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^{13}C-NMR Parameters of some Poly[Oligo(Ethylene Glycol) Dimethacrylates]

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^{13}C chemical shifts, $T_{1\rho}(^1H)$, $T_{1\rho}(^{13}C)$ and T_{SL} have been measured for some solid poly(ethylene glycol) dimethacrylate polymers. The chemical shifts obtained are compared with those of the monomers and with those of poly(methyl methacrylate). As expected, the ratios of T_{SL} to $T_{1\rho}$ (^{13}C) correlate with the measured T_g values.

Introduction

Polymerization of dimethacrylate esters yields highly cross-linked, insoluble polymers. Because of this, and the early onset of gelation in polymerization the usual methods of obtaining high resolution ^{13}C NMR spectra, using dilute solutions, are not valid and solid-state methods must be used. We have examined poly[tri(ethylene glycol) dimethacrylate], (PTRIGMA), and poly[tetra(ethylene glycol) dimethacrylate], (PTETGMA), which are glasses and poly[poly-600 (ethylene glycol) dimethacrylate], (P600GMA), a rubbery gel in which the cross-link has a number-average molecular-weight of 600 (ca. 14 ethylene glycol units). We have assigned the ^{13}C resonances of these polymers.

The bulk properties of the poly[oligo(ethylene glycol) dimethacrylate] series show systematic changes as the length of the flexible oxyethylene cross-link is increased. The changes of some, at least, of these properties must have their origin in changes in mobility of different segments of the network. We have determined the spin-lock cross-polarization time (T_{SL}) and the rotating frame relaxation times for ^{1}H and ^{13}C ($T_{1\rho}$(H) and $T_{1\rho}$(C)), using methods described by Schaefer (1,2), for various sites on the methacrylate back-bones and oxyethylene cross-links of each polymer.

The value of $T_{1\rho}$(H) is a measure of the rate of spin diffusion among the protons in the sample. This rate is influenced by the spatial mixing of polymer chains and so is a measure of the homogeneity of the polymer sample (3). The polymers used in the present measurements were pure and fully cured. $T_{1\rho}$(H) is of less interest than it would be in partially cured, plasticized or blended polymers.

$T_{1\rho}$(C) is of greater potential value in the investigation of motion in different parts of the molecular structure of the network. It is sensitive to motions in the 10-50 kHz range. There are two mechanisms which may make major contributions to $T_{1\rho}$(C), spin-spin and spin-lattice relaxation. The former is not very useful because the proton pool can act as a relaxation sink (4). The spin-lattice mechanism, however, is a motional one and so is of great value in any investigation of molecular dynamics.

The extent of the contribution of spin-spin relaxation to $T_{1\rho}$(C) has been controversial. Some rejected $T_{1\rho}$(C) as a measure of molecular motion (5).However Schaefer (6) finds that average $T_{1\rho}$(C)s around 35kHz at room temperature, conditions pertinent to our measurements, are predominantly spin-lattice and hence motional in character for a wide variety of glassy polymers.

The spin-lock cross-polarisation time (T_{SL}) is sensitive to static interactions and is a measure of the time taken for polarisation of the carbons by the proton pool via static dipolar interactions.

Schaefer and coworkers (7) have noted that the ratio $T_{SL}/T_{1\rho}$(C) correlated well with the impact strength of glassy polymers. The T_{SL} component was suggested to be a measure of the chain segment's ability to accommodate the near static components of impact, but not the high frequency components. The $T_{1\rho}$(C) component measures chain segments capable of dissipating energy in the 50kHz range. It was noted by Schaefer that, despite many potential flaws in the presented arguments, a very good correlation did exist between $T_{SL}/T_{1\rho}$(C) and impact strength. Schaefer pointed out that this did not necessarily imply a functional dependence.

Experimental

^{13}C high resolution solution spectra were obtained on a Bruker WP80 NMR spectrometer, operating at 1.8T. ^{13}C MAS spectra were obtained at ambient temperature with a Bruker CXP300 NMR spectrometer operating at 7.05T. CP/MAS spectra were obtained using a cross-polarisation time of 1 ms, a recycle time of 5-10s, and a data acquisition time of 30 ms. The proton decoupling field ranged from 5 to 6.7 mT. Spin-temperature alternation and phase cycling were used. The Andrew-Beams rotor was made of boron nitride with a Delrin or Kel-F base. The spin rate was 2.4kHz and in some cases spinning sidebands were suppressed using the TOSS sequence (7). Chemical shifts are quoted relative to tetramethyl silane using the Delrin resonance as a secondary reference at 88.5 ppm.

The measurement of T_{SL} and $T_{1\rho}(H)$ was performed by varying the cross-polarisation time (t_{cp}) of the standard CP/MAS experiment. Values for T_{SL} and $T_{1\rho}(H)$ were extracted by performing a least squares fit of equation (1) to data obtained for the peak intensity of each resonance as a function of t_{cp}. Some 500 transients were averaged for each of 11 different t_{cp} values in the range 20μs to 7 ms.

$$I_i = [S_a - (S_a - S_b) \exp(-t_{cp\,i}/T_{SL})]. \exp[-t_{cp\,i}/T_{1\rho}(H)] + S_b \qquad (1)$$

where I_i = intensity of resonance after a cross-polarisation time $t_{cp\,i}$, S_a and S_b are disposable parameters in which S_a = maximum intensity in the absence of $T_{1\rho}$ relaxation, S_b = intensity in the absence a cross polarisation pulse.

$T_{1\rho}(C)$ values were obtained by the method discussed by Schaefer (7). A cross-polarisation time of 1 ms was used. ^1H spoiling pulses were not used.

The poly(methyl methacrylate) used was a commercial sample obtained from Polysciences Inc., Warrington, Pa.

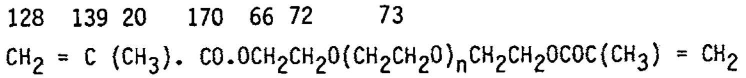
The dimethacrylate polymers were prepared from the appropriate monomers by radical polymerisation and were cast as sheets. Appropriately sized plugs were cut for the MAS samples.

T_g values were determined using a torsion pendulum; the methodology will be reported elsewhere.

Results and Discussion

1. ^{13}C Chemical Shifts of the monomers

We have found that very little change in solution ^{13}C chemical shifts occurs throughout the set of dimethacrylate monomers investigated. The average chemical shifts in $CDCl_3$ solution cited as ppm downfield of tetramethyl silane are shown in I.

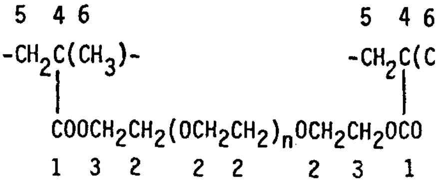


$$\overset{128}{CH_2} = \overset{139}{C}\ (\overset{20}{CH_3}).\ \overset{170}{CO}.\overset{66}{OCH_2}\overset{72}{CH_2}O(\overset{73}{CH_2CH_2O})_nCH_2CH_2OCOC(CH_3) = CH_2 \qquad (1)$$

Both resonances of the end - OCH_2CH_2 - groups were clearly resolved in all monomers investigated. All inner groups contributed to one resonance at 73 ppm. This is consistent with ^{13}C spectra at 20.1 MHz for poly(ethylene glycols).

2. Polymer ^{13}C chemical shifts

^{13}C chemical shifts for poly[oligo(ethylene glycol) dimethacrylates] can only be obtained in the solid state as these polymers are insoluble. However, in the early stages of cure, polymer resonances can be observed in solutions of the reaction mixture in dichloromethane. The most evident resonance is that of the acrylate backbone CH_2 at 44.7 ppm (C5 in II).



$$\begin{array}{lcl} 5\ 4\ 6 & & 5\ 4\ 6^{\bullet} \\ -CH_2C(CH_3)- & & -CH_2C(CH_3)- \\ \quad | & & \quad | \\ \multicolumn{3}{l}{\quad COOCH_2CH_2(OCH_2CH_2)_nOCH_2CH_2OCO} \\ \multicolumn{3}{l}{\quad 1\ \ 3\ \ 2\quad 2\ \ 2\quad 2\ \ 3\ \ 1} \end{array}$$

(II)

The gross chemical shifts are reported in Table 1. The assignments were made on the basis of those of poly (methylmethacrylate), PMMA, and, in case of those of oxyethylene, their relative integrated intensities and the assignments of oligo(ethylene glycols).

Somewhat lower resolution is observed in the solid polymer spectra. This is most evident in the CH_2O resonance at 70 ppm, which is that of all glycol resonances except C3(II), γ to the carbonyl. In monomer solution the β CH_2O is also resolved (I).

Table 1: ^{13}C chemical shifts of some glycol dimethacrylate polymers (II) PTRIGMA: n = 1, PTETGMA: n = 2, P600GMA: n = 12

GROUP		PTRIGMA	PTETGMA	P600GMA
1[a]	(CO)	178.3	177.4	176.3
2	(CH_2O)	70.2	70.3	70.9
3	(CH_2O)	65.1	67.8	66.3
4	(C)	56.4	55.3	56.7
5	(CH_2)	45.6	44.8	45.1
6	(CH_3)	29-15[b]	29-15[b]	29-15[b]

[a] see (II): [b] broad resonance, values define range.

The methyl resonance 6 is very broad and contains features consistent with steric triad structure. The observed methyl bandshape may be decomposed into 3 resonances of different linewidths, having chemical shifts as reported in Table 2.

Table 2: ^{13}C chemical shifts in ppm for glycol dimethacrylate polymer methyl resonance.

RESONANCE	PTRIGMA	PTETGMA	P600GMA
6a	25	22.5	22.3
6b	18.8	18.6	19.2
6c	17.5	16.2	16.7

These values are consistent with shift values reported for PMMA solutions and so may be assigned as follows; resonance 6a is isotatic (i), resonance 6b is heterotactic (h), and resonance 6c is syndiotactic (s) (8,9). No accurate determination of linewidth has been made at this time, however in all three cases, the width of the iso and syndiotactic resonances are approximately the same and are roughly double the width of the heterotactic resonance. It is interesting to note that the triad resolution is somewhat higher than in solid PMMA.

3. $T_{1\rho}(H)$

The mean values of $T_{1\rho}(H)$ for each polymer is presented in Table 3. We include the estimate for a PMMA determined under the same conditions.

Table 3: $T_{1\rho}(H)$/ms and standard errors for some polymers.

polymer	Delrin	PMMA	PTRIGMA	PTETGMA	P600GMA
$T_{1\rho}(H)$	.51	1.81	1.26	1.78	2.68
SE	.17	.52	.56	.51	1.05

The PMMA used in this determination has $\overline{M_W} \approx 790{,}000$ and a triad ratio i:h:s = 14:38:48. The mean $T_{1\rho}(H)$ is 1.81 ms. The dimethacrylates have $T_{1\rho}(H)$ ranging from 1.3 to 2.7 ms. The standard errors are interesting in that that of the rubbery P600GMA is nearly twice that of the other dimethacrylates, which are hard brittle glasses. There is an increase in $T_{1\rho}(H)$ with the increase in poly(ethylene glycol) chain length. The significance of this is as yet uncertain.

Table 4: $T_{1\rho}$(C)/ms for some polymers.

polymer group	PMMA	PTRIGMA	PTETGMA	P600GMA
1 (CO)	76	93	300	-
2 (CH_2O)	12[a]	6.3	6.1	5.3
3 (CH_2O)		6.0	5.8	1.6
4 (C)	30	10	14.8	4.1
5 (CH_2)	57	55	110	12
6[b] (hCH_3)	20	20	25	3.6

[a] for the $-OCH_3$ resonance, [b] determined at 19 ppm, i.e. the h triad resonance.

4. $T_{1\rho}$(C)

This parameter could be determined for all carbons except for the carbonyl group of the P600GMA. The values, presented in Table 4, all have standard errors of approximately 10%.

In general, the $T_{1\rho}$(C) values are in the order expected. The rubbery P600GMA has shorter $T_{1\rho}$(C) values for all resonances other than group 2 (CH_2O) for the P600GMA which is only slightly shorter than that of the other two dimethacrylates, suggesting that motion in the glycol crosslink is the same in all of them. This value is half that recorded for the CH_3O of PMMA.

The methyl $T_{1\rho}$(C) of P600GMA is also far shorter than for the glassy polymers. It is worth noting that for the heterotactic part of the methyl resonance, all glassy polymers had roughly the same $T_{1\rho}$(C).

5. T_{SL}

Values for all resonances that could be measured are presented in Table 5. As with $T_{1\rho}$(C), only values for h-CH_3 are given as not all those for i and s unit CH_3s could be calculated.

This parameter has an associated error of about 30%. This arises because of the comparatively few points dominated by T_{SL} in the fit. Thus, although general trends will be manifest, the nuances suggested by our data may not be accurate. Despite this, it is obvious that the P600GMA exhibits far longer T_{SL} values than do glassy polymers. As with

Table 5: T_{SL}/ms for some polymers.

polymer group	PMMA	PTRIGMA	PTETGMA	P600GMA
1 (CO)	.47	.31	.39	-
2 (CH_2O)	.048[a]	.029	.042	.84
3 (CH_2O)		.059	.030	.15
4 (C)	.095	.043	.017	.064
5 (CH_2)	.22	.23	.19	.81
6[b] (hCh_3)	.098	.17	.14	.40

[a] for the CH_3O resonance, [b] for the *h* triad resonance.

$T_{1\rho}$(C), the CH_3 values are the same for the glassy polymers. The acrylate backbone CH_2 is the same for the glassy polymers, but four times longer for P600GMA.

6. The ratio of T_{SL} to $T_{1\rho}$(C)

The values of this ratio, along with the measured glass transition temperatures (T_g) are presented in Table 6. Schaefer (1) has shown a correlation between this ratio for protonated main chain carbons and impact strength. The backbone methylene carbon (group 5) is therefore the initial target for comparison. There is an obvious rough correlation in that the 3 glassy polymers have values lying between 1.7×10^{-3} and 4×10^{-3}, whilst the rubbery polymer has a value of 7×10^{-2}. These values compare with that reported by Schaefer for PMMA of 1×10^{-2} for the backbone CH_2 resonance.

An even more striking correlation exists between $T_{SL}/T_{1\rho}$(C) for the bulk CH_2O resonance (group 2) and T_g. As it is the length of the crosslinking poly(ethylene glycol) chain that determines T_g within this set of dimethacrylate polymers, it is not surprising that this correlation should be most striking.

We would not expect an inverse correlation between the $T_{SL}/T_{1\rho}$(C) ratio determined at 295K and T_g to be quantitative as the bulk property (T_g) is not measured at the same temperature as the above ratio. The spectral distribution of motion for each group will alter with temperature so that the rigour of the correlation will alter.

Table 6: 10^3 $T_{SL}(C)/T_{1\rho}(C)$ for some polymers. Also noted are the T_g measured for each sample.

polymer group	PMMA	PTRIGMA	PTETGMA	P600GMA
1 (CO)	6.2	3.3	1.3	-
2 (CH_2O)	4.0^a	4.6	6.9	159
3 (CH_2O)		9.8	5.1	91
4 (CH_2)	3.2	4.3	1.2	15.6
5 (C)	3.9	4.1	1.7	68
6^b (hCH_3)	4.9	8.5	5.7	110
T_g/K	378	408	388	238.

Certainly, however, the fact that a correlation is observed suggests that the $T_{1\rho}(C)$ relaxation is dominated by molecular motion, not spin-spin interactions.

Acknowledgements

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