Gel-state NMR Investigation of Crosslinked Poly(methyl Methacrylate) Incorporating ^{13}C Labeled Ethylene Glycol Dimethacrylate

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SUMMARY: ^{13}C labeled ethylene glycol dimethacrylate (EGDMA) was used to form labeled crosslinked PMMA and model ^{13}C labeled pendant double bond copolymers. Solution NMR was possible on solvent-swollen samples containing less than 0.5% by weight EGDMA. Spectra confirm significant amounts of singly reacted EGDMA in fully polymerized networks. Peaks arising from the two most likely stereochemical triads (syndi- and heterotactic) were identified but no evidence of cyclic species was observed. Labeled EGDMA allowed observation of the crosslink site at concentrations as low as 0.02 wt-% EGDMA.

Introduction

Network formation in methyl methacrylate-ethylene glycol dimethacrylate systems has long been known to deviate significantly from gelation behavior predicted by the Flory-Stockmeyer equation.[1,2] Most explanations for this deviation center on two contributions: formation of cyclic species, and reduced reactivity of pendant vinyl groups (i.e., vinyl groups of singly-reacted EGDMA). Landin and Macosko[3] plotted pendant vinyl conversion verses monomer conversion for MMA-EGDMA systems incorporating less than 2% dimethacrylate. The polymers obtained at low conversion were swellable enough for proton NMR analysis. They observed that overall conversion versus time was insensitive to the amount of EGDMA present;

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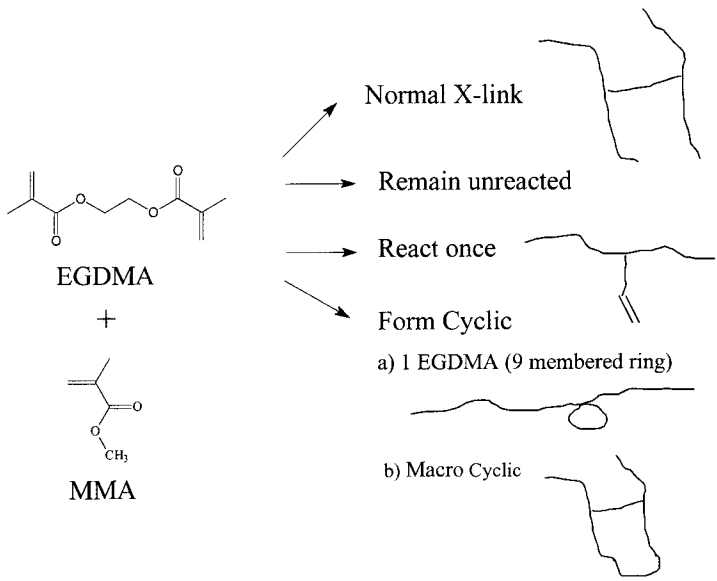
i.e. the reactivity of the first double bond of EGDMA was estimated to be identical to that of the monofunctional monomer (MMA). Proton NMR distinguished pendant vinyls from unreacted and incorporated monomer thus allowing conversion of pendants versus conversion of monomer to be plotted. All plots (from 0.0-1.7 mole-% EGDMA) had positive y-intercepts implying pendant conversions of 2% to 4% at time zero in the polymerization. It was concluded that this pendant conversion at zero monomer conversion was evidence of cyclization. The probability of crosslinking (i.e.; reaction of pendant vinyls with other chains) would be zero during the very beginning of polymerization and the pendant vinyls therefore had to be reacting with their own polymer chain ends.



The work reported here follows the fate of ethylene glycol dimethacrylate crosslinker incorporated into methyl methacrylate using ^{13}C-labeled EGDMA. The wider dispersion of chemical shifts afforded by carbon over proton NMR allows clearer observation of all species present, including resonances arising from repeat units of different tacticity. Central to the spectral analysis was the synthesis of PMMA with 100% ^{13}C- labeled pendant vinyls; i.e., soluble polymer containing labeled and singly reacted EGDMA along its backbone. This model polymer was used to obtain $^{13}C/^{13}C$ coupling constants and to deconvolute contributions from pendant vinyls in crosslinked systems. Concentrations of EGDMA were observable between 0.5 wt-%

down to 0.02 wt-%. Crosslinked PMMA containing more than 0.5 wt.-% EGDMA was not sufficiently swellable to afford well resolved spectra while 0.02 wt-% EGDMA was the practical limit of detection for 24 hour acquisition times.

Experimental

Methyl methacrylate, ethylene glycol dimethacrylate, hydroxyethyl methacrylate methacryloyl chloride, triethyl amine and bromine were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received except for methacryloyl chloride which was twice distilled under vacuum and HEMA which was extracted with heptane from H_2O to remove traces of EGDMA. Doubly ^{13}C-labeled ethylene glycol was obtained from Cambridge Isotope Laboratory (Andover, MA) and used as received. Spectra were acquired using Bruker AC300 and MSL400 spectrometers using standard solution pulse programs. Polymerizations were performed in bulk employing 0.5% AIBN as initiator.

Synthesis of labeled ethylene glycol dimethacrylate (EGDMA)

Methacryloyl chloride (3.7 g, 35 mmol) and 40 mL 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 and stirring begun. Ethylene glycol (1.0 g, 16 mmol); triethylamine (3.5 g, 35 mmol) and 25 mL methylene chloride were combined in a 100 mL Erlenmeyer flask and chilled in an ice bath. The chilled solution was transferred quantitatively to the addition funnel and added dropwise to the reaction flask. After addition was complete, the ice bath was removed and the reaction allowed to continue at room temperature for 1 h. The reaction mixture was placed in a 250 mL separatory funnel together with an additional 100 mL methylene chloride. The mixture was washed with two portions of dilute HCl followed by 1 portion of saturated KCl solution. The methylene chloride was removed with a rotary evaporator and the crude product dissolve in 150 mL diethyl ether. This solution was washed with 15 portions of dilute NaOH, 1 portion of H_2O and 1 portion of saturated KCl(aq). The ether layer was dried over $MgSO_4$ and solvent removed by rotary evaporation; yield 2.0 g.

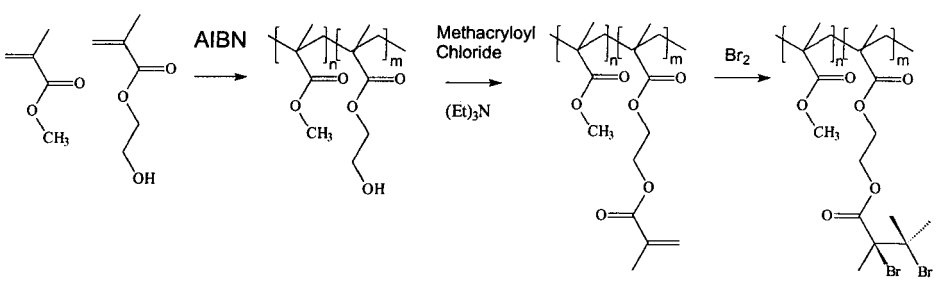
Synthesis of labeled hydroxyethylmethacrylate (HEMA)

Methacryloyl chloride (1.9 g, 18 mmol) and 40 mL 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 and stirring begun. 1,2$^{13}C_2$ -[ethylene glycol] (1.0 g, 16 mmol); triethylamine (1.8 g, 18 mmol) and 25 mL methylene chloride were combined in a 100 mL Erlenmeyer flask and chilled in an ice bath. The chilled solution was transferred quantitatively to the addition funnel and added dropwise into the reaction flask. After addition was complete, the ice bath was removed and the reaction allowed to continue at room temperature for 1 h. The reaction mixture was placed in a 500 mL separatory funnel together with 200 mL of additional methylene chloride. The mixture was washed with one portion of dilute HCl followed by removal of methylene chloride by rotary evaporator. The residue was dissolved in 200 ml H_2O and washed with 2 portions of heptane. The aqueous layer was then extracted with 7 portions of methylene chloride. The combined methylene chloride washings were dried over $MgSO_4$ and the solvent removed by rotary evaporation; yield 0.7 g ; 34 % .

Synthesis of model polymer containing pendant vinyls and bromine

MMA and HEMA were copolymerized in bulk at 60 °C using 0.05 wt-% AIBN as initiator. Extra purification measures were necessary to eliminate trace amounts of EGDMA in the commercial HEMA in order to obtain soluble copolymers. The polymer was purified via reprecipitation into MeOH. The dried polymer was then dissolved in CH_2Cl_2. A ten-fold excess of triethylamine was added to the solution based on the stoiciometric amount of HEMA units in the copolymer. Methacryloyl chloride, also in 10-fold excess, was diluted with CH_2Cl_2 and added in portions to the chilled copolymer solution. The reaction was stirred at room temperature overnight, then precipitated into a mixture of CH_3OH and H_2O, followed by repeated reprecipitation into CH_3OH fom $CHCl_3$. Bromination of pendant double bonds was accomplished by adding a 10-fold excess of Br_2 to a solution of the copolymer in CH_2Cl_2



Preparation of solvent swollen crosslinked polymethylmethacrylate samples for solution NMR

Solution spectra were possible with crosslinked poly(methyl methacrylate) samples containing less than 0.5 wt-% EGDMA. Polymer was first ground to a powder form in a stainless steel coffee grinder. The powder was then mixed with sufficient $CDCl_3$ to swell it below its equilibrium expansion level. Samples polymerized with 0.5 wt-% EGDMA swelled on the order of 200% while samples containing 0.02 wt-% and below behaved as soluble polymer. It was also necessary to ensure that all of the powder samples swelled to the same degree. This was accomplished by hand stirring of the swelling gel in the 10 mm nmr tube as it uptakes solvent, because samples do not reach equilibrium expansion levels for a number of hours. Stirring was applied continuously during the first few minutes of solvent uptake, followed by intermittent mixing applied between intervals of time spent suspended in a water bath held at 50 °C. After a number of hours, any air bubbles trapped in the gelled samples were shaken out by a whipping action. If the sample showed swollen particles suspended in a solvent-rich continuum, too much solvent had been used and the swelling process was started over from the beginning. Considerable time was spent shimming on a properly swollen sample to obtain the desired resolution. In general, shimming was easier on the more lightly crosslinked samples (below 0.2 wt-% EGDMA). The quality of the shim was conveniently judged at a low number of transients by viewing the linewidth of peaks arising from deuterated chloroform. After obtaining good separation of the solvent triplet peaks, the long term acquisition was carried out.

Results and Discussion

Figure 1 compares the ester region of samples of PMMA crosslinked with singly and doubly ^{13}C labeled EGDMA, (top and third trace) with that of singly and doubly labeled model polymers containing pendant vinyl segments, (second and fourth traces). It is clear that the finer spectral detail in the crosslinked PMMA spectra (top) is accounted for by singly reacted EGDMA incorporated into the polymer backbone. When labeled EGDMA (unincorporated) was added into the crosslinked PMMA (third trace from the top), the resulting peak was distinct from singly and doubly incorporated EGDMA indicating that the vast majority of EGDMA was incorporated into the polymer through at least one vinyl group.

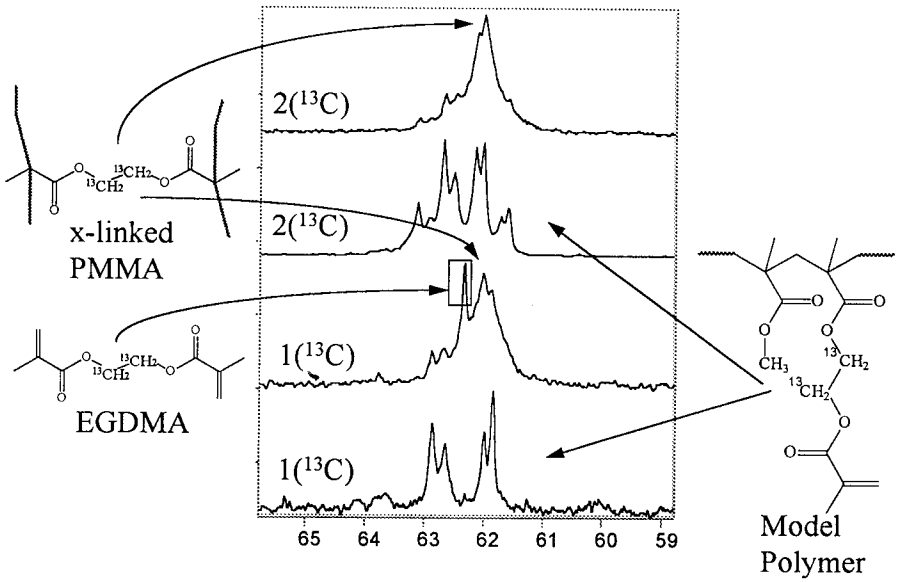


Figure 1 ^{13}C spectra of crosslinked PMMA and model pendant vinyl polymers

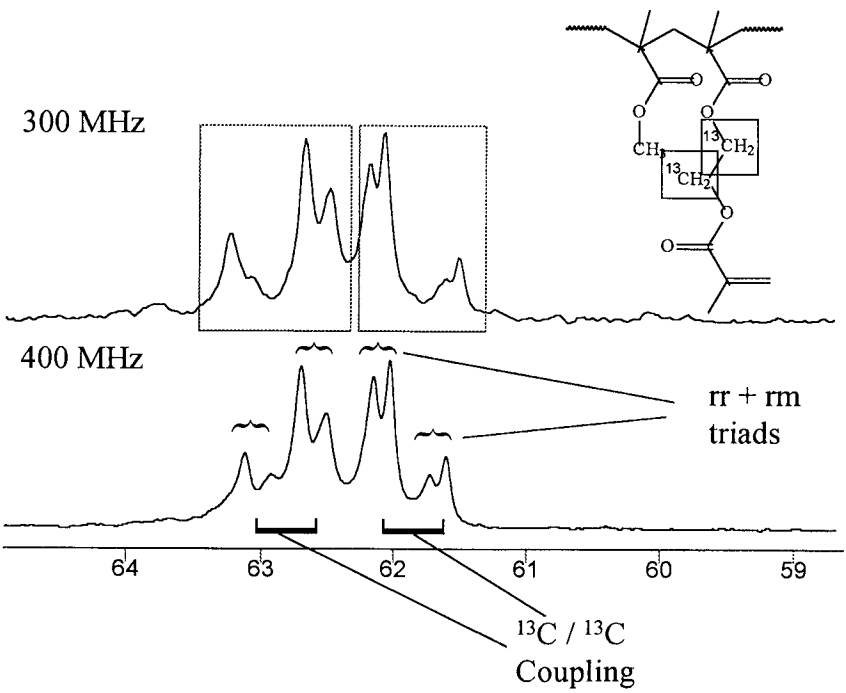


Figure 2 Ester region of di-labeled pendant vinyl model polymer acquired at 300 and 400 Mhz

Figure 2 illustrates how the pattern of 8 peaks arises from a singly incorporated di-labeled EGDMA segment of the polymer. Note that the ^{13}C-coupling is constant in hertz and thus gives a narrower pattern at higher magnetic field strength. Also, $^{13}C/^{13}C$ coupling between the two ester carbons approaches the limit of first order splitting, causing the carbon spectra to have intensity attenuations similiar to that of non-first order ^{1}H doublets. The fine splitting ({) is due to the two most probable stereochemical triads[4] (*rr* and *rm*). Reasoning that the tacticity would cause a greater chemical shift difference closer to the point of chiral attachment would support that the higher field ester peaks are those furthest away from the polymer backbone.

Polymerizations carried out at successively lower temperatures gave crosslinked networks that solvent swelled to differing degrees. The less swellable gels had main crosslink peaks that were attenuated as much as 75% (Figure 3). The attenuation was unaffected by increased recycle times and thus was not a result of rf saturation. Most probably, the less swellable gels were experiencing a decreased NOE enhancement. Quantitative comparison of data is therefore prohibited, at least with simple observation methods, and exact determination of crosslinker reaction product amounts was not possible.

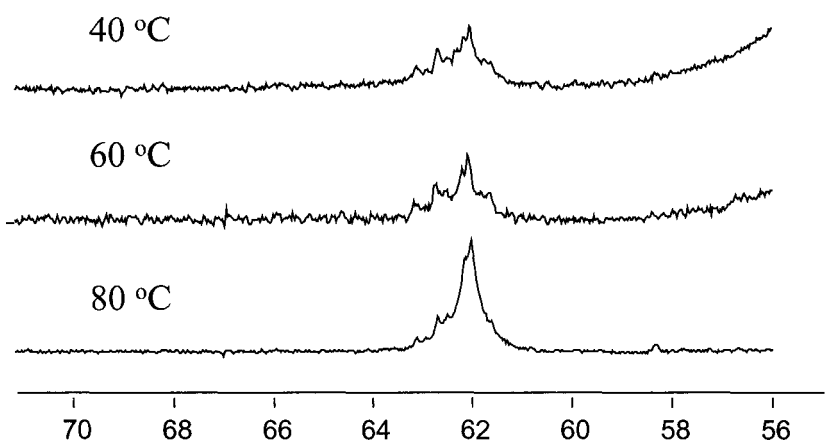


Figure 3 ^{13}C NMR spectra of PMMA crosslinked with di-^{13}C-labeled EGDMA at different temperatures.

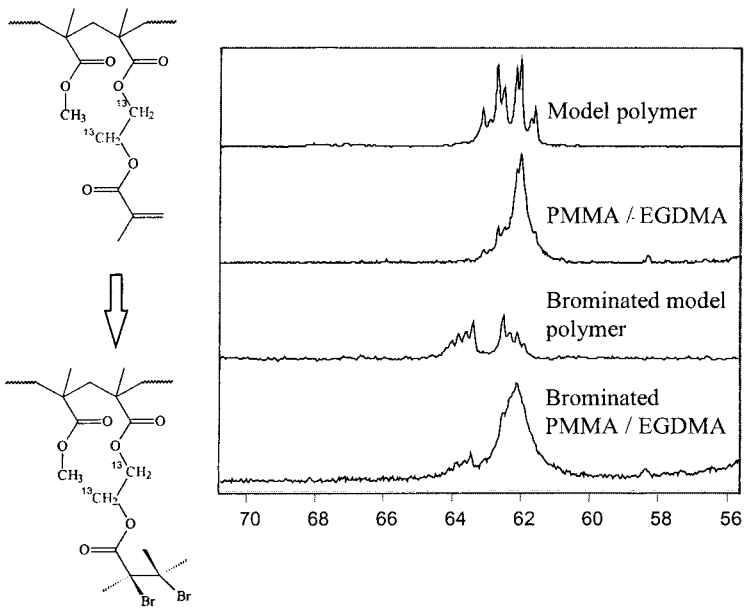


Figure 4 ^{13}C spectra of di-^{13}C labeled model pendant double bond polymer and PMMA / di-^{13}C 0.1 wt-% labeled EGDMA before and after bromination.

Figure 4 confirms the identity of pendant double bonds in the crosslinked networks and in the model polymers. Note the reaction with bromine shifted the ester peaks away from the first order limit compared to the pendant double bond model polymer. Addition of bromine to the double bonds allowed the peaks to be shifted and to possibly expose peaks due to cyclic species; the latter were not identified.

Conclusions

^{13}C-Labeled EGDMA allowed spectral monitoring of the crosslink site through a concentration range of (0.02-0.5) wt-% EGDMA. Crosslinker concentrations above 0.5 wt-% produced a polymer that was insufficiently swellable for solution NMR analysis. All peaks present were accounted for by either a doubly-reacted normal crosslink or a pendant vinyl resulting from a singly reacted EGDMA segment. Ongoing work is aimed at synthesis of a model polymer containing primary cyclic units (a cyclized EGDMA) which would allow

definitive observation of cyclic units and confirm whether or not ^{13}C NMR can be used to monitor cyclic formation in crosslinked PMMA samples.

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[1] Flory, P. J. *J. Am. Chem. Soc.* **1941**, 63, 3083, 3091,3097.
[2] Stockmeyer, W. H. *J. Chem Phys*. **1943**, 11,45.
[3] Landin, D. T. ; Macosko,C. W. *Macromolecules*.**1988** 21, 846.
[4] Bovey; F. A. *Chain Structure of Macromolecules*; **1982.** 47.