Polymer Vol. 38 No. 9, pp. 2041–2045, 1997
PII: S0032-3861(96)00764-1
0032-3861/97/$17.00 + 0.00

Determination of extent of reaction in poly(mono- and dimethacrylates) using n.m.r. Comparison of solid-state and solution-state methods

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(Received 13 March 1996; revised 10 May 1996)

The extent of reaction in lightly cross-linked poly(mono- and dimethacrylates) has been determined using solid- and liquid-state ^{13}C n.m.r. Three methods were used: (i) magic-angle spinning (MAS) with high-power decoupling of the solid; (ii) conventional liquid-state high-resolution n.m.r. of the samples swollen by $CDCl_3$; (iii) m.a.s. of the swollen samples. The three methods give comparable results, indicating that motional factors which may affect the solid-state method are not significant. © 1997 Elsevier Science Ltd.

(Keywords: poly(mono- and dimethacrylates); extent of reaction; n.m.r.)

INTRODUCTION

In a recent paper, we discussed an investigation of the instrumental conditions and techniques required for an accurate evaluation of the extent of reaction in dimethacrylate-based dental materials[1] using high-resolution solid-state magic-angle spinning (MAS) ^{13}C n.m.r. Clearly resolved carbonyl signals were observed for reacted and unreacted methacrylate groups at *ca.* 178 and 175 ppm respectively. Because of a large difference in the mobilities of reacted and unreacted methacrylate groups, the relaxation characteristics of nuclei in the two types of groups were found to be quite different. The consequence was that the commonly-used cross-polarization (CP) technique did not give reliable relative intensities, and the less sensitive and less efficient single-pulse excitation (s.p.e.) technique was preferred for quantitative measurements. However it was found that the amount of residual unreacted methacrylate groups determined by n.m.r. was only about one-half that determined using the more usual i.r. method.

In addition to differential relaxation times, the intensities and linewidths of high-resolution solid-state ^{13}C spectra may be affected strongly by interference between molecular motions and the MAS. or dipolar decoupling (d.d.) frequencies as discussed in the previous paper[1]. In that work, experiments were performed to check the effect of this interference, and it was concluded that the effect was minimal. Liquid-state n.m.r. techniques are considerably more reliable than solid-state n.m.r. for intensity measurements, but the dimethacrylate systems investigated previously were too highly cross-linked to dissolve or even swell to any extent. It was felt desirable to further evaluate the reliability of solid-state n.m.r. using samples which could be studied using both solid- *and* liquid-state methods. This note reports measurements on lightly crosslinked poly(methacrylate) samples consisting mostly of a mixture of a monomethacrylate (*ca.* 95%) and a dimethacrylate (*ca.* 5%). Swelling by, or dissolution in, a suitable solvent such as chloroform engenders considerable molecular motion resulting in almost complete averaging of dipole–dipole coupling and chemical shielding anisotropy which are present in solid-state spectra. This then allows the use of liquid-state techniques where the measurement of relative intensities is more reliable. Also, following a recent note[2] on the application of MAS in solid-phase synthesis based on cross-linked polystyrene, the use of MAS of the swollen poly(methacrylate) gels has been investigated.

In the earlier paper[1], it was noted that in the s.p.e. spectra a significant broad background peak was observed arising from materials in the MAS probe employed. Fortunately this did not materially affect the carbonyl peaks used to determine the extent of reaction in methacrylate based systems. However the background peak could potentially be intrusive in other applications, and we have therefore examined a simple method of reducing its effect, using a combination of 90° and 270° pulses.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from BDH

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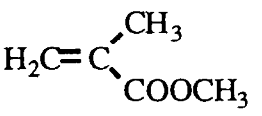
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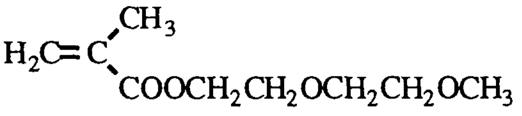
MMA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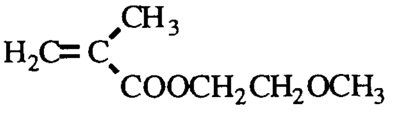
MEEMA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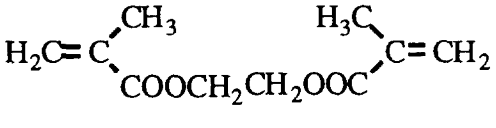
MEMA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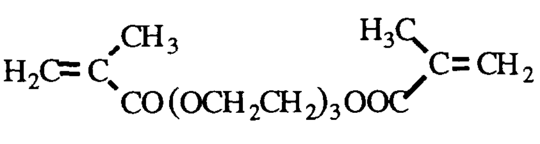
EGDMA


$H_2C{=}C(CH_3)CO(OCH_2CH_2)_3OOC(CH_3)C{=}CH_2$

TEGDMA

Figure 1 Structures of materials used

Table 1 Sample compositions, designations and unreacted methacrylate content

	Degree of conversion (% reacted methacrylate)		
		Swollen samples	
Sample composition (wt%)	Solid-state	Liquid-state	MAS
MMA 100%	96.8	96.7	
MMA 96.5% EGDMA 3.5%	94.3	93.5	94.7
MMA 95.0% TEGDMA 5.0%	96.5	95.5	
MMA 96.5%[a] TEGDMA 3.5%[a]	96.0	96.1	97.1
MMA 96.5%[a] TEGDMA 3.5%[a]	94.7	92.8	
MEMA 97.0% TEGDMA 3.0%	95.0	95.6	
MEEMA 100%	96.2	95.9	
PMMA 97.5%[b] TEGDMA 2.5%[b]	97.5	97.7	

[a] Two different preparations

[b] TEGDMA absorbed in PMMA—see text

Ltd., Poole, UK, methoxyethyl methacrylate (MEMA) was obtained from Lancaster Synthesis, Morecambe, UK, methoxyethoxyethyl methacrylate (MEEMA) was obtained from Monomer-Polymer & Dajac Laboratories, Inc., Feasterville, PA, USA, and tri-ethyleneglycol dimethacrylate (TEGDMA) was obtained from Aldrich Chemical Co., Ltd., Gillingham, UK; structures are shown in *Figure 1*. All were used as received, and were stored in the dark at ambient temperature prior to polymerization. Several homopolymer and lightly crosslinked copolymer systems were prepared as detailed in *Table 1* using a visible light initiator comprising a 50/50 (by weight) mixture of *dl*-camphoroquinone and 2-(dimethylamino)-ethyl methacrylate incorporated into the monomer at 2 wt%. Specimens were polymerized as discs 5 mm dia. × 2 mm thick in a plastic mould by illuminating with visible light from a Coltène® lamp, Coltolux curing unit Model 204, for *ca.* 60 s at ambient temperature (*ca.* 22°C). It was found advantageous for the more volatile, mobile monomers to perform a prepolymerization in a glass vial under natural light until the system had become sufficiently viscous to be retained in the mould without difficulty. The degree of polymerization using this method was somewhat irreproducible, but was sufficient for the purpose of comparing liquid- and solid-state n.m.r.

The final sample in *Table 1* was prepared simply by allowing TEGDMA (2.5% by weight) to penetrate

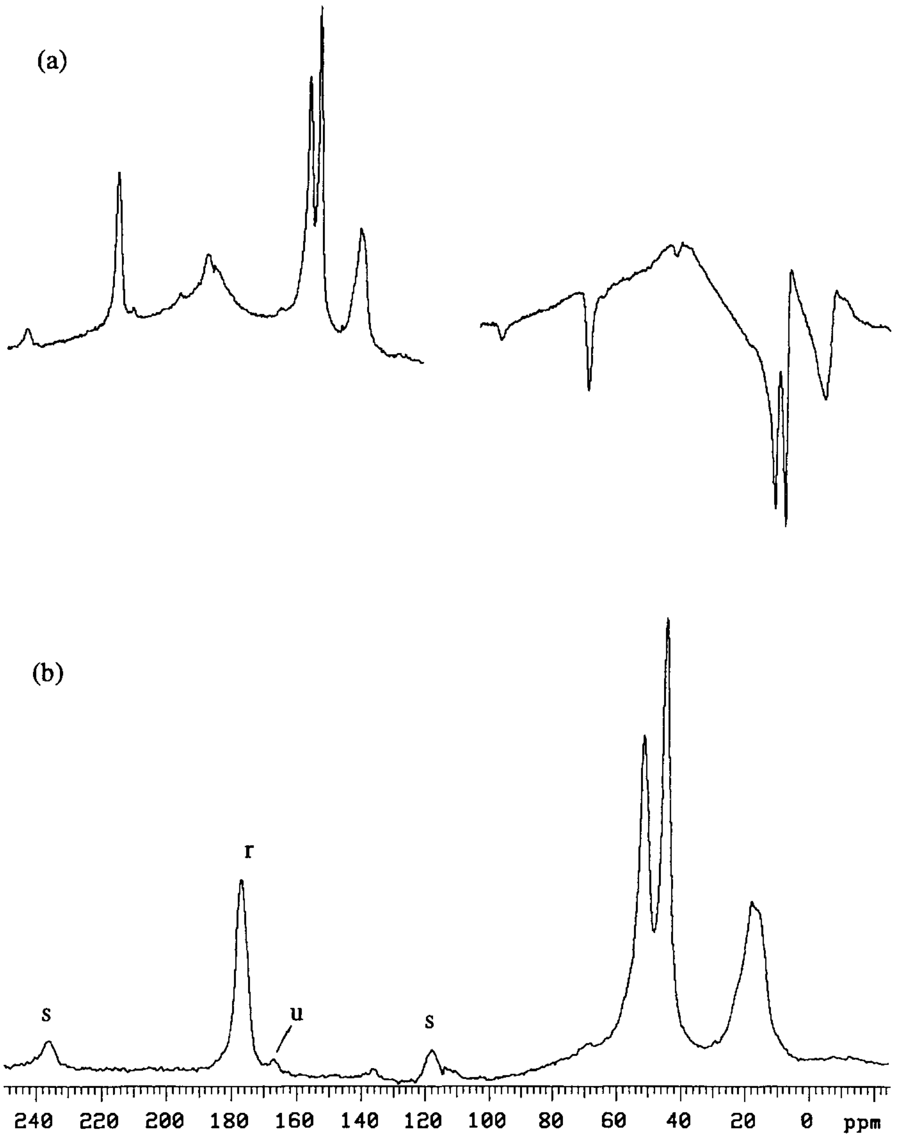


Figure 2 ^{13}C MAS/s.p.e. spectra of a MMA/TEGDMA copolymer (96.5 wt% MMA). (a) Spectra obtained with ^{13}C pulses of 90° (left) and 270° (right); (b) the difference of the two spectra in (a). The spinning speed was 4.8 kHz. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively; and the label s indicates spinning sidebands of the reacted carbonyl

poly(methyl methacrylate) at ambient temperature for three weeks; this sample was fully soluble in $CDCl_3$.

N.m.r. spectroscopy

^{13}C high-resolution spectra were obtained using a Varian Associates Unity 500 spectrometer operating at 125.7 MHz. Samples in 10 mm n.m.r. tubes were dissolved or swollen in $CDCl_3$ to which was added a small amount of hydroquinone inhibitor. The excitation pulse width was 10 μs corresponding to a 40° flip angle to give reasonably uniform excitation over the spectrum frequency range of 21 kHz. The nuclear Overhauser effect was suppressed by using inverse gated decoupling[3]. The question of the pulse interval required to allow complete relaxation is dealt with in Results and Discussion. Also as described below, the swollen lightly cross-linked samples showed fairly broad linewidths compared to solutions, and a spectral width and filter bandwidth of 50 kHz were used to minimize loss of signal between the end of the pulse and the start of data acquisition.

^{13}C MAS spectra were obtained using a Varian Associates Unity 300 spectrometer operating at 75.5 MHz and equipped with a Doty Scientific Industries 7 mm high-speed MAS probe. Solid-state spectra were obtained using s.p.e. excitation with MAS at *ca.* 4.8 kHz and a pulse interval[1] of at least 40 s; the total experiment time was *ca.* 8 h. The radio-frequency field strength used for ^{1}H d.d. was *ca.* 50 kHz. Spectrum deconvolution was performed using manufacturer-supplied software. Swollen gel spectra were obtained using s.p.e. excitation with MAS at *ca.* 2 kHz ^{1}H decoupling at a radio-frequency field strength of *ca.* 10 kHz, operating in single-frequency mode. Decoupling was applied only during the acquisition period giving spectra without nuclear Overhauser enhancement. The question of the pulse interval required to allow complete relaxation is dealt with in Results and Discussion. The gels were packed into the standard sample rotors with press-in Kel-F end caps.

RESULTS AND DISCUSSION

Suppression of background signals

In the previous paper[1], it was noted that a broad background signal was observed in s.p.e. spectra from

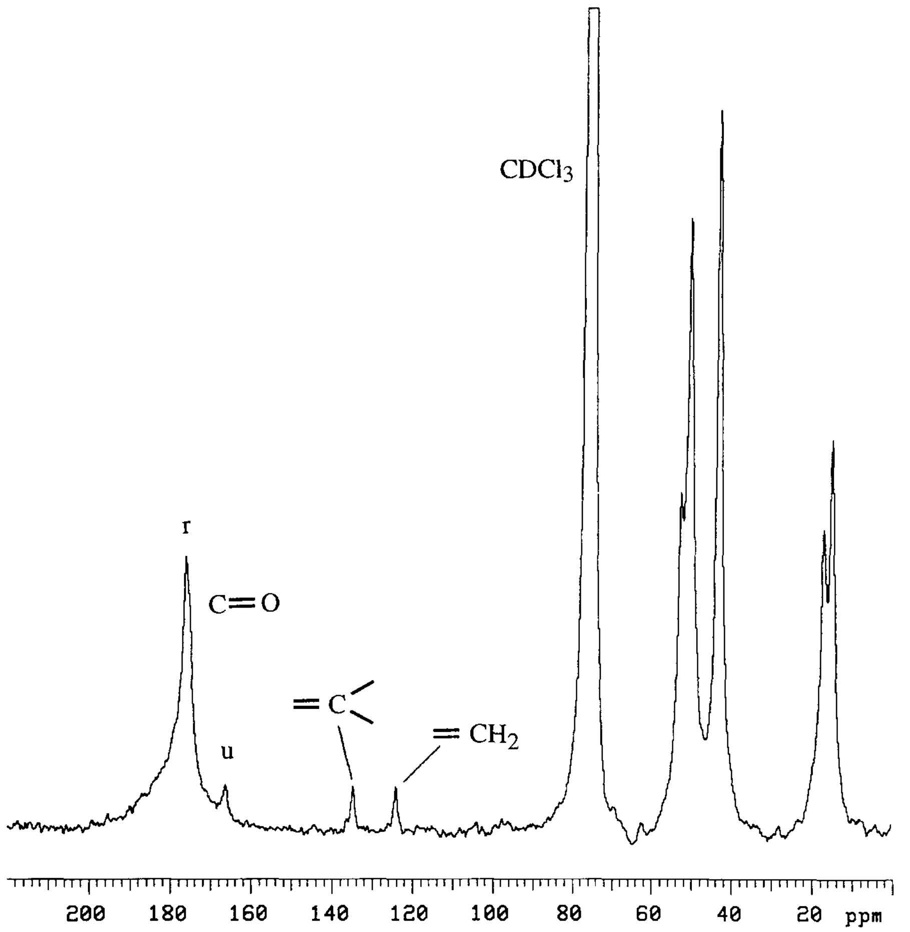


Figure 3 The liquid-state n.m.r. ^{13}C spectrum of a MMA/TEGDMA copolymer (96.5 wt% MMA) swollen in $CDCl_3$. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively

fluorinated polymer in the probe. This did not materially affect the analysis of the centreband carbonyl peaks which covered a narrow range of frequencies but did interfere with analysis of their spinning sidebands. The method used to reduce this background was the simple subtraction of two spectra obtained using 90° and 270° flip angles for nuclei within the sample rotor. The sample signals are of opposite sign in the two spectra, whereas the background signal arising from nuclei well outside the radiofrequency coil and therefore experiencing a much lower B_1 field strength, remains of the same sign and substantially of the same magnitude, and is largely eliminated by subtraction. *Figure 2* demonstrates the efficiency of this technique. In the difference spectrum, the polymer peaks were observed much more clearly than in a single s.p.e. spectrum.

Comparison of liquid- and solid-state techniques

The form and analysis of solid-state spectra have been described previously[1], and these will not be discussed in detail. Values of the proportion of reacted methacrylate groups are given in *Table 1*.

In 'liquid-state' spectra, the soluble samples showed the expected narrow lines and excellent resolution, but the lightly cross-linked gel samples showed broader lines due to motional restrictions as illustrated in *Figure 3* for a MMA/TEGDMA sample. Peaks from the polymer backbone were significantly broader than those from more mobile side-groups. In particular, the carbonyl peak from reacted methacrylate groups was much broader than that from unreacted groups. Sidebands arising from chemical shielding anisotropy in solid-state spectra were of course absent. In spite of the broadening, it was possible to obtain a reasonably accurate value for the degree of conversion from peak integrals using the reacted carbonyl and unreacted methacrylate carbonyl and alkene peaks; results are given in *Table 1*. It was found that the relaxation times of the unreacted methacrylate peaks were considerably greater than those of the reacted carbonyl peaks due to greater molecular mobility. For the alkene CH_2 peak, a pulse interval of 10 s was sufficient to allow complete relaxation, but for the alkene quaternary and unreacted carbonyl peaks, a pulse interval of at least 75 s was necessary.

The effect of MAS of gel samples is shown in *Figure 4* for the sample used in *Figure 3*. Compared to the 'liquid-state' spectra, a considerable reduction in linewidth of the backbone carbons was apparent, presumably indicating that the broadening observed in the 'liquid-state' spectra arose largely from residual dipole–dipole coupling which was not removed either by ^1H decoupling or by the molecular motion engendered by swelling by $CDCl_3$. However the sensitivity of this experiment was considerably less than that of the liquid-state experiment, partly because of the lower resonance frequency, partly because of the smaller sample diameter, and partly because of the lower degree of coupling between sample and receiver coil in the MAS probe. An interesting feature revealed by the increase in resolution is that in the

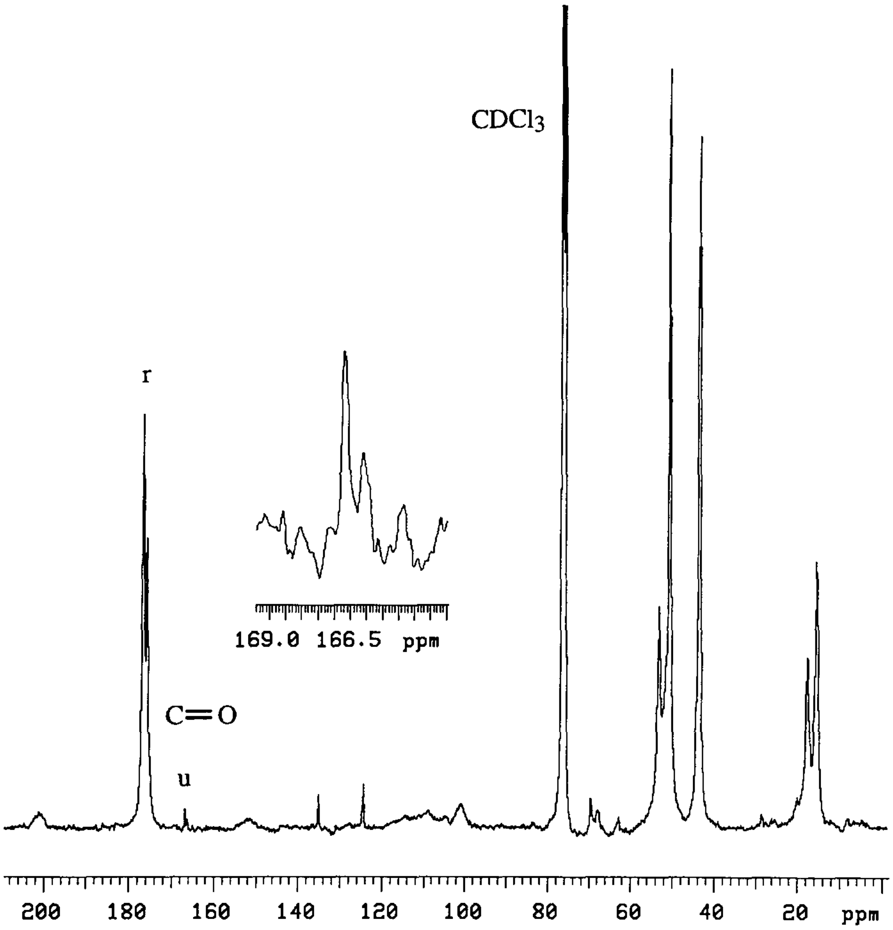


Figure 4 The MAS (2.2 kHz) ^{13}C spectrum of a MMA/TEGDMA copolymer (96.5 wt% MMA) swollen in $CDCl_3$. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively. The inset shows an expansion of the unreacted methacrylate carbonyl peaks

MMA/dimethacrylate systems, *two* peaks arising from unreacted methacrylate carbonyl carbons were clearly observed, as illustrated in the inset expansion in *Figure 4*. One of these presumably arises from unreacted MMA monomer and the other from dimethacrylate species which either remained entirely unpolymerized or which polymerized at only one methacrylate group. The lower frequency peak (165.9 ppm in EGDMA and 166.1 ppm in TEGDMAA) was identified as arising from the dimethacrylate component on the basis of comparison of its chemical shift with that of unreacted monomer in a sample of poly(methoxyethoxy-methacrylate), and also on the basis that its longitudinal relaxation time was significantly less than that of the higher frequency peak (166.7 ppm). From the fact that the intensities of the two peaks are comparable in spite of the 30-fold excess of MMA in the monomer mixture, it is clear that the extent of reaction of the MMA is much greater than that of the dimethacrylate.

The pulse intervals required for complete relaxation of the unreacted peaks were similar to those for the 'liquid-state' experiments. The degrees of conversion measured for those samples studied by this technique are given in *Table 1*.

Pairwise non-parametric statistical analysis of the solid-state and liquid-state measures of degree of conversion was made by the Wilcoxon matched-pairs signed-ranks test[4]. This yielded a two-tailed probability of 0.4008, thus confirming the null hypothesis that there was no significant difference between the two methods. Comparison of the data from liquid- and solid-state n.m.r. thus shows acceptable agreement between the two methods, indicating that solid-state n.m.r. does indeed provide a reasonably accurate method for determining the extent of reaction in these systems provided the s.p.e. technique with a sufficient long pulse interval is employed.

ACKNOWLEDGEMENTS

The authors are grateful to the EPSRC and the University of Manchester for the provision of n.m.r. facilities.

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