ALMA resonances are very weak by comparison. Although the unreacted vinyl resonances can be detected by ^{1}H NMR, the level cannot be quantified accurately because there are no resolved resonances from the reacted species to scale them by. If, however, the polymer is synthesized with ALMA containing deuterium in the allyl positions, the deuterium NMR spectrum will reveal resolved resonances for both reacted and unreacted species.

Isotope labeling has also been used to address whether side chain branching occurs in acrylate polymers. Gel permeation chromatography (GPC) data before and after hydrolysis[8] indicate that molecular weight increases associated with branching are reversible by hydrolytic cleavage. This would seem to imply that the alkyl side chain is involved in the branching reaction. Thus, deuterated butyl acrylate, with the deuteration in the alkyl side chain, was prepared to investigate side chain abstraction.

Initially, it seems that proton NMR should reveal the presence of new, though small, resonances if side chain branching occurs. However, in proton NMR spectra of polymer samples, there are invariably unassigned resonances that can be attributed to a variety of low-level additives, impurities, and derivatives that are present in the sample. By using a polymer containing a deuterated side chain, however, all additional resonances in the deuterium NMR spectrum can be safely attributed to modifications of the BA side chain.

Experimental Section

Deuterated Monomer Preparation. To a 30-mL single-neck flask, 20.0 g of MMA and a few crystals of butylated hydroxytoluene were added. Using a short-path distillation apparatus with a nitrogen blanket, the MMA was refluxed until approximately 5 g was removed (to dry the system). Then 2.0 g of deuterated allyl alcohol (MSD Isotopes) and 15 drops of titanium tetraisopropoxide were added, and the mixture was heated back to reflux. The methanol was collected until the temperature increased back to 80 °C. A gas chromatography determination for allyl methacrylate showed 23% ALMA-d_5 in MMA.

Polymer Preparation. Polymers were prepared by standard semicontinuous emulsion polymerization methods utilizing 0.25% dodecyl benzenesulfonate as surfactant and 0.3% ammonium persulfate as initiator (all weight percent compositions are based on monomer). The monomers were fed over 2.5 h while maintaining a polymerization temperature of 85 °C. The final particle sizes were approximately 269 nm, and the final polymer content approximately 36%.

NMR Sample Preparation. For the ALMA-d_5 monomer, a solution of about 1 mg/mL was prepared in tetrahydrofuran-d_8 (MSD Isotopes). For the polymer samples containing ALMA-d_5, between 50 and 100 mg of each polymer sample was placed in a 5-mm NMR tube, and about 0.7 mL of $CDCl_3$ (MSD Isotopes) was added. The samples were allowed to swell for 4–24 h. Some samples were mixed with a copper wire to ensure good dissolution. The pBA sample containing 10% BA-d_9 was swelled in $CHCl_3$ for several days and transferred as a viscous solution to a 10-mm NMR tube. For the ^{13}C NMR spectrum, an insert containing $CDCl_3$ was used to afford locking.

NMR Spectroscopy. All data were acquired on either a Varian XL400 spectrometer equipped with a 5-mm switchable probe tunable to the deuterium frequency (61.40 MHz) or a Bruker AMX500 NMR spectrometer equipped with a 10-mm broad-band probe tuned to the deuterium frequency (76.77 MHz). On both spectrometers, the lock channel was disengaged, and data were collected in unlocked mode. For the ALMA-d_5, 1693

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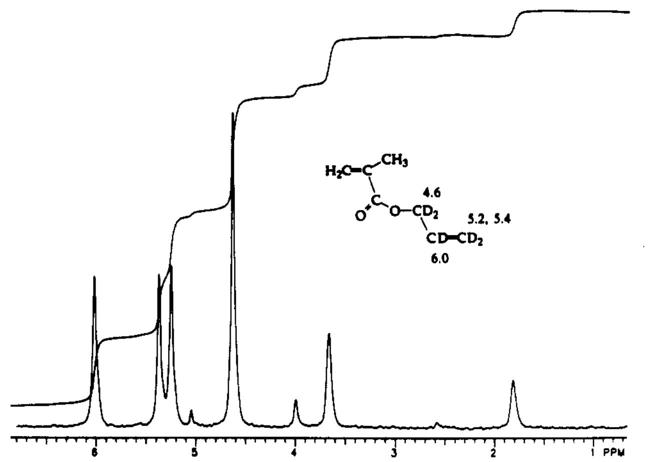

Figure 1. Solution-state deuterium NMR spectrum of ALMA-d_5 in THF and chemical shift assignments. Also observed are allyl alcohol (4.0 and 5.05 ppm) and the natural-abundance deuterium in the solvent (1.8 and 3.65 ppm).

transients were collected on the Varian XL400 using a 16K data set, a 90° pulse width (20 μs), a sweep width of 1470 Hz (at 400 MHz), and an acquisition time of 5.4 s with no additional relaxation delay. For the polymer samples, spectra were collected on both instruments, using 10000–65000 transients, 2–16K data sets, 45° pulse widths ($\sim$10 μs), sweep widths of 921–2326 Hz, and acquisition times of 1–2 s with 1-s relaxation delays. ^{13}C spectra were obtained with these same probes, appropriately tuned and were proton decoupled (WALTZ16) during the acquisition only.

Results and Discussion

Deuterium NMR of ALMA-d_5. The solution-state deuterium NMR spectrum of allyl-d_5 methacrylate (ALMA-d_5) is shown in Figure 1. This spectrum served as control and as a method of verifying the structure and purity. The chemical shifts and relative integral intensities of the major peaks are consistent with ALMA-d_5, and the assignments are shown in the figure. As expected, the chemical shifts are analogous to those observed in the ^1H NMR spectrum of ALMA.[9] Additional resonances are observed at 1.8 and 3.65 ppm, which can be assigned to the natural-abundance deuterium in the THF solvent. (The natural abundance of deuterium is 0.015%.) Other unassigned resonances are observed at 5.05, 4.0, and 2.6 ppm. The assignment of the peaks at 5.05 and 4.0 ppm to the unreacted allyl alcohol is verified by the solution-state deuterium NMR spectrum of allyl alcohol (data not shown).

Deuterium NMR Spectra of Polymer Samples Containing ALMA-d_5. The initial attempts to obtain solution-state deuterium NMR spectra of polymers containing ALMA-d_5 were made on a system with a weight percent composition of 52 BA/46.4 MMA/1.5 MAA/0.1 ALMA-d_5 (polymers A and B, respectively) as 6% solutions in tetrahydrofuran and then in $CHCl_3$. Unfortunately, only the natural-abundance deuterium resonances from the solvent and a very small hump in the vinyl region were observed (data not shown). The observation of these resonances indicates that at least some of the ALMA has not cross-linked. The lack of other resonances makes unambiguous interpretation of the data impossible, though it could be argued that the cross-linked groups have broadened to the point of being undetectable, while the vinyl portion of the non-cross-linked groups retain sufficient mobility to be observed.

Table I
Weight Percent Composition of the Polymers Analyzed in the Study

polymer	BA	MMA	MAA	ALMA	ALMA-d_5	DDM[a]
A	52	46.4	1.5		0.1	
B	52	46.4	1.5		0.1	
C	52	46	1.5		0.5	2
D	52	45.5	1.5		1	3
E	52	46	1.5	0.5		2

[a] The level of DDM (dodecyl mercaptan), a chain transfer agent, is given relative to a comonomer composition totaling 100%.

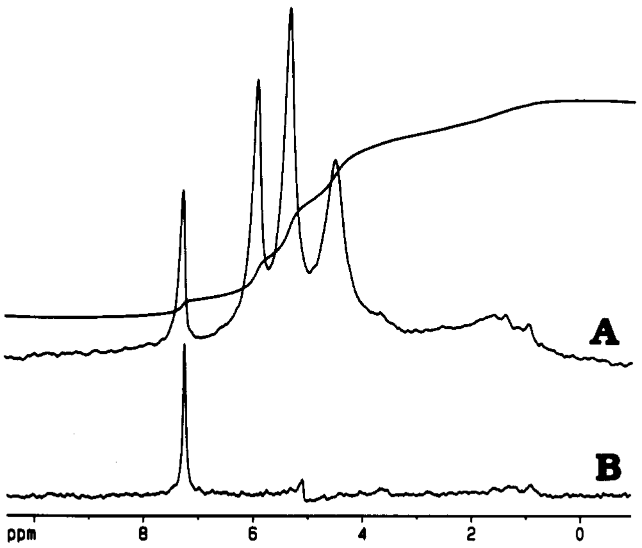

Figure 2. Solution-state deuterium NMR spectrum of polymer D in $CHCl_3$. The natural-abundance $CDCl_3$ is observed at 7.2 ppm. Residual vinyl deuterons are observed between 5.0 and 6.5 ppm, and the $-OCD_2-$ deuterons are seen at 4.5 ppm. The alkyl deuterons are observed between 0.0 and 3.0 ppm. (B) The solution-state deuterium NMR spectrum of polymer E in $CHCl_3$, which contains no deuterated ALMA. The broad resonances between 0.0 and 3.0 ppm are from the natural-abundance deuterium in the polymer.

To improve the signal-to-noise in the samples, the level of ALMA-d_5 was boosted to values of 0.5% or 1% (instead of 0.1%). Unfortunately, the associated increase in cross-linking caused reduced solubility of the polymer, which caused broadened NMR resonances. Consequently, dodecyl mercaptan (DDM) was added as a chain transfer agent to reduce the molecular weight of the polymers. (Some danger does exist, however, that the DDM could terminate the cross-linking reaction.) Two samples were prepared, polymer C and polymer D, the compositions of which are shown in Table I.

Figure 2A shows the solution-state deuterium NMR spectra of sample polymer D in $CHCl_3$. This spectrum, which is representative of both samples, shows resonances corresponding to the natural-abundance $CDCl_3$ and the unreacted ALMA-d_5. As in the spectrum of the monomer, the unreacted ALMA-d_5 is observed as three vinyl resonances (two of which are not resolved) and two equivalent $-OCD_2-$ resonances. The broadness of the resonances most likely reflects the hindered mobility of these nuclei that are now associated with the polymer chain. A new, broad peak is observed in the alkyl region (0.5–3 ppm), which must represent resonances from a reacted species.

To obtain good signal-to-noise, especially in the broad alkyl region, data were acquired for about 15 h on these samples. Because the data were acquired in the unlocked mode, the possibility existed that static field drift would cause significant broadening of the resonances. (The instrument specification for this is 15 Hz/h, and the line width of the sharper resonances is about 50 Hz.) To test this possibility, data for polymer C were acquired in 15 consecutive 1-h blocks. Comparison of the 15 spectra

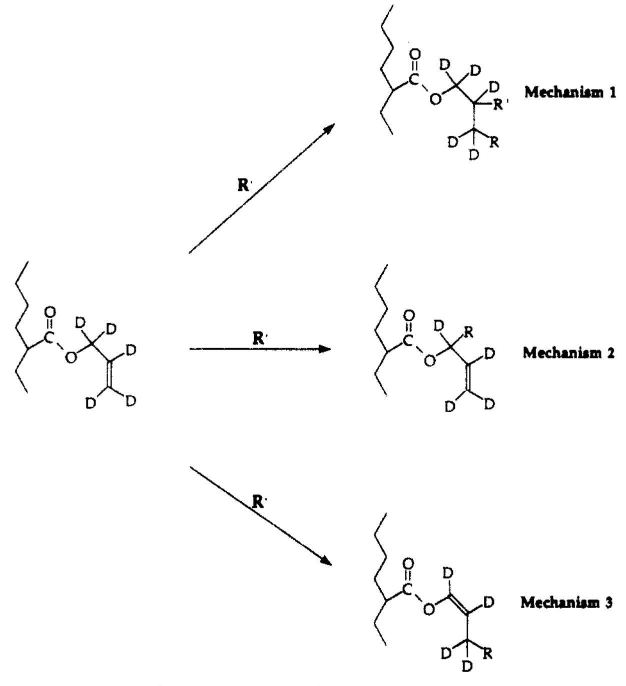

Figure 3. Possible mechanisms by which the ALMA-d_5 can react.

Table II
Calculations Based on Integration of the Deuterium NMR Spectra[a]

polymer	V_1/V_2	$(V_1 + V_2)/M$	$(A + V)/M$	$A/(A + V)$
C	1.8	1.2	1.7	0.24
D	1.6	1.3	1.9	0.33
theoretical[b]	2.0		1.5	

[a] V_1 = vinyl intensity at 5.0 ppm, V_2 = vinyl intensity at 5.8 ppm, M = methylene intensity ($-OCD_2-$), and A = alkyl intensity (0.5–2.0 ppm). V_1/V_2: should be 2.0; used as a test of integration accuracy. $(V_1 + V_2)/M$: if mechanism 2 is dominant, this ratio should be >1.5 (see text). $(A + V)/M$: should be 1.5, assuming mechanism 1 dominates. $A/(A + V)$: shows fraction of cross-linked ALMA in samples, assuming mechanism 1. [b] Assuming mechanism 1.

shows no significant shifting of the resonances (data not shown). Consequently, subsequent data were collected in single blocks only.

Determination of the Mechanism of Allyl Methacrylate Cross-Linking. The resulting spectra provide insight into the mechanism by which the cross-linking occurs and subsequently allow calculation of the percent of the ALMA-d_5 that cross-linked. The allyl group in ALMA-d_5 presumably reacts with a growing radical chain by one of the three possible routes shown in Figure 3. If mechanism 3 were dominant, new vinyl resonances should appear downfield in the spectrum, because a vinyl deuteron would now be adjacent to an oxygen. No such resonances are observed, so this pathway cannot be contributing in a significant way. If mechanism 2 prevailed, then the ratio of vinyl intensity to $-OCD_2-$ intensity (initially at 1.5) should continually increase as the fraction of reacted ALMA-d_5 increases, to a theoretical limit of 3.0. The data in Table II show that this ratio is always less than 1.5, suggesting that this mechanism is not the main reaction pathway.

If mechanism 1 were dominant, then several new resonances should be observed in the 1–2 ppm region. Clearly, some broad resonances have appeared. In addition, the ratio of the sum of the vinyl and alkyl intensity to the methylene intensity should remain at 1.5, regardless of the amount of ALMA-d_5 that has cross-linked. Table II shows that this is true within experimental error.

Determination of Cross-Linking Efficiency. Assuming that mechanism I was indeed the dominant pathway, the level of the ALMA-d_5 that has cross-linked was calculated by comparing the alkyl intensity (representing three reacted deuterons per unit) to the sum of the vinyl intensity (representing three deuterons per unreacted unit) and the alkyl intensity. These results, which are summarized in Table II, show that about 24% and 33% of the ALMA has reacted in polymer C and polymer D, respectively. Clearly, a limitation in the accuracy of the calculation results from the incomplete resolution of the resonances. To test the accuracy of integrating these broad resonances, two internal consistency checks were performed. First, the ratio of the two vinyl resonances were compared to the expected 2:1 ratio. Second, the sum of the vinyl and alkyl groups was compared to the intensity of the $-OCD_2-$, which should have a 3:2 ratio. These results are summarized in Table II.

One ambiguity in the analysis is the contribution of the natural-abundance deuterium from the polymer backbone to the broad hump in the alkyl region. If it is significant, then the values obtained for the fraction of the ALMA-d_5 that has cross-linked would be too high. Fortunately, the internal controls should also be distorted, and this does not appear to be the case. To address this question directly, a new sample (polymer E), which was identical to polymer C except for the presence of fully protonated ALMA instead of ALMA-d_5, was synthesized and analyzed. The deuterium NMR spectrum is shown in Figure 2B. The broad peak is indeed visible, but the integral intensity was measured to be about 28% of the natural-abundance $CDCl_3$ resonance. In all the samples of interest, the alkyl region integral value was at least 2 times larger than the natural-abundance $CDCl_3$ peak. Thus, since this systematic error was within the experimental error of the analysis, it was ignored.

A final question concerned whether some of the cross-linked ALMA-d_5 could become so rigid that the deuterium NMR resonances would broaden beyond the point of detectability in the spectrum. This issue was addressed by comparing the intensity of the natural-abundance $CDCl_3$ peak to the ALMA-d_5 peaks. The $CDCl_3$ concentration was approximated from the natural abundance of deuterium, and the ALMA-d_5 concentration was calculated from the weight of polymer added and the weight percent contribution of the ALMA-d_5. Though the calculations were approximate, they indicated that all of the ALMA-d_5 was accounted for.

Branching in pBA. As an independent application of selective labeling in combination with solution-state deuterium NMR, a set of experiments was performed to investigate the level of side chain branching in poly(butyl acrylate). A sample of pBA was prepared in which 10% of the BA monomers contained a fully deuterated side chain (Figure 4). The deuterium NMR spectrum of this sample, swelled in $CHCl_3$, is shown in Figure 5. The four main resonances can be assigned to the three methylene groups and the one methyl group of the BA side chain. Again, the chemical shifts are nearly identical to those observed in the proton spectrum and are summarized in the figure. A small resonance from the natural-abundance $CDCl_3$ is observed at 7.2 ppm.

The lack of other resonances indicates that no significant amount of side chain branching has occurred during synthesis. Since no new resonances are observed, only an upper limit on the amount of side chain branching can be calculated based on the signal-to-noise of the observed

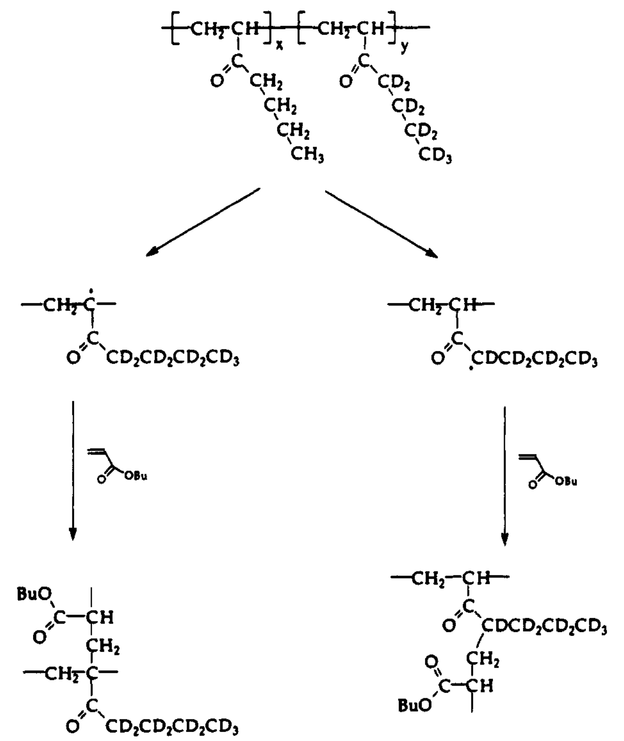

Figure 4. Structure of poly(butyl acrylate) containing 10% fully deuterated side chains, and the mechanism of side chain and backbone branching in poly(butyl acrylate).

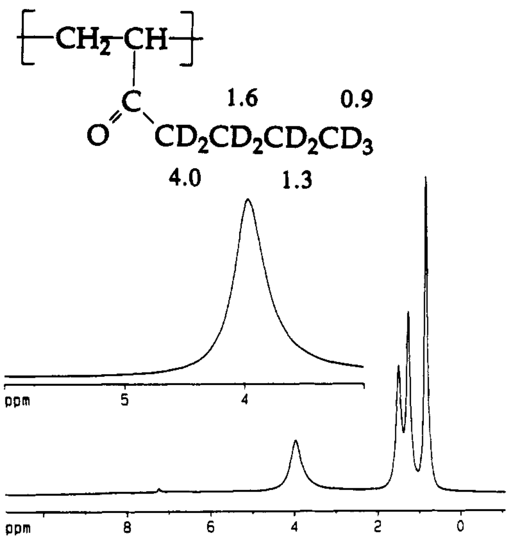

Figure 5. Solution-state deuterium NMR spectrum of poly(butyl acrylate) containing 10% butyl-d_8 acrylate. The inset shows an expansion of the region containing the $-OCD_2-$ resonance.

resonances. If branching had occurred by proton abstraction on the side chain, a methine group would result (see Figure 4). If this occurs at the $-OCD_2-$ group, which seems most likely due to the neighboring oxygen, a new resonance should appear near 5 ppm (in analogy to the proton spectrum of isopropyl acrylate[9]).

The inset in Figure 5 shows an amplification of the $-OCD_2-$ region of the spectrum. To calculate the maximum level of side chain branching, several assumptions must be made. First, it is assumed that a signal-to-noise ratio of 3:1 is necessary for a resonance to be observed. This is somewhat on the conservative side; it could be argued that a signal-to-noise of 2:1 is indeed observable. Additionally, it was assumed that the line width of the branched resonance could be up to 5 times larger than the measured line width of the $-OCD_2-$ peak, because the hindered mobility of the quadrupolar deuterium nuclei can result in increased line width. This assumption seemed reasonable and somewhat conservative, based on the observed line width of the cross-linked sites of the samples containing ALMA-d_5 described above. With these assumptions accounted for, calculations yielded an upper limit of 0.2% for the amount of side chain branching present in pBA. The true value, of course, could be considerably lower. One additional point to consider here is that because proton/deuteron abstraction may be involved in the rate-limiting step of the reaction, deuterium isotope effects may alter the chemistry of interest. A 3- to 7-fold decrease in the rate of the reaction is possible.

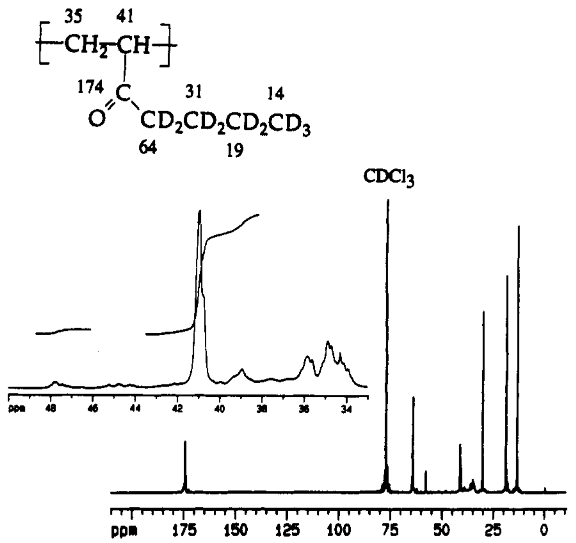

Figure 6. ^{13}C NMR spectrum of poly(butyl acrylate) containing 10% butyl-d_8 acrylate. The inset shows an expansion of the backbone region, showing the side chain branching peak at about 48 ppm, the methylene peaks at 34–36 ppm, and methine peaks at 39–41 ppm.

If little or no side chain branching were present, then branching must be occurring at the backbone. The dominant mechanism is thought to be through abstraction of the α proton, as depicted in Figure 4. The resulting quaternary carbon can be observed in the ^{13}C NMR spectrum of pBA as a broad resonance at about 48 ppm, and its quaternary nature has been identified by an APT or DEPT experiment.[1] Figure 6 shows the ^{13}C NMR spectrum of the sample containing the butyl-d_9 acrylate, and the backbone branching peak is indeed observed. The amount of backbone branching can be estimated by comparing the integral intensity of this resonance to the remaining methine intensity at about 41 ppm (inset, Figure 6); a value of 4% was obtained. Thus, the level of backbone branching is considerably higher than the amount of side chain branching.

Conclusion

Solution-state deuterium NMR offers the potential to spectroscopically address identification of components and reaction mechanisms in synthetic polymer systems. Using deuterium isotope labeling, it was determined that less than half of the ALMA used as a cross-linking agent in acrylic copolymers actually forms the intended cross-links, and the mechanism of cross-link formation was verified. Additionally, labeling a small percentage of the side chains in poly(butyl acrylate) demonstrated that side chain reactions are not the dominant mechanism of branching in these polymers. Previous work has shown the utility of this approach for biopolymers and small molecules.[2-7] Clearly, the same principle can be applied to probe interesting questions in synthetic polymers. However, the effect of replacing hydrogen with deuterium must be accounted for.

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References and Notes

(1) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Commun.* **1991**, *32*, 98.

(2) Akasaka, K.; Inoue, T.; Tamura, A.; Watari, H.; Abe, K.; Kainosho, M. *Proteins: Struct. Funct. Genet.* **1988**, *4*, 131.

(3) Johnson, R. D.; La Mar, G. N.; Smith, K. M.; Parish, D. W.; Langry, K. C. *J. Am. Chem. Soc.* **1989**, *111*, 481.

(4) Bendel, P.; Murphy-Boesch, J.; James, T. L. *Biochim. Biophys. Acta* **1983**, *759*, 205.

(5) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Mendeleev Commun.* **1991**, *1*, 24.

(6) Pitner, T. P.; Edwards, W. B., III; Bassfield, R. L.; Whidby, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 246.

(7) Tokles, M.; Hensley, D. R.; Hatvany, G. S.; Harwood, H. J.; Rinaldi, P. L., manuscript in preparation.

(8) A polybutyl acrylate ($M_w = 2.1 \times 10^6$ by THF GPC, $M_w/M_n = 36$) was subjected to alkaline hydrolysis (potassium hydroxide in ethanol/water solution, 150 °C for 3 days) to yield a poly(acrylic acid) ($M_w = 1.6 \times 10^5$ by aqueous GPC, $M_w/M_n = 5.5$).

(9) Rouchert, C. J. *The Aldrich Library of NMR Spectra: Edition II*; Aldrich Chemical Co.: Milwaukee, 1983.