

## Biomedical Polymers: Solid-State Studies in the Centre- and in the Stray-Field of a 7 T Magnet

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**Abstract:** The performance of dental materials containing dimethacrylate polymers is strongly dependent on the extent of polymerization, which is difficult to measure accurately. In this study we have used solid-state  $^{13}\text{C}$  CP/MAS NMR/ $^1\text{H}$  stray-field MRI techniques in order to obtain quantitative evaluation of unreacted methacrylate moieties in resin networks and to relate these data with local mobility in the kHz frequency range.

**Resumo:** O desempenho de materiais dentários contendo polímeros com grupos metacrilato depende muito da extensão de polimerização, em geral difícil de obter com exactidão. Neste estudo usámos técnicas de observação de RMN de  $^{13}\text{C}$  por CP/MAS e de IRM de  $^1\text{H}$  na região de stray-field, para quantificar os grupos metacrilato que não reagiram em resinas reticuladas e para relacionar esta informação com a mobilidade local na gama dos kHz.

### Introduction

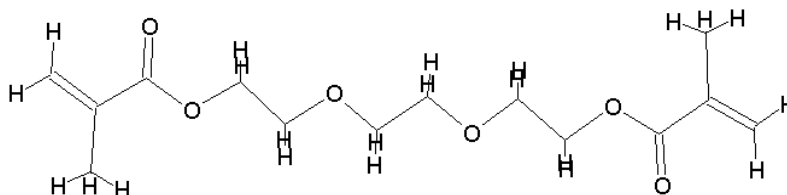
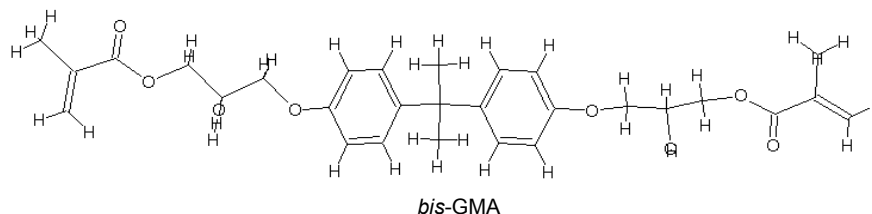
Polymers with methacrylate groups are, in general, biocompatible. Accordingly, they are used in Restorative Dentistry, for example, to promote adhesion of the restorative material to dentin. The most widely used copolymers contain 2,2 - bis-(4-(2-hydroxy-3 -methacryloxy prop-1-oxy) phenyl) propane), bis-GMA, which has a number of disadvantages including high viscosity ( $1.2 \times 10^6$  cp).

The addition of a diluent such as TEDMA (triethylene glycol dimethacrylate) is thus required to reduce the viscosity and the glass

transition ( $T_g$ ), in order to increase the degree of conversion (DC) and to allow adequate filler content.<sup>1</sup>

### Experimental

The samples were prepared, as previously described, with bis-GMA/TEDMA (w%/w%) ratios 100/0, 85/15, 75/25, 70/30 and 50/50, using 1 mol% azobisisobutyronitrile as initiator; <sup>1</sup>the polymerization reaction was performed in glass tubes at 80°C, over 6 h, and post-cured at 120°C for 2 h.  $^{13}\text{C}$  CP/DD ( $B_1=50$  kHz) -MAS (4.3 kHz) spectra



were recorded at 75.47 MHz using a Bruker MSL 300P spectrometer, at C-H contact times from 100  $\mu$ s to 10 ms. A wideline probe-head was used for  $^1\text{H}$  observation at 123 MHz, in the stray-field of the 7 T magnet.<sup>2</sup> The static magnetic field gradient of 3750 G/cm, present outside the superconducting coil, was employed to select a slice of the material. The protons in the selected slice were submitted to a radio frequency (RF) pulse sequence (see reference 3 for details) and the magnetization was recorded as long multiple spin-echo decay.<sup>4</sup>

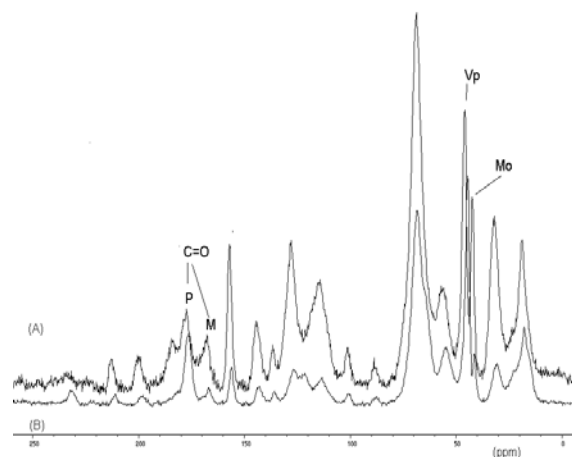
## Results and Discussion

Figure 1 shows typical  $^{13}\text{C}$  CP/DD MAS spectra, obtained from the indicated samples. Well-resolved signals are identified for the carbons in the carbonyl groups of unreacted (M) and polymerized (P) methyl methacrylate moieties. The other labeled signals in figure 1 are: signals from  $\text{CH}_2$  in the polymer backbone ( $\text{V}_\text{p}$ ) and from quaternary C bonded to two methyl groups (Mo), in the bisphenol moiety.

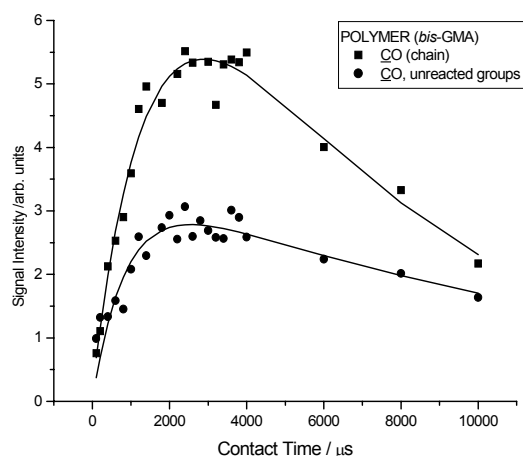
Figure 2 shows the plots obtained for the signal intensity of the carbonyl groups in poly *bis*-GMA, as a function of contact time.

The ratio of the maximum intensities (well defined by extrapolation to zero-contact time of the linear part of the curves) yields the extent of polymerization, that is DC, which for poly *bis*-GMA is 66 %. From similar plots obtained for the other samples, we have determined DC as a function of the amount of TEDMA (Table 1); the data presented here agrees well with previous reported results.<sup>1</sup> In particular, it should be noted that similar DCs were obtained with 15% and 50% TEDMA.

In all the samples, the variation of the  $^{13}\text{C}$  signal intensity (Y) with contact time (x) is in agreement with the presence of two dominant regions, A and B, with different mobility; in fact, the function that best fits the experimental data is  $Y = (I_A + I_B) * \exp(-x/T_{1\rho}) - (I_A * \exp(-x/T_{\text{CHA}}) + I_B * \exp(-x/T_{\text{CHB}}))$ , where



**Figure 1.**  $^{13}\text{C}$  CP/DD-MAS typical spectra obtained with the contact times: A) Polymer *bis*-GMA, 2 ms and B) Copolymer *bis*-GMA-TEDMA (50/50), 2.4ms.



**Figure 2.** Variation of the indicated signal intensities with contact time obtained for the polymer *bis*-GMA

**Table 1.** Viscosity and degree of conversion (DC) obtained for the mixtures *bis*-GMA/TEDMA with the indicated monomer ratios.

<i>Bis</i> -GMA/TEDMA (w%/w%)	Viscosity* (cp)	DC (%)
100/0	$1.2 \times 10^6$	61.7 <sup>*</sup> 66
85/15	-	- 86
75/25	~5200	85.9 <sup>*</sup> 85
50/50	282	84.2 <sup>*</sup> 85

\* reference 1

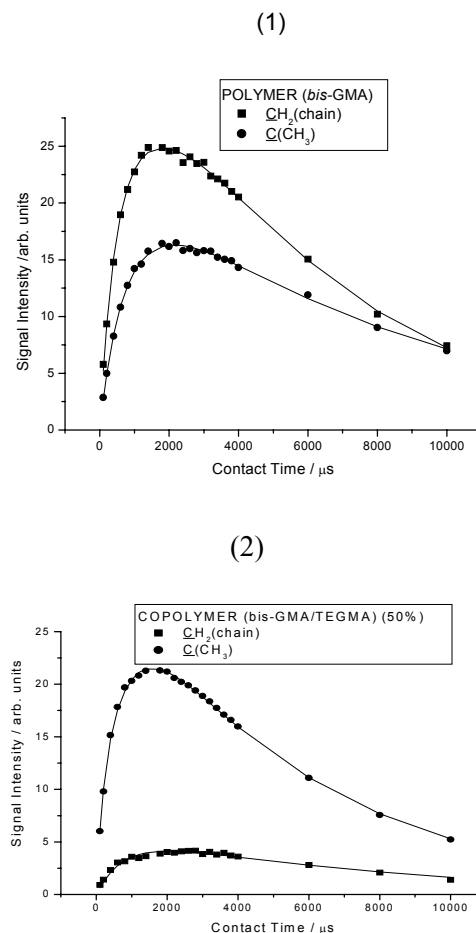
$^H T_{1\rho}$  represents the  $^1H$  spin-lattice relaxation time in the rotating frame,  $I_A$  and  $I_B$  are, respectively, A and B magnetizations at thermal equilibrium,  $T_{CHA}$  and  $T_{CHB}$  the contact time-constants for the carbon-proton magnetization transfer in A and B domains, respectively. The first part of the curve is related to very fast processes in rigid molecules containing protonated carbons, and the maximum magnetization is reached in a very short time (very short  $T_{CH}$ ). The decreasing part of the curve, mainly dependent on  $^H T_{1\rho}$ , is essentially related with mobility in the kHz range only when local magnetic field fluctuations in the same frequency range are induced by molecular motion not by H-H spin-diffusion.

Figure 3 shows the variation of  $\underline{CH}_2$  (Vp) and  $\underline{C}(\underline{CH}_3)$  (Mo) intensities with the contact time, recorded for the polymer *bis*-GMA and for a copolymer; particularly Mo in the copolymer shows a behavior closer to a rubbery phase ( $T_{CHA}$ ,  $T_{CHB}$  and  $^H T_{1\rho}$  are  $1.04 \pm 0.01$ ,  $0.40 \pm 0.02$ ,  $8.2 \pm 0.1$  ms and  $1.57 \pm 0.02$ ,  $0.3 \pm 0.01$ ,  $7.3 \pm 0.2$  ms, respectively). Consequently, this fact leads to the conclusion that the bisphenol group is more mobile in the copolymer.

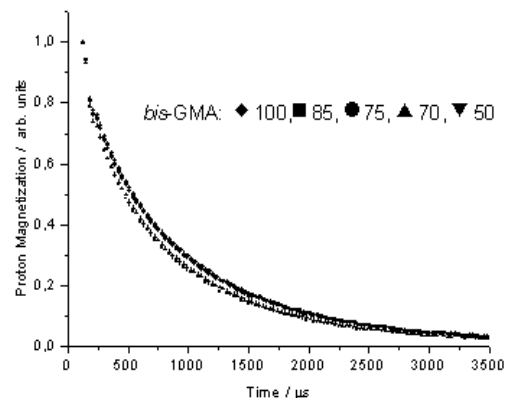
DCs were also correlated with proton magnetization decays, recorded in the stray-field of the 7 T magnet, using long spin-echo train acquisition (256 echoes, Figure 4);<sup>4</sup> bi-exponential functions were used to fit the decays and the short- and the long- time constants were assigned to domains A and B, respectively, due to the fact that the first echoes refocus magnetization from all the protons in the samples, while only magnetization from mobile regions contribute to the last echoes. In all the samples studied here, similar time-constants were used in the fitting functions.

For example, while for poly *bis*-GMA the time-constants were  $1.03 \pm 0.01$  (61%) and  $0.21 \pm 0.01$  (39%), for the copolymer with 50% TEDMA we have found  $1.04 \pm 0.01$  (58%) and  $0.19 \pm 0.01$  (42%). The same technique yielded for

an elastomer (commercial rubber)  $4.0 \pm 0.5$  (82%) and  $0.3 \pm 0.1$  (18%).



**Figure 3.** Variation of the indicated signal intensities with contact time: 1) Polymer *bis*-GMA 2) Copolymer *bis*-GMA/TEGMA (50/50).



**Figure 4.** Long  $^1H$  spin-echo train decays obtained from the samples with the indicated *bis*-GMA content (W%).

## Conclusions

DC obtained for poly bis-GMA was lower (66%) than DCs obtained for the copolymers (86% for 50/50 copolymer), as expected. NMR data presented here agree well with previous reported results.<sup>1</sup> The comparison of the variation of the intensity of (CH<sub>3</sub>)<sub>2</sub>C in the bisphenol group obtained for poly bis-GMA and for the copolymers is in agreement with a plasticizing effect of TEDMA. However, the mobility of the polymer backbone, probed by the evolution of CH<sub>2</sub> magnetization with contact time, is similar in poly bis-GMA and in the copolymers. According to the combined solid-state <sup>13</sup>C CP/MAS NMR/stray-field MRI observations, the extent of polymerization and the local mobility in the kHz frequency range do not change significantly for TEGMA>15%.

## Acknowledgements

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