Evaluation of Reactions of a Dilute Cross-Linker Using Solution Nuclear Magnetic Resonance Spectroscopy with Isotopically Labeled Cross-Linkers

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ABSTRACT: Cross-linked poly(methyl methacrylate) (PMMA) was synthesized to high conversion with 0.02−0.5 wt % ^{13}C- or ^{2}H-labeled ethylene glycol dimethacrylate (EGDMA). Samples were analyzed with a variety of NMR techniques to examine different cross-linker reaction products (or architectures), i.e., pendant EGDMA methacrylates, cyclized EGDMA, and cross-linked EGDMA. Solid-state ^{13}C NMR spectroscopy was not applicable because poor peak resolution masked the cross-linker architecture peaks. Solid-state ^{2}H NMR spectroscopy of deuterium-labeled EGDMA was also not useful because the deuterium line shape was convoluted by signals from natural abundance deuterium in the polymer. Solution ^{13}C NMR analysis of solvent swollen polymers (gel-state ^{13}C NMR spectroscopy) produced well-resolved spectra of copolymers containing less than 0.5 wt % ^{13}C-labeled EGDMA. These spectra confirm that significant amounts of EGDMA were singly reacted, resulting in large numbers of pendant methacrylate units. Non-cross-linked and completely soluble model PMMA copolymers containing 0.1 wt % ^{13}C-labeled pendant EGDMA methacrylates units (incorporated in a postpolymerization reaction) were used to identify the ^{13}C NMR signals characteristic of EGDMA pendant units. Signals from the stereochemical triads (syndio- and heterotactic) were identified, but specific peaks for nine-membered cyclic EGDMA units were not observed. The detection limit of gel-state ^{13}C NMR analysis on these MMA/EGDMA copolymers was as low as 0.02 wt % ^{13}C-labeled EGDMA, which demonstrates the utility of this approach for characterizing lightly cross-linked polymers.

Introduction

Cross-linked PMMA is used in a variety of commercial materials such as membranes,[1] dental fillings,[2] dentures,[2] latex coatings,[3] computer-to-sensor data transmission links,[4] composites,[5] optically clear sheeting, limb prostheses, bathtubs, bathroom sinks, and shower surrounds where cross-linking plays a vital role in both processing and ultimate properties. A better understanding of cross-linking effects on polymerization kinetics and cross-linker architectures would provide insight into optimizing the industrial processes and maximizing performance.

Several researchers since the 1970s have investigated the polymerization kinetics of cross-linked PMMA.[6−12] For example, Haung and co-workers[12] used DSC to determine monomer conversion, rate of polymerization, reaction rate constants, and reaction orders during the copolymerization of EGDMA and 2-hydroxylethyl methacrylate (HEMA). This detailed research revealed trends in reaction parameters that were dependent on both EGDMA concentration and temperature. However, the architectures of incorporated EGDMA and their combined effects on the kinetics of the polymerization were not determined.

Landin and Macosko[6] used ^{1}H NMR spectroscopy to observe pendant methacrylates in soluble samples of poly (MMA-*co*-EGDMA). They constructed a series of pendant conversion vs monomer conversion plots for low conversion polymerizations of PMMA (<33.3%) containing 0.57−1.7 mol % EGDMA. From the positive *y*-intercept on these graphs they concluded that the extrapolated loss of pendant methacrylates at the onset of polymerization was a result of primary EGDMA cyclization (3−4 mol %). Primary cyclization was explained as the formation of 9- or 10-membered EGDMA rings generated before reaction with monofunctional monomer, similar to deliberately obtained ring structures in linear polymers via cyclopolymerization.[13] The apparent content of primary cyclization product was unaffected by EGDMA concentration but increased with dilution. These researchers also reported that the total conversion of pendant methacrylates increased with an increase in EGDMA concentration and dilution of reactants and that the reactivity of pendant methacrylates was half that of monomeric methacrylates. A kinetic model was constructed to estimate the number of cyclics, cross-links, and pendant methacrylates at selected monomer conversions less than 30%; no high conversion samples were analyzed.

This research provided an excellent understanding of the fate of EGDMA in *soluble* PMMA copolymers at *low* conversion. However, the results will not accurately represent the EGDMA architecture in MMA/EGDMA

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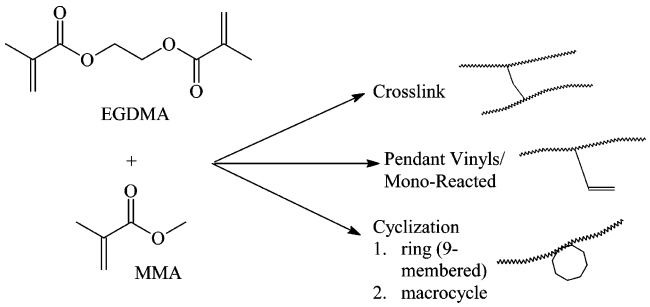

Figure 1. Possible EGDMA architectures in MMA/EGDMA copolymers.

copolymerizations where high monomer conversion occurs. This is due to inherent limitations in analysis of cross-linked and insoluble polymers, even when polymerizations are stopped at conversions well below those used in industry. Low conversion PMMA copolymers do not experience the Trommsdorff effect (autoacceleration) or significant changes in monomer concentration, viscosity, and temperature, which will affect the individual incorporation amounts for products from various competing pathways of the propagating radicals. As a result, much of the research in this area has been based on soluble polymers with results extrapolated to insoluble cross-linked systems without taking into account the large changes in rates, molecular weights, and cross-link densities that occur in the latter stages of reaction.

The overall goal of our work in this area is to explore and develop methods for analyzing insoluble cross-linked polymers to elucidate how changes in reaction conditions *during* polymerization affect molecular composition and ultimate properties. This paper is aimed at identifying dimethacrylates comonomer architectures, i.e., pendant methacrylates, cyclized and cross-linked (Figure 1). We targeted PMMA copolymerizations with 0.02−0.5 wt % EGDMA carried to 100% conversion. Possible NMR techniques for characterization of such systems include solid-state ^{13}C NMR, solid-state ^{2}H NMR, and high-resolution ^{13}C NMR spectroscopy performed on solvent swollen samples.

This paper will first briefly discuss problems with traditional solid-state ^{13}C NMR and solid-state ^{2}H NMR methods for such analyses and then detail successful use of gel-state ^{13}C NMR spectroscopy for identifying EGDMA comonomer architectures. With the last method, the EGDMA peaks were identified using high-resolution (solution) ^{13}C NMR analysis of solvent swelled copolymers but only after overcoming considerable difficulties with sample preparation and related problems with NMR shimming. The majority of this paper will discuss the synthesis of various labeled monomers, labeled polymers, NMR sample preparation, and the results of gel-state ^{13}C NMR analysis.

Results and Discussion

The three main architectures of dimethacrylates, such as EGDMA, generated during copolymerization with monofunctional monomers, such as MMA, are cross-linked (incorporation of a single dimethacrylate monomer into two different PMMA chains), pendant methacrylates (one end of a dimethacrylate monomer incorporated into a PMMA chain and the other end unincorporated), and cyclized (incorporation of both ends of a dimethacrylate unit into the same PMMA chain as adjacent units) (Figure 1). Identification of these three

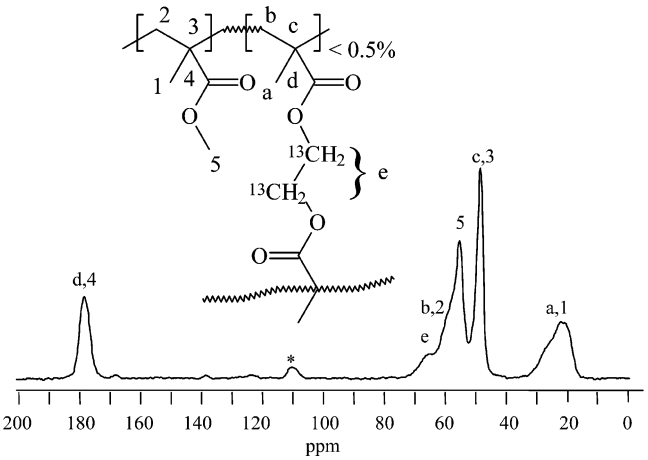

Figure 2. Solid-state ^{13}C CP/MAS NMR of poly(MMA-*co*-1,2-^{13}C-EGDMA) with 0.1 wt % EGDMA. ∗indicates spinning sidebands.

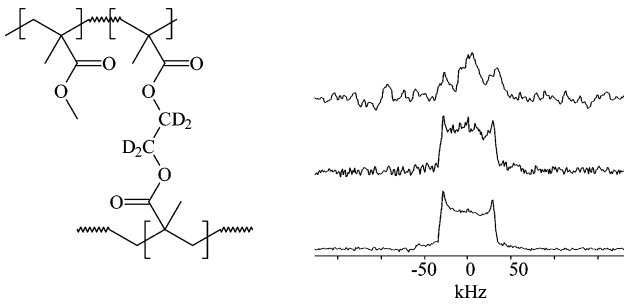

Figure 3. Solid-state ^{2}H NMR spectra of PMMA containing 0.1 wt % (top), 1.0 wt % (middle), and 5.0 wt % (bottom) 1,1,2,2-^{2}H-EGDMA.

architectures in EGDMA/MMA copolymers was attempted first by solid-state ^{13}C NMR spectroscopy, then solid-state ^{2}H NMR spectroscopy, and finally high-resolution gel-state ^{13}C NMR spectroscopy. Observation of EGDMA units at concentrations as low as 0.02−0.5 wt % and differentiation of cross-linked and pendant EGDMA NMR peaks was only achieved using solution ^{13}C NMR spectroscopy on solvent swollen copolymers.

Solid-State ^{13}C NMR and Solid-State ^{2}H NMR Analysis. Initially, traditional solid-state NMR characterization techniques of polymers (^{13}C and ^{2}H NMR spectroscopy) were used to analyze PMMA copolymers containing 0.02−0.5 wt % ^{13}C- or ^{2}H-labeled EGDMA. Solid-state ^{13}C CP/MAS and HPD NMR spectroscopy are extremely powerful techniques because of the flexibility of the pulse programs and the plethora of polymers that have been investigated. However, EGDMA ester methylene signals were convoluted by polymer backbone carbon peaks at concentrations less than 5 wt % ^{13}C-labeled EGDMA (Figure 2), which is at least an order of magnitude greater than the EGDMA concentrations of interest.

Solid-state ^{2}H NMR analysis of $^{2}H_4$-labeled EGDMA in PMMA resulted in a static ^{2}H line shape (Figure 3) with a splitting of 110 kHz between 90° asymptotes. However, at concentrations below 1 wt % the amount of naturally abundant ^{2}H in the PMMA chain was on the same order as the amount of labeled EDGMA. Thus, the signal from these deuterons (a narrow peak ∼35 kHz in width and a 125 kHz wide-line line shape) began overlapping with the EDGMA line shape. In addition, this technique was time-consuming; averaging between 4 and 8 days and 60−80 000 scans per sample.

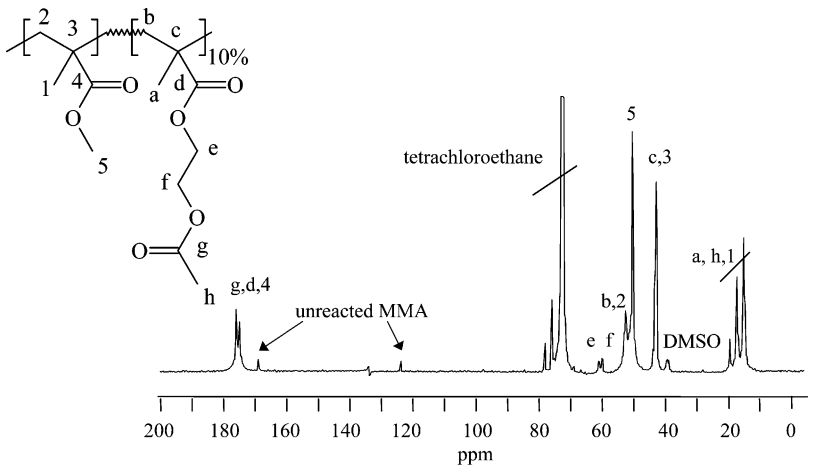

Figure 4. Solution ^{13}C NMR spectrum of poly(MMA-*co*-AE-HEMA).

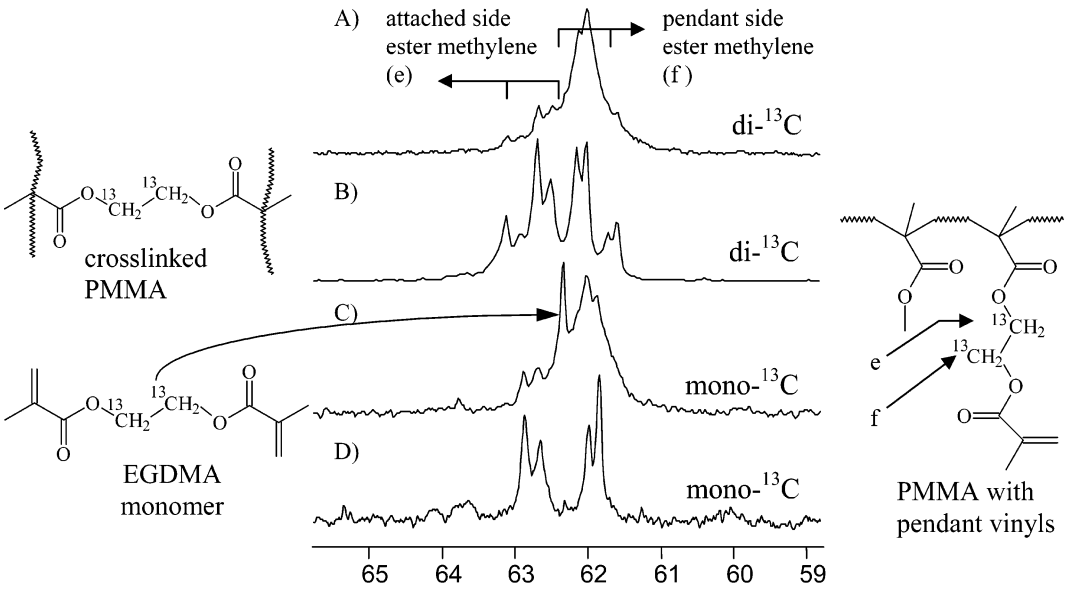

Figure 5. Gel-state ^{13}C NMR spectra of ^{13}C-labeled poly(MMA-*co*-EGDMA) (A, C) and ^{13}C-labeled pendant EGDMA methacrylate model copolymers (B, D).

An alternative method was sought that would provide a faster and more sensitive analysis of PMMA copolymers containing extremely low EGDMA content (0.02−0.5 wt %). This technique not only had to be sensitive enough to observe extremely low EGDMA concentrations but produce well-resolved NMR signals in order to distinguish between the different EGDMA architectures (cyclized, cross-linked, and pendant methacrylate). Thus, we examined the potential of solvent-swollen NMR analysis.

Gel-State ^{13}C NMR Analysis. Solution ^{13}C NMR spectra of solvent swollen cross-linked copolymers could be acquired within a reasonable period of time (∼12 h). In addition, EGDMA ester methylene signals (∼62 ppm) were sufficiently resolved to distinguish different EGDMA-based structures. Assigning the splitting of the ester peaks to specific architectures therefore became the focus of this study. The assignments were obtained through a series of model copolymers containing only pendant methacrylate architecture and isotopically labeled EGDMA.

PMMA copolymers containing pendant EGDMA methacrylates was first modeled using an analogue copolymer based on the acetate ester of HEMA, poly(MMA-*co*-AE-HEMA) (Figure 4). Peaks labeled e and f were assigned to the ester methylene units on the attached side and pendant side, respectively, of incorporated AE-HEMA. This model copolymer lead to the first inclination that not only could EGDMA cross-linker be observed by solution ^{13}C NMR spectroscopy but also the attached methacrylate peaks could be distinguishable from pendant methacrylates peaks (Figure 4, peaks e and f).

The poly(MMA-*co*-AE-HEMA) solution ^{13}C NMR spectra indicated the possibility of studying the nature of the cross-link sites provided the signal of those positions could be increased. Therefore, singly and doubly ^{13}C-labeled EDGMA was used to synthesize poly(MMA-*co*-EGDMA), including a model system with pendant vinyl groups. The use of labeled material permitted observation of peaks at levels of EGDMA incorporation approaching 0.02 wt %.

Figure 5 summarizes the NMR results for PMMA polymers cross-linked with singly and doubly ^{13}C-labeled EDGMA. The spectrum of the model copolymer synthesized with mono-^{13}C-labeled EDGMA (Figure 5D) show two doublets centered at 62.4 ppm. Using data from poly(MMA-*co*-AE-HEMA) spectra as well as previously acquired spectra for substituted MMA/HEMA systems[14] as a guide, the upfield doublet is assigned to

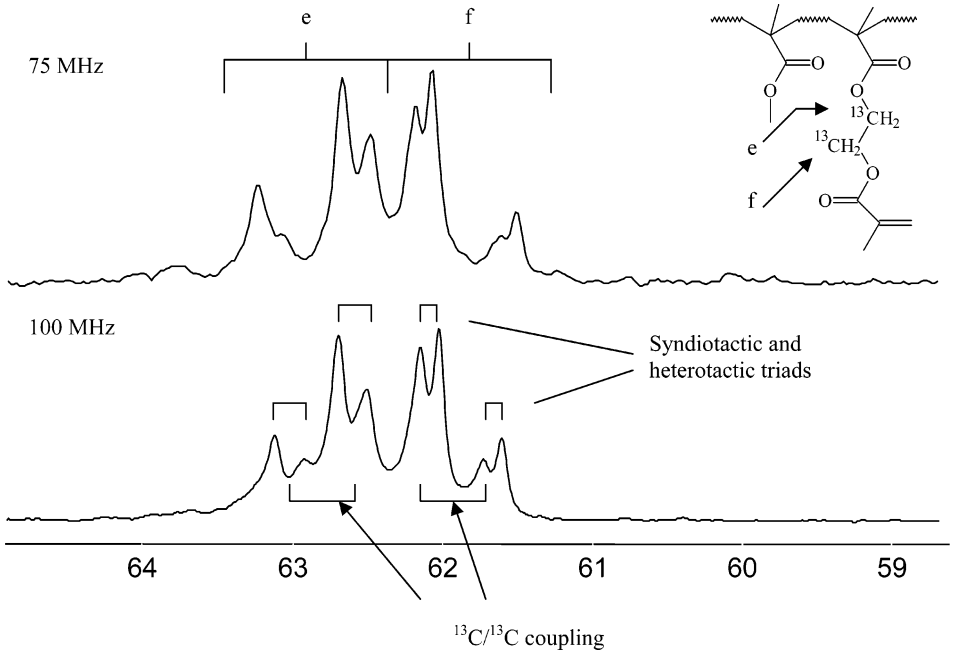

Figure 6. Ester region of a model PMMA copolymer containing di-^{13}C-labeled pendant EGDMA methacrylates, acquired at 75 and 100 MHz for carbon.

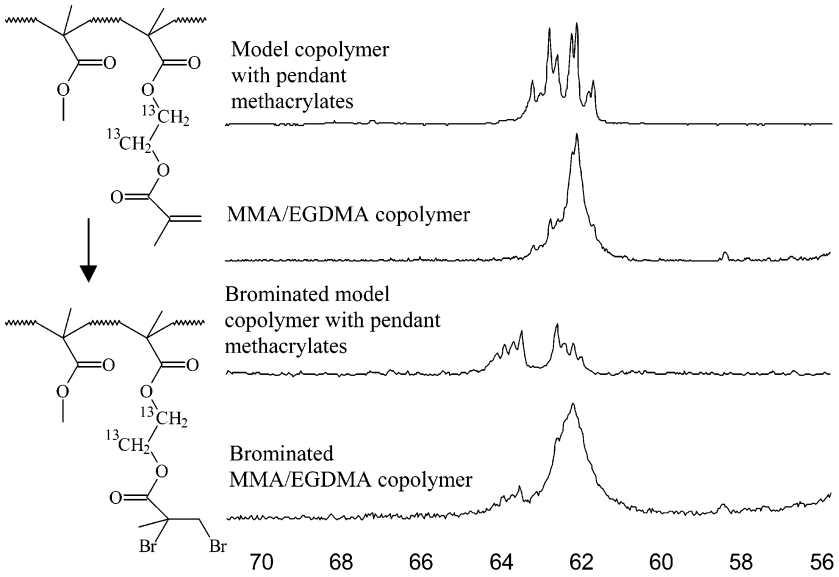

Figure 7. Solution ^{13}C NMR spectra of poly(MMA-*co*-1,2-^{13}C-EGDMA$_p$) and poly(MMA-*co*-1,2-^{13}C-EGDMA) before and after bromination (0.1 wt % labeled EGDMA).

the ester methylene unit closest to the unreacted vinyl group. The downfield doublet is associated with sites closest to the polymer backbone. The peaks are split into doublets due to tacticity. The splitting pattern for the pendant doublet is consistent with a heterotactic structure (*mr*), while the downfield peak exhibits a syndiotactic pattern (*rr*), with a greater degree of splitting due to its proximity to the polymer chain.[15] The spectrum of the model copolymer with doubly labeled material (Figure 5D) exhibits a set of eight overlapping peaks due to the addition of $^{13}C-^{13}C$ coupling ($J \sim 50$ Hz). Spectra acquired at 75 and 100 MHz for carbon confirm this explanation (Figure 6).

Figure 5A,C shows the spectra for PMMA cross-linked with singly and doubly labeled EDGMA. Both clearly show the presence of fully reacted EDGMA (singlet at ~62 ppm) as well a relatively large percentage of EDGMA units with pendant methacrylates. Here it important to note that the data are not completely quantiatitve. No attempts were made to remove NOE effects, which enhances sites with differing degrees of mobility unequally. In addition, fully reacted EDGMA units may be in regions of sufficient rigidity as to broaden the signal to the point of undetectability. However, it is believed that sufficient amount of local mobility is present in the gel to permit these results to be interpeted semiquantitatively.

At this point key questions concerning the assignments of the ester methylenes e and f as well as the presence of cyclic EDGMA structures need to be addressed. To confirm our previous spectral assignments, the pendant methacrylates were brominated (Figure 7). Referring to published tables of ^{13}C NMR shifts,[16] bromine subsitution in delocalized systems such as $CH_2Br-C_6H_5$ will move resonances for sites β, γ, and δ from the site of halogenation approxiamately 1.2−0.7

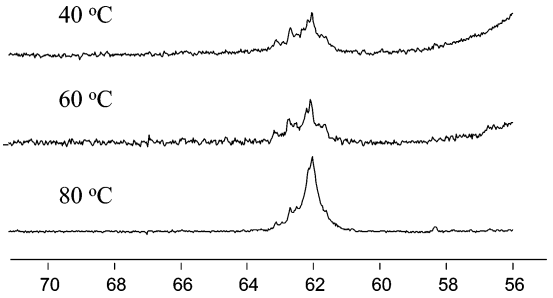

Figure 8. ^{13}C NMR gel-state spectra of EDGMA cross-linked PMMA polymerized at 40, 60, and 80 °C.

ppm downfield. In contrast, for aliphatic systems sites that are two or more bonds removed from the bromine position tend to shift upfield by approximately 1 ppm. Using these trends as a guide, it is expected that the pendant $-CH_2O-$ position will be significantly shifted downfield, while the other site will be moved upfield. The spectrum of the bominated model system in Figure 7 confirms these predictions. The pendant site shifted ~2 ppm downfield, and the site adjacent to the main chain moved upfield by ~1 ppm, creating a pair of quartet structures separated by 1 ppm. Bromination of the MMA/EGDMA copolymer also yields a similar quartet pattern characteristic of pendant methacrylate groups, with the upfield peaks obscured by the cross-linking EGDMA moeity. This again clearly shows that a significant number of EDGMA units are not involved in cross-linking.

It was hoped that bromination would shift unreacted EGDMA peaks enough to reveal the presence of any possible cyclic structures. However, no additional peaks were observed. In addition, all attempts to synthesize cyclic EGDMA model compounds by varying EGDMA concentrations, solvent, temperature, or reaction time failed. These facts strongly suggest that cyclic units are not present. Nevertheless, the only definite conclusions are that pendant and cross-linked EGDMA units are observed for EDGMA cross-linked PMMA, with cyclic structures either absent or obscured by cross-link and pendant peaks.

Temperature Effects in Polymerizations and Gel-State ^{13}C NMR Analysis. Polymerizations of 0.1 wt % 1,2-^{13}C-EGDMA and MMA carried out at various temperatures produced cross-linked networks with differing degrees of swellability. Specifically, samples prepared at 40 °C swelled much less than those obtained at 80 °C. This indicates a higher cross-link density and cross-linking efficiency for EGDMA at lower temperatures. The MMA monomer conversion also decreased at lower polymerization temperatures, consistent with observations of Huang and co-workers,[12] who used DSC and FTIR to follow monomer conversion isothermally and nonisothermally. They reported that for EGDMA and HEMA copolymerizations lower monomer conversion was observed at lower temperatures.

Figure 8 shows the ^{13}C NMR spectra of the labeled systems described above. Differences in these spectra may be due to changes in NOE enhancements because of lower mobility. However, the most probable explanation is that the local mobility has been decreased to the point where broadening mechanisms such as residual dipolar coupling become significant. This is particularly true for systems with low solvent uptake. This prohibited semiquantitative comparison of the data.

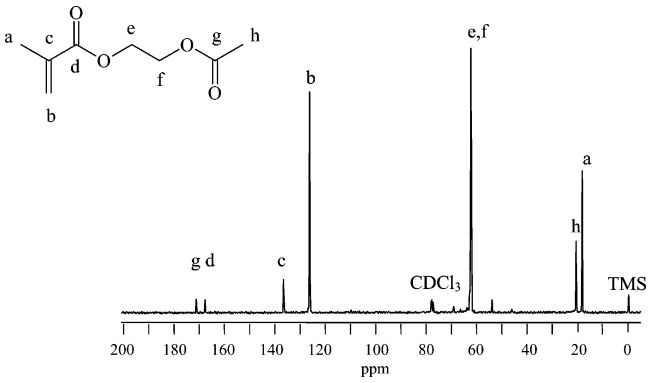

Figure 9. Solution ^{13}C NMR spectrum of the acetyl ester of HEMA.

Conclusions

Gel-state ^{13}C NMR analysis was performed on polymers containing between 0.02 and 0.5 wt % ^{13}C-labeled cross-linker, indicating a range of applications that should be general to other vinyl systems. Cross-linker concentrations higher than 0.5 wt % produced polymers that did not swell sufficiently to resolve cross-linker NMR signals in the system described here. Use of ^{13}C-labeled cross-linkers with gel-state ^{13}C NMR analysis of MMA/EGDMA copolymers confirmed significant amounts of mono-reacted EGDMA. Peaks for pendant EGDMA methacrylates and cross-linked EGDMA were assigned and included splitting caused by tacticity in the backbone. These assignments were based on model copolymers synthesized specifically to mimic systems with pendant methacrylate units. There was no evidence of cyclic EGDMA units because their concentration was too low to detect or their peaks were obscured. Finally, these results clearly demonstrate the capability of the gel-state NMR method to see very small amounts of appropriately labeled segments in cross-linking groups that are normally not observable using traditional solid-state and solution methods.

Experimental Section

A. Synthesis. All reagents were used as received from Aldrich Chemical Co. (Milwaukee, WI) unless specified otherwise. ^{13}C- and ^{2}H-labeled ethylene glycol samples were purchased from Cambridge Isotope Laboratory (Andover, MA) and used as received.

Monomers. All isotopically labeled comonomers were synthesized using a similar procedure. Only the synthesis of di-^{13}C-labeled HEMA (1,2-^{13}C-HEMA) and di-^{13}C-labeled EGDMA (1,2-^{13}C-EGDMA) comonomers will be discussed in detail. All other labeled comonomer synthesis descriptions will contain only information pertinent to the synthesis of those moieties.

Synthesis of the Acetate Ester of 2-Hydroxyethyl Methacrylate (AE-HEMA). A 100 mL round-bottom flask was charged with HEMA (2.01 g, 0.015 mol), triethylamine (2.01 g, 0.02 mol), and 40 mL of methylene chloride. The flask was capped with an addition funnel and cooled in an ice bath for 20 min. Through the addition funnel, acetyl chloride (2.02 g, 0.02 mol) was added dropwise over 45 min to the stirring solution. The reaction proceeded in an ice bath for 2 h and then at room temperature for an additional 2 h. The reaction mixture was washed with three 25 mL portions of 0.1 M NaOH. The water layers were combined and washed with three 25 mL portions of ethyl ether. The ether layers and the organic layer were combined and solvents were removed under high vacuum at 30 °C, leaving a clear liquid (1.98 g, 0.011 mol, 58%); 100% purity by GC. The ^{13}C NMR spectrum (TMS, $CDCl_3$) is provided in Figure 9.

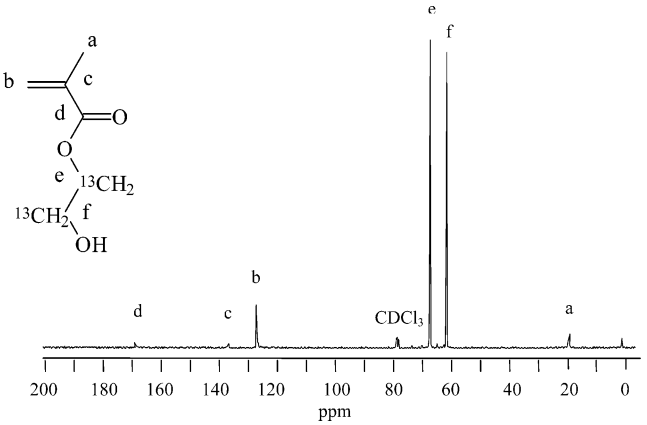

Figure 10. Solution ^{13}C NMR spectra of 1,2-^{13}C-HEMA.

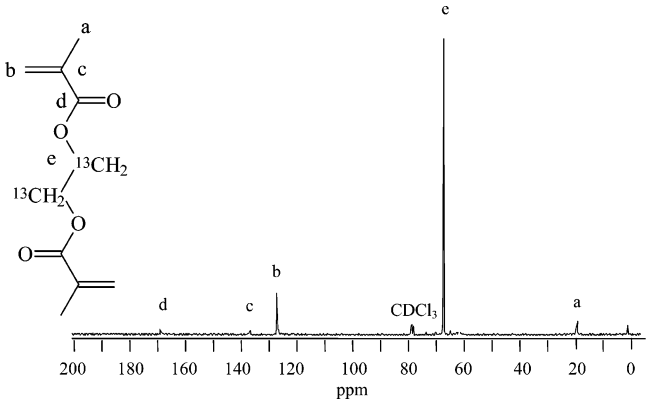

Figure 11. Solution ^{13}C NMR spectra of 1,2-^{13}C-EGDMA.

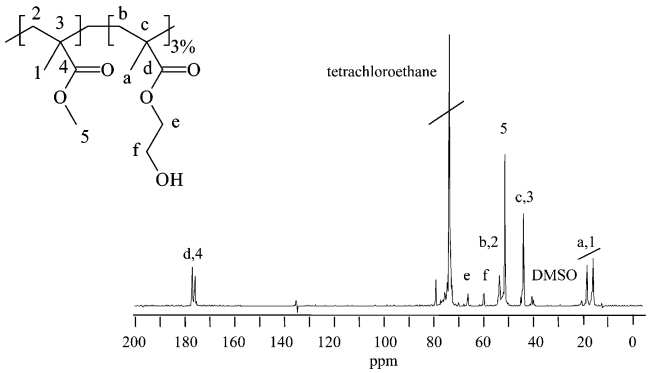

Figure 12. Solution ^{13}C NMR spectra of poly(MMA-*co*-HEMA) containing 3 wt % HEMA.

Synthesis of Di-^{13}C-Labeled HEMA (1,2-^{13}C-HEMA). Methacryloyl chloride (1.9 g, 18 mmol) and 40 mL of methylene chloride were combined in a 150 mL round-bottom flask fitted with an addition funnel and magnetic stir bar. The flask was placed in an ice bath for 25 min, and then a cooled solution of 1,2-^{13}C-ethylene glycol (1.0 g, 16 mmol), triethylamine (1.8 g, 18 mmol), and 25 mL of methylene chloride were dropwise added through the addition funnel over 30 min. The ice bath was then removed, and the reaction proceeded at room temperature for an additional hour. The reaction mixture was combined with 200 mL of methylene chloride and washed with 50 mL of 0.1 N HCl. Methylene chloride was removed by rotary evaporator, and the residue was dissolved in 200 mL of H_2O and washed with four 50 mL portions of heptane, thus removing all EGDMA formed during acylation. The aqueous layer was extracted with seven 50 mL portions of methylene chloride, which separated HEMA from any residual ethylene glycol. The combined methylene chloride washings were dried over $MgSO_4$, and the solvent was removed by rotary evaporation to give a clear liquid (0.7 g, 34%); 100% purity by GC. The ^{13}C NMR spectrum (TMS, $CDCl_3$) of the ester methylene region is provided in Figure 10.

Synthesis of Di-^{13}C-Labeled EGDMA (1,2-^{13}C-EGDMA). Refer to the synthesis of di-^{13}C-labeled HEMA (1,2-^{13}C-HEMA). A 150 mL round-bottom flask was charged with methacryloyl chloride (3.7 g, 35 mmol) and 40 mL of methylene chloride. A chilled solution of 1,2-^{13}C-ethylene glycol (1.0 g, 16 mmol), triethylamine (3.5 g, 35 mmol), and 25 mL of methylene chloride was dropwise added, and the reaction proceeded for an hour at room temperature. After washing with dilute acid, the methylene chloride layer was removed with a rotary evaporator, leaving crude solid product which was dissolved in 150 mL of diethyl ether and washed with 15 25 mL portions of a 0.1 N NaOH(aq), 25 mL of H_2O, and saturated KCl(aq). The ether layer was dried over $MgSO_4$, and diethyl ether was removed with a rotary evaporator to give a clear liquid (2.0 g, 58%); 98% purity by GC. The ^{13}C NMR spectrum (TMS, $CDCl_3$) is provided in Figure 11.

Synthesis of Mono-^{13}C-Labeled EGDMA (1-^{13}C-EGDMA). Refer to the synthesis of di-^{13}C-labeled EGDMA (1,2-^{13}C-EGDMA). The product, 1-^{13}C-EGDMA, was a clear liquid (2.1 g, 65%); 97% purity by GC.

Synthesis of $^2H_4$-Labeled EGDMA (1,1,2,2-^2H-EGDMA). Refer to the synthesis of di-^{13}C-labeled EGDMA (1,2-^{13}C-EGDMA). 1,1,2,2-^2H-ethylene glycol was used instead of ^{13}C-labeled ethylene glycol. The product, 1,1,2,2-^2H-EGDMA, was a clear liquid (2.3 g, 65%); 98% purity by GC.

Copolymers. All PMMA copolymers were polymerized free radically in bulk using thermal initiation, as described in the procedure for the synthesis of poly(MMA-*co*-AE-HEMA). The poly(MMA-*co*-AE-HEMA) procedure will be discussed in detail, and all polymerization descriptions will contain only information pertinent to the synthesis of that copolymer.

Synthesis of Poly(MMA-co-AE-HEMA). A large Pyrex test tube was charged with AE-HEMA (0.5 g, 0.003 mol), MMA (5.01 g, 0.05 mol), and 0.5 wt % AIBN. The reaction vessel was capped with a septum and purged under nitrogen for 30 min. The polymerization proceeded at 65 °C overnight in a nitrogen atmosphere. The transparent copolymer plug was dissolved in chloroform, reprecipitated into methanol, and dried overnight under high vacuum to give a hard white solid (4.5 g, 81%); 10% AE-HEMA incorporated by ^1H NMR. The ^{13}C NMR spectrum (tetrachloroethane, DMSO-d_6 inset) is provided in Figure 4.

Synthesis of Poly(MMA-co-HEMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). EGDMA impurity was removed from commercial HEMA by extracting a HEMA/water solution with heptane. The polymerization was conducted in a test tube charged with purified HEMA (0.15 g, 1.2 mmol), MMA (5.01 g, 0.05 mol), and 0.5 wt % AIBN. The product was a hard white solid (4.4 g, 93%); 3 wt % HEMA by ^1H NMR. The ^{13}C NMR spectrum (tetrachloroethane, DMSO-d_6 inset) is provided in Figure 12.

Synthesis of a Model Copolymer Containing Pendant EGDMA Methacrylates: Poly(MMA-co-EGDMA$_p$). Reactant concentrations were based on the stoichiometric content of HEMA in a copolymer. For example, a 25 mL round-bottom flask was charged with poly(MMA-*co*-HEMA) (0.5 g, 3 wt % HEMA) and a 3 wt % excess of triethylamine at a 25 wt % concentration in chloroform. The round-bottom flask was capped with an addition funnel, and the reaction mixture was stirred in an ice bath for 20 min under nitrogen. A 10 wt % excess of methacryloyl chloride (which had been distilled twice under vacuum before use in chloroform) was added dropwise over 30 min, and the reaction was allowed to proceed for 6 h in an ice bath. The copolymer was precipitated in a mixture of methanol and water, reprecipitated into methanol from chloroform, and then dried overnight under high vacuum at room temperature. The product was a hard white solid (0.5 g, 95%); 100% conversion of pendant HEMA alcohols to methacrylate esters (3 wt % pendant methacrylate units) by ^1H NMR.

Synthesis of Poly(MMA-co-1,2-^{13}C-HEMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). The product was a hard white solid (1.5 g, 95%); 0.1 wt % 1,2-^{13}C-HEMA by ^1H NMR.

Synthesis of a Di-^{13}C-Labeled Model Copolymer Containing Pendant EGDMA Methacrylates: Poly(MMA-co-1,2-^{13}C-EGDMA$_p$). Refer to the synthesis of poly(MMA-*co*-EGDMA$_p$) from poly(MMA-*co*-HEMA). HEMA pendent alcohol groups in poly(MMA-*co*-1,2-^{13}C-HEMA) were converted to pendant EGDMA methacrylates by postpolymerization reaction with methacryloyl chloride. The product was a hard white solid (0.7 g, 90%); 100% conversion of alcohols to methacrylate ester groups by ^{1}H NMR. The ^{13}C NMR spectrum (TMS, $CDCl_3$) of ester methylene region is provided in Figure 5b.

Synthesis of Poly(MMA-co-1-^{13}C-HEMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). The product was a hard white solid (1.8 g, 92%); 0.1 wt % 1-^{13}C-HEMA by ^{1}H NMR.

Synthesis of a Mono-^{13}C-Labeled Model Copolymer Containing Pendant EGDMA Methacrylates: Poly(MMA-co-1-^{13}C-EGDMA$_p$). Refer to the synthesis of poly(MMA-*co*-EGDMA$_p$) from poly(MMA-*co*-HEMA). HEMA pendent alcohol groups in poly(MMA-*co*-1-^{13}C-HEMA) were converted to pendant EGDMA methacrylates by postpolymerization reaction with methacryloyl chloride. The product was a hard white solid (0.9 g, 94%); 100% conversion of alcohols to ester groups by ^{1}H NMR. The ^{13}C NMR spectrum (TMS, $CDCl_3$) of ester methylene region is provided in Figure 5d.

Synthesis of Poly(MMA-co-1,2-^{13}C-EGDMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). The product was a hard white solid (1.0 g, 90%); 0.1 wt % 1,2-^{13}C-EGDMA by ^{1}H NMR. The ^{13}C NMR spectrum (TMS, $CDCl_3$) of the ester methylene region is provided in Figure 5a.

Synthesis of Poly(MMA-co-1-^{13}C-EGDMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). The product was a hard white solid (0.8 g, 83%); 0.1 wt % 1-^{13}C-EGDMA by ^{1}H NMR. The ^{13}C NMR spectrum (TMS, $CDCl_3$) of the ester methylene region is provided in Figure 5c.

Synthesis of Poly(MMA-co-1,1,2,2-^{2}H-EGDMA). Refer to the polymerization of poly(MMA-*co*-AE-HEMA). Insoluble copolymers were synthesized containing 0.02, 0.1, 1.0, and 5.0 wt % 1,1,2,2-^{2}H-EGDMA. The products were hard white solid (average 90% yield). The solid-state ^{2}H NMR spectrum is provided in Figure 3.

Bromination and Titration of Model PMMA Copolymers Containing Only EGDMA Pendant Methacrylates. The bromine, catalyst, titration, and iodide solutions were independently prepared according to previous work.[17,18] The preparation of the solutions, the bromination of the pendant methacrylates, and the titration of I_2 were all performed under red lights to eliminate photochemical reactions.

A 10 mL round-bottom flask was charged with poly(MMA-*co*-EGDMA$_p$) (0.5 g, 3 wt % pendant EGDMA methacrylates) at 10 wt % concentration in chloroform. The reaction vessel was placed in an ice bath, and the bromine solution (10 g, 0.1 equiv) and catalyst solution (50 mL, 30 mol % mercuric acetate) were added. The reaction proceeded in the dark for 10 h in an ice bath, and then a KI solution (20 g, 0.2 equiv) was added. Aliquots were removed every 30 min, and excess I_2 was titrated with a 0.1 N $Na_2S_2O_4$ solution.

Results from these measurements were not quantitative or reproducible. Further studies were carried out involving bromination of pendant methacrylates using a dilute Br_2 solution with out concern for quantifying pendant methacrylate content. Bromination of poly(MMA-*co*-1,2-^{13}C-EGDMA$_p$) and poly(MMA-*co*-1,2-^{13}C-EGDMA) was performed with 10 wt % excess Br_2 in relation to the total content of ^{13}C-labeled EGDMA. Solution ^{13}C NMR spectra (TMS, $CDCl_3$) of the ester methylene region of the brominated copolymers are provided in Figure 7.

Attempted Synthesis of Cyclic EGDMA (EGDMA$_c$). Several 10 mL round-bottom flasks were charged with EGDMA and AIBN. The reactants were diluted to 100, 50, 3, 2, 1, 0.1, and 0.01 wt % concentrations in various dried solvents, i.e., benzene, chloroform, methylene chloride, dioxane, and tetrahydrofuran. The reaction vessels were sealed with a septa and degassed under nitrogen. The reactions proceeded for 48 h at 65 °C. All reactions gave cross-linked gels of EGDMA and unreacted EGDMA.

B. NMR Spectroscopy. *Preparation of Solvent Swollen Cross-Linked PMMA Copolymers for Solution ^{13}C NMR Spectroscopy.* High-resolution solution ^{13}C NMR analysis was conducted on $CDCl_3$ swollen cross-linked PMMA copolymers containing less than 0.5 wt % labeled EGDMA. Copolymer plugs were broken into small chunks using a hammer and a stainless steel compartment equipped with a stainless steel piston. The polymer chunks were then chopped to a powder in a coffee grinder and initially swollen with $CDCl_3$ in a scintillation vial while vigorously agitating with a stir bar. This preswelling enabled more efficient mixing and dissolution compared to a one-step preparation in NMR tubes. After preswelling for 15 min, the swollen copolymers were transferred to a 5 mm NMR tube and continuously hand agitated for 5−10 min. To increase solvent uptake, the samples were suspended in a water bath held at 50 °C for several hours (8−24 h, as needed) and intermittently mixed using a thin metal wire. If a sample contained swollen particles suspended in a solvent-rich continuum, excess solvent was present that interferes with the NMR analysis (shimming problems). The swelling process was started over from the beginning using a new sample. Samples polymerized with 0.5 wt % EGDMA swelled on the order of 800% while samples containing 0.02 wt % or less EGDMA behaved as totally soluble polymer. Air bubbles trapped in gelled samples were removed by a downward whipping action of the NMR tubes.

Considerable time was spent shimming on a properly swollen sample to obtain the desired resolution. In general, shimming was easier on lightly cross-linked samples (below 0.2 wt % EGDMA). The quality of shim was judged at a low number of scans by viewing the line width of the $CDCl_3$ peaks. Shim adjustments were made until good resolution of the solvent triplet peaks was obtained, and then long-term acquisition was carried out.

Solid-State ^{13}C NMR (CP/MAS and HPD) Spectroscopy. Solid-state ^{13}C NMR spectra were acquired on a 200 MHz Bruker MSL NMR spectrometer at a spectral frequency of 50.31 MHz for carbon using a 7 mm multinuclear probe. Routine cross-polarization/magic angle spinning (CP/MAS) pulse program was used with a 5 μs 90° pulse, 5 s recycle time, 40 μs pulse delay, and a 3 ms contact time. A routine high-power decoupled (HPD) pulse program was also used with a 5 μs 90° pulse, 3 s recycle time, and 40 μs pulse delay. The average number of scans was 15 000.

Solid-State ^{2}H NMR Spectroscopy. Solid-state ^{2}H NMR spectra were acquired on a 400 MHz Bruker MSL NMR spectrometer operating at a spectral frequency of 64.4 MHz for deuterium. A routine quadrapolar spin-echo pulse program ($90_{+x}-\tau-90_{+y}-\tau$) was used with 90° pulse durations of 3.8 μs, τ of 25 μs, recycle time of 3 s, and 60−80 000 average number of transients. Raw data were shifted so that the FID was Fourier-transformed at the top of the spin echo.

Gel-State ^{13}C NMR Spectroscopy. Routine high-resolution solution ^{13}C NMR analysis of solvent swollen copolymers was conducted on a 300 MHz Bruker AC NMR and 400 MHz Bruker MSL NMR spectrometers using a 5 mm probe and operating for carbon at 75.5 and 100.13 MHz spectral frequencies, respectively. Instrument shimming was crucial to obtaining well-resolved spectra. Long recovery times after adjusting shim settings, plus high lock power and gain needed to obtain a good lock signal, made shimming on the swollen polymer networks especially tedious. The best spectral resolution was obtained by first shimming on pure $CDCl_3$ and then making slight adjustments of the shim settings for the swollen polymer samples.

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