

# Determination of Residual Unsaturation in Highly Crosslinked, Dough-moulded Poly(methyl methacrylate) Dental Polymers by Solid-State $^{13}\text{C}$ NMR

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## Synopsis

Methyl methacrylate has been copolymerized with eight multifunctional, cross-linking comonomers in mixtures containing poly(methyl methacrylate) to give highly crosslinked polymers for trial as dental resins. These insoluble, optically opaque polymers have been characterized by solid-state  $^{13}\text{C}$  Nuclear Magnetic Resonance spectroscopy. The crosslinking comonomer could be identified from the appropriate resonances in the solid-state spectra. Unreacted methacrylate groups could be determined quantitatively from the resonance at 167 ppm due to C=O adjacent to C=C at concentrations down to at least 0.5% of the total C=O. The final conversion of C=C double bonds in the comonomer depended on the nature and length of the spacer segment between the reactive methacrylate groups.

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is widely used in the construction of dentures and other prostheses. The material is supplied commercially in two components: a liquid composed essentially of methyl methacrylate, and a powder of poly(methyl methacrylate) beads produced by suspension polymerization and containing up to about 1% by weight of benzoyl peroxide as a polymerization initiator. The liquid and the powder are mixed in the proportions of about 1 : 2.5 by weight, and this forms a soft "dough" by swelling and softening of the polymer beads and their partial dissolution to form a viscous liquid phase. This dough is packed into a mould cavity under pressure and heated to initiate polymerization (heat curing).

In commercially available denture-base polymers, cross-linking agents such as ethylene glycol dimethacrylate are added to the monomer component to improve the resistance of the cured polymer to crazing by solvents. The concentration of cross-linking agents is usually limited to less than 15% by weight of the monomer<sup>1</sup> because higher concentrations reduce the tensile strength<sup>2</sup> and increase the brittleness of the cured material. At this level of crosslinking, solvent crazing is reduced but not eliminated.

An investigation has been made<sup>3</sup> to establish whether the use of alternative cross-linking monomers with longer and more flexible chains between functional groups would avoid the reduction in strength properties, including, in particular, impact resistance, and so allow a higher level of crosslinking to be used and eliminate susceptibility to solvent crazing. To confirm that any improvement in impact resistance resulted from crosslinking rather than from other effects, the degree of crosslinking was determined by estimating the concentration of residual double bonds in the polymerized specimens used for the strength measurements.

These polymers contain pigments such as cadmium sulfide, cadmium selenide, and titanium dioxide for aesthetic reasons, and the consequent opacity, combined with the insolubility of the polymer matrix caused by the high level of crosslinking, precludes solution methods and normal spectroscopic techniques for this investigation.

The aims of the present work were to determine by solid-state <sup>13</sup>C Nuclear Magnetic Resonance spectroscopy (NMR) (1) the identity of the cross-linking monomer, and (2) the proportion of unreacted C=C bonds in the polymer.

## EXPERIMENTAL

Poly(methyl methacrylate) powder was mixed to form a viscous dough with a liquid containing methyl methacrylate monomer and one of eight multifunctional cross-linking agents listed in Table I. This dough was mixed in the proportion 2.4 powder : 1 liquid by weight. The concentration of cross-linking comonomer in the liquid was 50% by weight for the present study. Moulds containing the dough were immersed in a water bath at  $70 \pm 2^\circ\text{C}$  for 1.5 h; then the temperature was raised to  $100^\circ\text{C}$  and maintained there for 18 h, to ensure a high conversion to polymer. This produced a rigid cross-linked polymer matrix in which the original PMMA beads were discernible.

In addition to the heat-cured polymers described above, specimens for analysis were also prepared from a commercially available cold-cured repair material. The powder consisted of PMMA beads containing benzoyl peroxide, while the liquid consisted of methyl methacrylate monomer containing by weight 9% EGDMA (1.3 mole% of the total polymer) and about 1% *N,N*-dimethyl-*p*-toluidine, as an activator of polymerization. Polymerization took place at ambient temperature ( $21 \pm 1^\circ\text{C}$ ) by a redox reaction involving a one electron transfer mechanism.<sup>4</sup> Dental polymers cured by this method are known to contain a large number of unreacted C=C bonds.<sup>5</sup>

Solid-state <sup>13</sup>C NMR spectra were obtained at  $25\text{--}30^\circ\text{C}$  with a Bruker CXP300 spectrometer operating at 75.46 MHz. Machined rods or powdered turning were packed into boron nitride or partially stabilized zirconia rotors, which were spun at the magic angle at 2.5–3 kHz; the Dixon sequence<sup>6</sup> was used to suppress the spinning sidebands. The zirconia rotors were obtained from Nilcra Ceramics, Melbourne, Australia. Spectra were recorded with dipolar-decoupling and cross-polarization (contact time of 2 msec) and a pulse recycle time of 5 sec. Contact time experiments by Schaefer et al.<sup>7</sup> have indicated that quantitative peak areas can be obtained from the spectra of PMMA using a cross-polarization contact time of 2 msec. The incorporation of cross-linking comonomer in our samples alters the bulk physical properties

TABLE I  
Cross-Linking Monomers Used in This Study

Monomer	Abbreviation	Chemical structure
1. Ethylene glycol dimethacrylate	EGDMA	
2. Hexamethylene glycol dimethacrylate	HMGDMA	
3. Decamethylene glycol dimethacrylate	DMGDMA	
4. Tetraethylene glycol dimethacrylate	TEGDMA	
5. Polyethylene glycol 600 dimethacrylate	PEGDMA	
6. Divinyl benzene	DVB	
7. Ethoxylated bisphenol A dimethacrylate	EBADMA	
8. Trimethylol propane trimethacrylate	TMPTMA	

of the polymers,<sup>3</sup> and also the NMR relaxation behavior. Quantitative areas for all peaks could not generally be obtained from a single spectrum. However the concentration of unreacted double bonds could be determined quantitatively, by comparison of the area of the peak due to C=O adjacent to C=C with the polymer C=O peak, since the relaxation times of these carbon atoms, and hence the areas of the respective peaks, should be directly comparable.

## RESULTS AND DISCUSSION

**Cold-Cured Poly(methyl methacrylate).** The sample of polymer prepared by cold curing PMMA beads with MMA at 21°C is expected to contain a relatively large proportion of unreacted double bonds. The solid-state <sup>13</sup>C NMR spectrum of this polymer is shown in Figure 1. The main features are the peaks due to the α-methyl carbon at 15–28 ppm, the quaternary carbon at 48 ppm, the methoxy at 55 ppm, and the carbonyl at 172 ppm. The methylene carbon peak is a broad underlying peak at 45–60 ppm. The cold-cured resin also contained 1.3 mole% of EGDMA comonomer; however no well-resolved peaks assignable to this minor component can be observed.

The conversion at 21°C would be expected to cease at the glass transition before all of the C=C bonds in the monomer molecules have reacted. No resonances around 100–130 ppm due to doubly bonded carbons were observed. This is the region where spinning sidebands occur and suppression by the Dixon sequence was incomplete, thus making observation of C=C more difficult. However, a distinct resonance was observed at 167 ppm, attributable to C=O adjacent to C=C, namely due to unreacted methacrylate groups. Quantitative comparison with the main C=O resonance at 172 ppm gave a value of  $1 \pm 0.5\%$  for the unreacted methacrylate groups in the sample shown in Figure 1. The unreacted methacrylate groups may include unreacted MMA monomer, unreacted EGDMA, and particularly, partially reacted EGDMA. The concentration of unreacted groups corresponds to 37% of the double bonds in the EGDMA monomer having not reacted, or 74% of the EGDMA molecules having only one of its C=C bonds reacted.

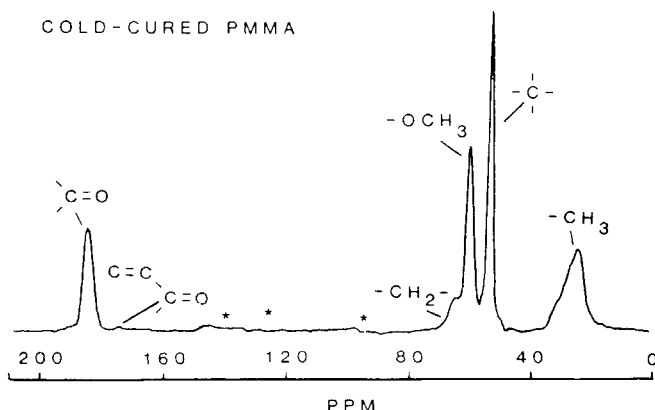


Fig. 1. Solid-state <sup>13</sup>C NMR spectrum of cold-cured poly(methyl methacrylate). The asterisks indicate peaks due to residual spinning sidebands or arcing.

TABLE II  
Compositions of Copolymers Analyzed in this Study, and the Proportions  
of Unreacted C=C Double Bonds Determined by Solid-State  $^{13}\text{C}$  NMR

Comonomer	Molecular weight	Composition (mole%)	Mole% MA groups from comonomer	% Unreacted groups in polymer <sup>a</sup>	% Comonomer with an unreacted C=C bond <sup>b</sup>
1. EGDMA	198	8.2	15.1	4.3 ± 0.5	60 ± 6
2. HMGDMA	254	6.5	12.2	0.9 ± 0.5	15 ± 8
3. DMGDMA	282	5.9	11.1	0.8 ± 0.5	14 ± 9
4. TEGDMA	330	5.1	9.7	< 0.5	—
5. PEGDMA	754	2.3	4.5	< 0.5	—
6. DVB	130	12.0	21.4	—	—
7. EBADMA	452	3.8	7.3	< 0.5	—
8. TMPTMA	339	4.9	13.4	3.2 ± 0.5	72 ± 11
9. MMA	100	15	15	1.0 ± 0.5	7 ± 4

<sup>a</sup>% of unreacted methacrylate groups (i.e., C=C) obtained from the area of the peak at 167 ppm, due to C=O adjacent to C=C, compared with the total area due to C=O (167 and 172 ppm).

<sup>b</sup>% of multifunctional monomers with at least one unreacted methacrylate group.

**Glycol Dimethacrylates.** A series of glycol dimethacrylates with spacer segments containing 2 to 10  $\text{CH}_2$  units (see Table I) were investigated. The variation in mechanical properties with the length of the spacer segment in the crosslink between PMMA chains has been reported elsewhere.<sup>3</sup>

The  $^{13}\text{C}$  NMR spectrum of the copolymer containing 8.2 mole% EGDMA (Tables I and II, is shown in Figure 2(a). The spectrum is similar to the spectrum of cold-cured PMMA (Fig. 1) except for a resonance at 62–70 ppm due to  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  in the EGDMA. As the length of the glycol segment increases, for example in DMGDMA [Fig. 2(b)], a new resonance appears at 34 ppm. This has been assigned to  $-\text{CH}_2-$  in the glycol segment removed from  $-\text{O}-$ .

Figures 2(a) and (b) both show evidence of unreacted double bonds by the peak at 167 ppm due to C=O adjacent to C=C. Although these systems were polymerized at 100°C, which is close to the glass transition temperatures of the copolymers, a significant proportion of the double bonds remained unreacted. However, the reactions did proceed to a higher conversion than for the cold-cured sample (Fig. 1). It would be expected that as the length of the glycol segment—and hence the chain flexibility—increased, the residual double bond concentration would decrease. This result was observed—as shown in Table II—for samples 1, 2, and 3 in order of increasing  $\text{CH}_2$  segment length, with the proportion of unreacted C=C in the crosslinking comonomer decreasing from 29% to 7%.

The importance of the flexibility of the comonomer spacer on the reactivity of the C=C bonds was demonstrated by samples 4 and 5 (Table II) containing 1, 4, and about 13  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  units in the spacer. These spacers will have increased flexibility compared with samples 2 and 3 because of less hindered bending of the C—O—C bonds, and therefore would be expected to show increased conversion of C=C bonds. This is confirmed by the  $^{13}\text{C}$  NMR spectra. Thus, the copolymer containing TEGDMA [Fig. 2(c)] shows a peak at

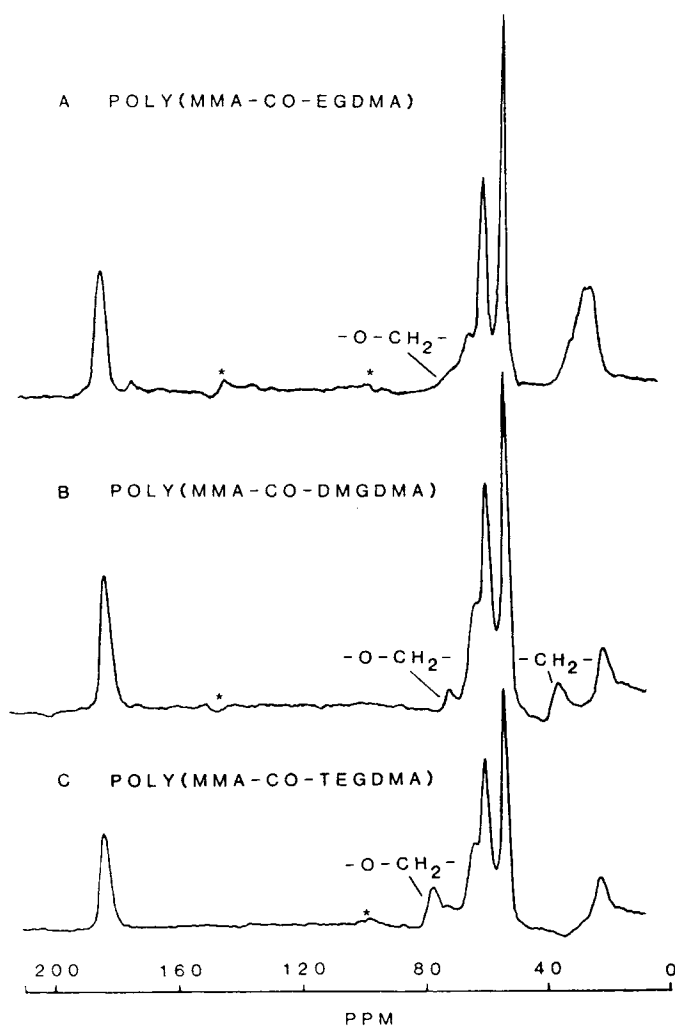


Fig. 2. Solid-state  $^{13}\text{C}$  NMR spectra of (a) poly(methyl methacrylate-co-ethylene glycol dimethacrylate), (b) poly(methyl methacrylate-co-decamethylene glycol dimethacrylate), and (c) poly(methyl methacrylate-co-tetraethylene glycol dimethacrylate).

70 ppm due to  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  carbon atoms, but there is no observable peak at 167 ppm, indicating that the concentration of unreacted double bonds in this sample must be very small (Table II).

**Other Comonomers.** The trifunctional monomer, TMPTMA can be identified from the resonances due to  $-\text{O}-\overset{*}{\text{C}}\text{H}_2-\text{C}-$  at 65 ppm and to  $-\overset{*}{\text{C}}\text{H}_2-\text{CH}_3$  at 42 ppm. This tristar monomer with short arms has an unfavorable structure for the complete reaction of its  $\text{C}=\text{C}$  groups. This is confirmed by the appropriate  $\text{C}=\text{O}$  resonance at 167 ppm in Figure 3(a), which corresponds to 3.2% unreacted  $\text{C}=\text{C}$ , or 24% of the  $\text{C}=\text{C}$  bonds in the comonomer remaining unreacted at  $100^\circ\text{C}$ .

Divinyl benzene (DVB) is frequently used as a cross-linking monomer. The solid-state  $^{13}\text{C}$  NMR spectrum [Fig. 3(b)] has characteristic resonances at

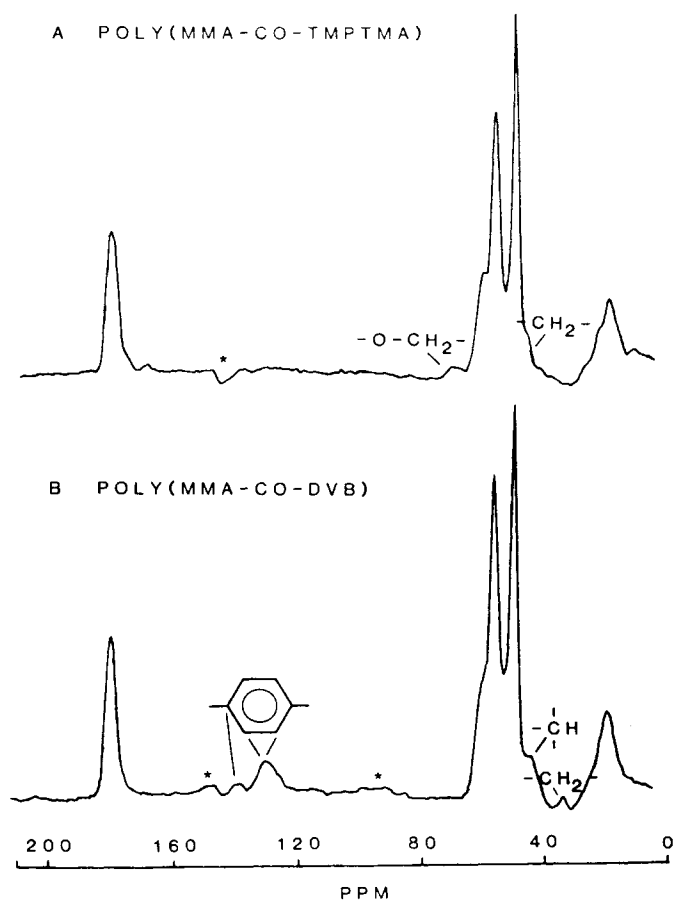


Fig. 3. Solid-state  $^{13}\text{C}$  NMR spectra of (a) poly(methyl methacrylate-co-trimethylol propane trimethacrylate) and (b) poly(methyl methacrylate-co-divinyl benzene).

120–135 and 135–140 ppm due to protonated and nonprotonated aromatic carbons, respectively, which can be used for identification of the comonomer. There are also resonances at 30 and 42 ppm due to  $\text{CH}_2$  and  $\text{CH}$  from the DVB after reaction of the double bonds. Any resonances due to unreacted  $\text{C}=\text{C}$  bonds are obscured, this time by the aromatic DVB resonances, but the  $\text{C}=\text{O}$  peak at 165 ppm indicates that the proportion of unreacted methacrylate groups is less than 0.5%.

### CONCLUSIONS

1. Solid-state  $^{13}\text{C}$  NMR can be used to analyze opaque dental copolymers.
2. The identity of the comonomer and the concentration of unreacted double bonds can be determined by this method.
3. The conversion of multifunctional comonomers increases with increasing length and flexibility of the spacer between the methacrylate double bonds.
4. Observation of the  $\text{C}=\text{C}$  resonances might be achieved by complete suppression of the spinning sidebands, subtraction procedures utilizing differ-

ent spinning rates, or from spectra obtained at lower field strengths, although sensitivity would then be diminished.

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