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Dynamic-Mechanical Properties and Cross-Polarized, Proton-Enhanced, Magic Angle Spinning ^{13}C NMR Time Constants of Poly[oligo(ethylene glycol) dimethacrylates]

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ABSTRACT: Dynamic-mechanical and fracture properties and proton-enhanced, magic angle spinning ^{13}C NMR time constants for polymers of the $CH_2{=}C(CH_3)CO(OCH_2CH_2)_xOCOC(CH_3){=}CH_2$ series (x = 1 to $\bar{x}$ = 22) and poly[tetrakis(ethylene glycol) diacrylate] have been measured. The effects of increasing length of the soft oxyethylene chain, $\bar{x}$, undercure (x = 1–4), and oxyethylene crystallization ($\bar{x}$ = 22) were observed. The results are interpreted in terms of the contributions of components of group motion to the cooperative motion of segments of the network which control the response to a macroscopic deformation.

Introduction

We present the results of dynamic-mechanical and fracture tests on glycol dimethacrylate networks prepared from a homologous series of monomers: $CH_2{=}C(CH_3)$-$CO(OCH_2CH_2)_xOCOC(CH_3){=}CH_2$. In the series the soft oxyethylene chains were cross-linked by hard methacrylate links. The increasing length, x, of the oxyethylene link is a measure of M_c, the molecular weight between cross-links. We have varied this from x = 1 in poly(ethylene glycol dimethacrylate) (PEGDMA) to a number-average $\bar{x}$ = 22 in P1000EGDMA.

The increasing flexibility of the network was due to both the decrease in cross-link density and the dilution of stiff methacrylate chains by flexible oxyethylene links. The trend was opposed by the onset of crystallization of the oxyethylene chain in P1000EGDMA and by the diminishing effects of residual monomer at ultimate cure in the glassy samples from PEGDMA to PTetEGDMA (poly[tetrakis(ethylene glycol) dimethacrylate]). Cross-polarized, proton-enhanced, magic angle spinning (CP/PE/MAS) ^{13}C NMR was applied to measure the unsaturation at ultimate cure and estimate the proportions that corresponded to free monomer. The PE/MAS ^{13}C NMR time constants T_{SL} and $T_{1\rho}(C)$ were also measured. These parameters are sensitive to molecular motion at and around the C-atoms responsible for the NMR line under observation.

Experimental Section

Materials. Ethylene glycol dimethacrylate (EGDMA), tris- and tetrakis(ethylene glycol) dimethacrylates (TriEGDMA and TetEGDMA), and tetrakis(ethylene glycol) diacrylate (TetEGDA) were obtained from Fluka. Bis(ethylene glycol) dimethacrylate

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Table I
Extent of Undercure at Ultimate Cure and Dynamic-Mechanical Properties of Poly(glycol dimethacrylates) (and One Diacrylate) as a Function of the Number of Oxyethylene Groups in the Soft Link of the Network ($\bar{x}$)[a]

	PEGDMA	PDEGDMA	PTri-EGDMA	PTet-EGDMA	P400-EGDMA	P600-EGDMA	P1000-EGDMA	PTet-EGMA
$\bar{x}$	1	2	3	4	9	13	22	4
cure, by PE/MAS NMR, %	85	82	88	98	100	100	100	100
constrained unsaturation, %	5	5	5	2	0	0	0	0
unconstrained unsaturation, %	10	13	7	0	0	0	0	0
T_g, °C		160*	135, 125*	115, 105*	−5, −12*	−35, −36*	−53	27, 20*
T_g half-width, °C			162	153	30	28	15	25
log (G'/Pa)								
at T_g + 50 °C		8.5*	8.3	8.1	7.2	7.0	6.8	8.1
at 20 °C		8.9*	9.0	9.0	7.5	7.0	6.8	8.2
tan δ, at T_g			0.10	0.11	0.51	0.55	0.27	0.25
log (G''/Pa) at 20 °C		8.1*	7.7	7.8	6.8	4.5	6.0	7.6
Poisson's ratio			0.20	0.25	0.41	0.30		0.50
T_γ, °C			−132	−132	−130	−133	−129	−129
tan δ, at T_γ			0.05	0.05	0.06	0.05	0.06	0.05

[a] Measured by a 1-Hz torsion pendulum or (*) dynamic mechanical thermal analysis at 0.33 Hz.

(DEGDMA) came from Polyscience, as did the oligo(ethylene glycol) dimethacrylate monomers: 400EGDMA, 600EGDMA, and 1000EGDMA, where the number indicates the number-average molecular weight of the oligo(ethylene glycol) link. Monomers were dried and stored over molecular sieves but were not deinhibited. It was ascertained that passing TetEGDMA through an activated alumina column to remove inhibitor had no significant effect on polymers prepared from it. The polymerizations were initated by *tert*-butyl 2-ethylperoxyhexanoate (Interox Australia) usually at 0.2% by weight.

Curing Procedures. Polymerizations were carried out under air-free conditions. It has been reported[1] that oxygen causes an increase in soluble polymer early in the cure and delays gelation to higher conversions. High purity, oxygen-free dry nitrogen was bubbled through the monomers to expel oxygen before the samples were sealed. The exact method of casting was dependent on the sample shape required. A sheet, 2 mm thick, suitable for dynamic mechanical analysis, was cast by Cowperthwaite's method[2] between glass sheets using Silastic tubing as a gasket. These sheets, crumbled, finely ground, or cut into disks could be used for other tests such as DSC and NMR measurements. Polymers were stored in vacuum desiccators—the higher homologues absorbed water readily.

The cure cycle depended on the monomer. The higher homologues, which yielded polymers that were rubbery at room temperature, required an initial temperature of 70 °C, increased in steps up to 150 °C. The lower homologues required an initial temperaure of 55 °C and postcuring at 150 °C. The limit to the postcure temperature is set by degradation, which is reported to set in above 200 °C.[2,3]

NMR Spectrometry. Details of PE/MAS ^{13}C NMR procedures and the assignments for PTetEGDMA have been published.[4] Assignments for other GDMA polymers are given in an earlier publication, but note that data for the acrylate backbone carbons is transposed in all tables.[5]

Dynamic-Mechanical Measurements. Torsion braid analysis was used in preliminary tests of cure cycles. When larger samples were required a curing pot which could be mounted on a torsion pendulum was used. The method used and that for determining the compression moduli have been described.[4]

Torsion pendulum tests of cured materials were carried out on 1.5 × 9 × 30 mm samples cut from cast sheet. The inertial arm was pulsed electromagnetically and the decay monitored by a light beam reflected from a mirror and detected by a photoresistor. The amplified signal was processed through a 12-bit A–D converter and a microcomputer. The pendulum had a natural frequency between 0.5 and 1 Hz. The mean deviation in T_g measurements was 3 °C; in the log decrement of the decay, Δ, 4.7%; and in the modulus, G', 4.73%, which are within the standards expected of these instruments.[6] Sample temperature was maintained by circulating dry N_2 at a controlled temperature.

Some samples were tested on a PolyLab Dynamic Mechanical Thermal Analyser (DMTA). Samples were scanned at 5 °C/min at 0.33, 3, and 30 Hz.

Differential scanning calorimetry was carried out on a Perkin-Elmer DSC2 as described.[4]

X-ray Laue and precession photographs were made with a Mo source operating at 45 kV and 20 mA and recorded by a reciprocal lattice explorer camera on Polaroid film.

Results and Discussion

Cure Characteristics. We could not find a cure cycle or casting geometry which yielded uncracked samples of PEGDMA. This appears to be a general experience,[7-10] attributed to the brittle nature of the polymers and the large contraction on polymerization (15.7 vol %[11]). The only report of a large uncracked sample would appear to be that of Atsuto and Turner,[12] obtained by slow, adventitious polymerization of monomer in the absence of added initiator. Most samples of PDEGDMA cracked during postcuring at 150 °C. Only one sample was suitable for testing on the torsion pendulum and by DMTA. P-, PD-, PTri-, and PTetEGDMA were rigid glasses, P400-, P600-, and P1000EGDMA were soft rubbers, and PTetEGDA was leathery at ambient temperature.

Ultimate Cure. All polymers were postcured at 150 °C until they showed no residual exotherm during DSC tests. PEG-, PDEG-, PTriEG-, and PTetEGDMA could not be driven to full cure by postcuring at 150 °C. This appeared to be the ultimate state of cure; continuing the DSC scan up to 277 °C produced no further exotherm even though residual unsaturation could be detected by PE/MAS ^{13}C NMR. As predicted,[13] these oligo(ethylene glycol) links are too short to give the networks sufficient flexibility for all vinyl groups to react. Within the dimethacrylates and diacrylates of our experience, those which are glassy at ambient temperature do not go to full cure.

In Table I two estimates of unsaturation are presented. Cure, by PE/MAS NMR, was calculated from the integrated intensity of the quaternary C resonance relative to the integrated intensity of all α-methyl resonances. The second estimate is based on the integrated intensity of the carbonyl resonance at ca. 168 ppm, assigned to unreacted methacrylate groups, relative to the total integrated intensity of the whole carbonyl resonance which includes that of saturated methacrylate groups at ca. 177 ppm. In this case we were able to distinguish between two types of unsaturated groups—constrained and unconstrained (Table I). The criterion of distinction is whether the group was sufficiently constrained from isotropic molecular tumbling to preclude cross-polarization of its C-atom by nearby protons during the pulse of the PE/MAS experiment.[4] Agreement between the two methods was good.

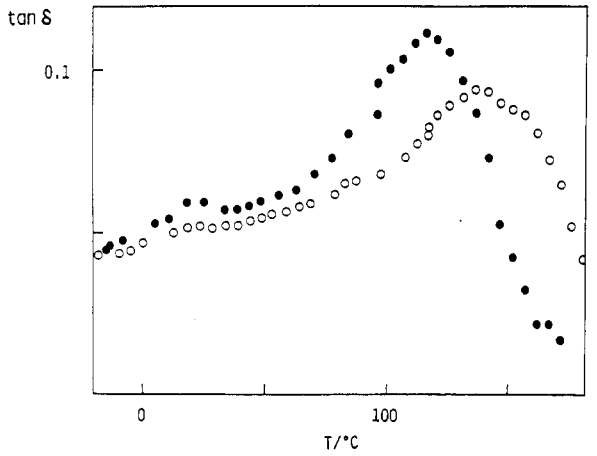

Figure 1. Dynamic-mechanical loss tangent (tan δ)–temperature (T) scans of PTriEGDMA (○) and PTetEGDMA (●) at ultimate cure measured on a torsion pendulum.

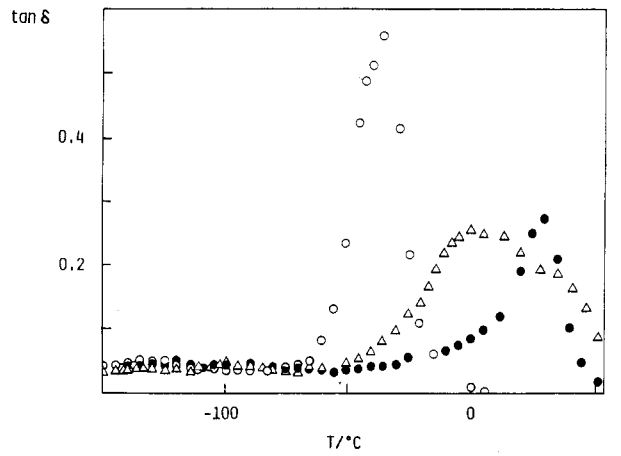

Figure 2. Dynamic-mechanical loss tangent (tan δ)–temperature (T) scans of fully cured P400EGDMA (△), P600EGDMA (○), and PTetEGDA (●) measured on a torsion pendulum.

Reasonable agreement was also found when samples of PTetEGDMA at different states of cure were tested.[4]

In tighter networks the constrained unsaturation can reasonably be identified with unsaturated pendant groups and the unconstrained with free monomer. Complications could arise with the higher homologues where the pendant double bond is on the end of a long flexible chain and its resonance might appear with unconstrained unsaturated groups. PTetEGDMA at ultimate cure has 2% unsaturation—all constrained. PEGDMA and PD- and PTriEGDMA at ultimate cure retained 5% constrained unsaturation and respectively 10, 13, and 7% unconstrained unsaturation. These are all glassy polymers and it is reasonable to assign unconstrained unsaturation to the free monomer.

Previous workers have reported undercuring at ultimate cure. The most unambiguous results were those depending on infrared spectroscopy of PEGDMA and PTriEGDMA (20 and 4% unsaturation, respectively).[12] Our results showed the distribution of this unsaturation and demonstrated that in the three lowest homologues some monomer molecules survived in an environment sufficiently fluid for the cross-polarization interaction to be averaged out. This was direct evidence supporting predictions that rigid monomers form inhomogeneous glasses with high density clusters of tight, fully polymerized networks and pools of monomer.[14] A computer model which simulates the formation of high density, fully polymerized clusters, monomer pools, and unsaturated pendant groups during cure gives a good fit if the observed, constrained unsaturation is assigned to pendant groups and the unconstrained to monomer pools.[15]

The Effects of Extent of Cure. We reported in an earlier paper[4] that some correlations could be observed between changes in bulk properties during cure and changes in the PE/MAS ^{13}C NMR time constants T_{SL} and $T_{1\rho}(C)$ of individual groups of the network.

The stiffening of the network early in the cure, manifested in the early sharp rise in T_g was, following Schaefer's interpretation of T_{SL} magnitudes,[16] associated with an increasing restraint of the low-frequency components of group motion while midkilohertz components were unaffected. Network stiffening after vitrification, manifested in the late sharp increase in T_g and a sudden rise in the compression modulus at ambient temperature,[4] is associated with a sudden constraint of midkilohertz components of group motion. We were observing the restraining of the high-frequency *group* motions which contribute to the low-frequency *cooperative* motions which determine the bulk response to low-frequency torsion or compression. In this context it should be recalled that the action of plasticizers in polycarbonates has been correlated with the release of midkilohertz components of group motion.[17]

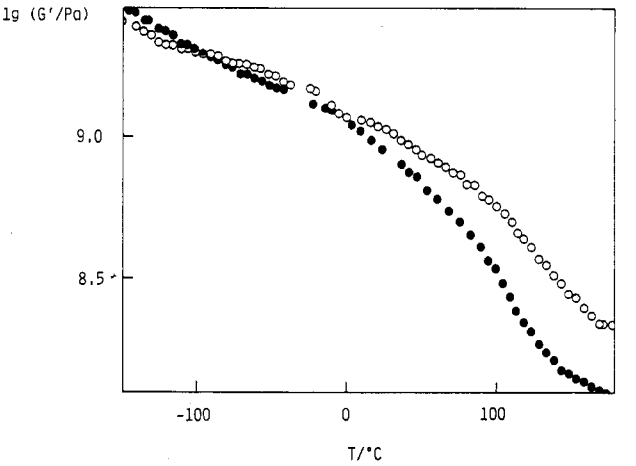

Figure 3. Temperature dependence of the shear storage modulus (G') for PTriEGDMA (○) and PTetEGDMA (●) at ultimate cure.

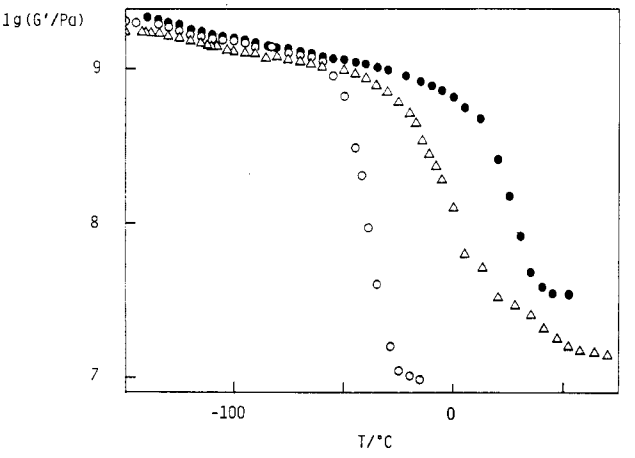

Figure 4. Temperature dependence of the shear storage modulus (G') for fully cured P400EGDMA (△), P600EGDMA (○), and PTetEGDA (●).

Dynamic-Mechanical Properties at Ultimate Cure. Figures 1–4 show the loss tangent, tan δ, and the shear storage modulus, G', as a function of temperature over the glass-transition region, determined on a torsion pendulum. The glass-transition temperature (T_g) is recorded in Table

I. In all five polymers the modulus–temperature curves, Figures 3 and 4, showed the beginnings of rubbery plateaux. The failure to observe this made previous workers[18,19] reluctant to assign values of T_g. Independent values of T_g were obtained for P400EGDMA and P600EGDMA by DSC: 259 and 240 K, respectively. The DSC trace of PTetEGDMA was featureless. A DMTA scan of PDEGDMA gave no conclusive evidence for the existence of a glass transition. The value of T_g given in Table I was obtained by extrapolation of the T_gs of six DEGDMA–600EGDMA copolymers obtained from dynamic-mechanical measurements. Values of G' and tan δ were taken from DMTA scans of PDEGDMA.

There is a smooth correlation of T_g with the number of oxyethylene groups ($\bar{x}$) in the glycol chain—a sharp decline from PD to P400EGDMA leveled out with P600- and P1000EGDMA (Table I). The decrease in T_g reflected both the decreasing cross-link density and the increasing flexibility of the oligo(oxyethylene) chain from PD- to P1000EGDMA and greater flexibility of an acrylate compared with a methacrylate chain (PTetEGDA and DTetEGDMA). The effects of residual monomer in PD- and PTriEGDMA are obscured by the other two effects. The storage modulus, G', 50 °C above T_g (Table I), declines in much the same way as T_g as the oxyethylene chain is increased but is unaffected by the change from an acrylate to methacrylate chain. The similarity of G' at ambient temperature of the three glassy polymers might be due to the effects of incomplete cure. The values are comparable with those of Katz and Tobolsky;[18] Atsuta and Turner[10] found a slightly lower room temperature value for PTriEGDMA by compression measurements: log (G'/Pa) = 8.8.

It has been suggested[20] that the height of the glass-transition peak in the tan δ–temperature plot depends on the number of kinetic units mobile enough to contribute to the transition. The breadth depends on the distribution of environments in which these units are located. Andrady and Sefcik[21] found that the glass-transition peak height in cross-linked poly(propylene glycol) increased as the mean chain molecular weight between cross-links, M_c, increased, leveling off in rubbery samples. Amine-cured epoxides behave similarly.[22] This is precisely what was observed (Table I) in the glycol dimethacrylate series: PTriEGDMA–P600EGDMA. The presence or absence of an α-methyl group on the acrylic link (Table I, PTetEGDMA and PTetEGDA) had a much smaller effect on peak height than it did on T_g. The half-width of the glass transition (Table I) declined with increasing chain flexibility, with the greatest change between the hard glasses (PTri- and PTetEGDMA) and the rest. The former obviously contained a much wider range of segmental environments and density domains than the rest.

The dynamic mechanical behavior of P1000EGDMA deviated from the pattern of the lower homologues in three respects. The increase in tan δ at T_g with $\bar{x}$ ceased; the peak height (Table I) was lower than those for P400- and P600EGDMA. There was also a steady rise in tan δ above T_g, from −37 °C upward (Figure 5), and an increase in the room temperature modulus during testing; log G' (20 °C) was 6.83 initially, 7.19 and 7.4 after successive subambient scans. These were the results of crystallization. The reversal of the increase of tan δ at T_g with increasing $\bar{M}_c$ was due to crystallinity augmenting the diminishing dynamic constraints of the cross-links. The effect has been observed with poly(ϵ-caprolactones).[23] Crystallization of poly[oligo(ethylene glycol) dimethacrylates] has been well established by Berlin and co-workers.[24-27] It involves the oxyethylene chain and occurs increasingly when the length of this chain increases from $\bar{M}_c$ = 1500.[25] Lamellar structures[25,26] have been reported.

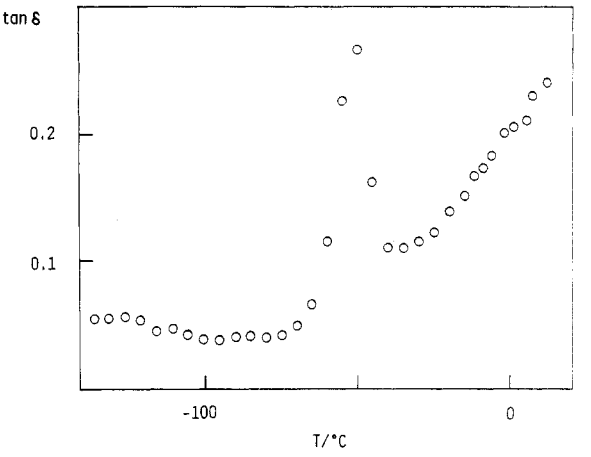

Figure 5. Dynamic-mechanical loss tangent (tan δ)–temperature (T) scan of fully cured P1000EGDMA measured on a torsion pendulum.

Crystallization of P1000EGDMA was manifest under a cross-polarizing, optical microscope and in X-ray Laue and precession photographs. P600EGDMA showed no trace of spherulites, though they have been observed in samples polymerized at −65 °C.[28] Only oligo(ethylene glycols) of MW 400 or higher are crystallizable.[29]

Young's storage modulus E' was determined by DMTA. T_g measured at 0.33 Hz corresponded well with torsion pendulum measurements. Poisson's ratio ν was determined from E' and G' from torsion pendulum measurements and the relationship $G' = E'/2(1 + \nu)$. They are shown in Table I.

The β-transitions, just visible at ~25 °C in the torsion pendulum scans of PTri- and PTetEGDMA (Figure 1), were more prominent in the DMTA scans at 0.33 Hz. DMTA scans of PDEGDMA also showed a β-transition in this temperature range; we could not cast a suitable sample for a torsion pendulum test. Linear regression analysis was used to estimate Arrhenius energies of activation for the β-transition from the transition temperatures at 0.33, 3.0, and 30 Hz. They were 105 ± 9, 128 ± 10, and 138 ± 8 kJ/mol for PD-, PTri-, and PTetEGDMA, respectively. An activation energy for the β-transition of PTriEGDMA of 103 kJ/mol has been obtained by dielectric measurements.[30] The β-transition is usually ascribed to localized group motion, in methacrylates to rotation of the –COOR group.[30-33] This is impossible in glycol dimethacrylate networks, nor does it seem likely that it is due to motion within the $-COO(CH_2CH_2O)_xCO-$ cross-links because the energies of activation increase with x, i.e., with increasing flexibility of these links. Furthermore T_β is not the same, lower in fact, in the diacrylates compared with the corresponding dimethacrylates.[32] It has been associated with the beginnings of vitrification[30] and of localized oxyethylene chain motion coupled with motion of the acrylate chain, the precursors of the larger scale cooperative motions responsible for the glass-transition.[31]

P400EGDMA showed a prominent tan δ peak at −90 °C and there were small peaks around −100 °C with PTri- and PTetEGMDA, due to moisture in the polymers. P600EGDMA showed no transition in this region unless water was deliberately introduced, when the peak appeared at −90 °C.

The next subambient peak, around −130 °C, is generic to the polymers themselves and listed as the γ-transition in Table I. The γ-transition in methacrylate polymers has

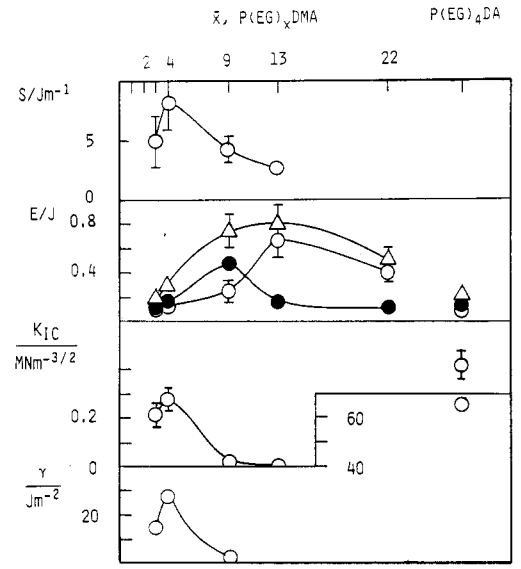

Figure 6. Fracture-mechanical parameters as a function of $\bar{x}$, the number of oxyethylene groups in the soft link of the networks of poly(glycol dimethacrylates), and one diacrylate at full or ultimate cure: short-cylinder, fracture-test parameters K_{IC}, the critical stress intensity, and γ, the surface energy of fracture; Hounsfield test impact strength, S; IIT energy, E, to fracture (△) and of initiation (○) and propagation (●).

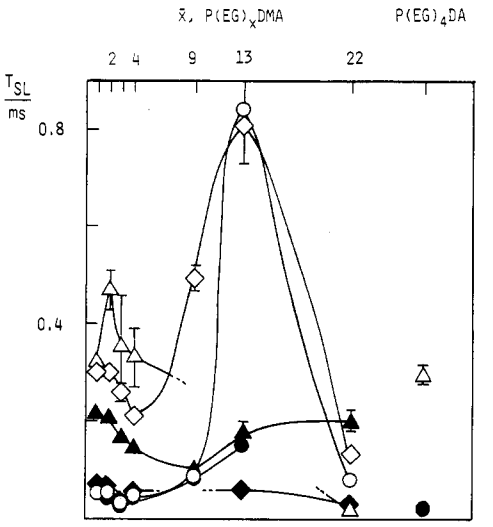

Figure 7. Spin-locked, cross-polarization time constants, T_{SL}, for full or ultimate cure poly(glycol dimethacrylates) and one diacrylate as a function of $\bar{x}$: inner CH_2O (○), end CH_2O (●), acrylate CH_2 (◆), quaternary C (◇), α-CH_3 (▲), and CO (△). Error bars are shown where the standard error, estimated from the rms deviation of the fit, overlaps the bounds of the symbol used for the data point.

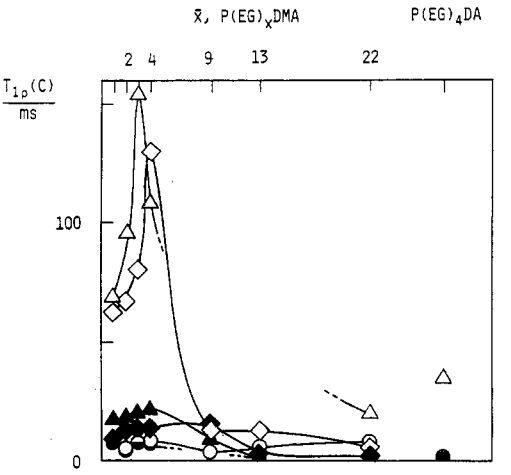

Figure 8. Relaxation time of ^{13}C resonances in a 60-kHz rotating field, $T_{1\rho}(C)$, plotted as in Figure 7.

been attributed to rotation of α-methyl groups and local motion within the -COOR group.[32,33] However, we found it present in PTetEGDA at much the same temperature as in PTetEGDMA. Berlin and Matvejeva[24] also found that this transition occurs at the same temperature in both dimethacrylate and diacrylate networks with oligo(ethylene glycol) ester cross-links. Comparison of the tan δ peak heights of PTetEGDA and PTetEGDMA (Table I) leaves no margin for a contribution from an α-methyl group. The increase in the series PTriEGDMA–P1000EGDMA is consistent with contributions from local motion within the $(-OCH_2CH_2)_n-$ link.

DMTA measurements on PTetEGDA gave an activation energy of 43.6 ± 4 kJ/mol to be compared with 46 kJ/mol for PTriEGDMA,[30] 45 kJ/mol for poly(2-hydroxyethyl methacrylate) and 29 kJ/mol for poly(*n*-propyl methacrylate).[33] If we follow Cowie's estimations[34] for poly[bis[methyl oligo(ethylene glycol)] itaconates] the energies of activation are consistent with motions involving only 2–3 adjacent bonds.

We conclude that the γ-transition observed around −130 °C in 1-Hz dynamic tests on poly(diacrylates) and poly(dimethacrylates) arises wholly, or almost wholly, from group motion in the oxyethylene links. No transition appears to have been observed between −180 and −5 °C in low-frequency dynamic tests on PMMA and poly(ethyl methacrylate).[33] However, transitions in this range have been observed when the carboalkoxy group is longer, e.g., poly(2-hydroxyethyl methacrylate) and poly(*n*-propyl methacrylate).[33] The dependence on the size of the group indicates that the transition may have its origins in cooperative small-group motion of the carboalkoxy chain, as occurs in the dimethacrylate networks. In the 20–30-kHz range the situation is different. PMMA shows two transitions in this temperature, which NMR measurements (see below) assign unambiguously to α-methyl rotation.

Fracture Properties. The impact strength, determined in a Hounsfield test; the critical stress-intensity for failure (K_{IC}) and the energy required to form the new surface (γ, the surface energy of fracture), determined in a short-cylinder fracture test; and the energy-to-fracture, partitioned into the proportions absorbed in crack initiation and propagation are shown in Figure 6. The latter measurements were made on a commercial instrumented impact tester (IIT) designed by ICI Australia, Scientific Instruments Division.[35]

The results for the series PTri- to P1000EGDMA are plotted in Figure 6 against $\bar{x}$, the number-average degree of polymerization of ethylene glycol residues in the soft links of the network. We could not prepare coherent samples of PEGDMA and PDEGDMA. Only the IIT was applicable to all the soft samples. The pattern of the parameters measured was also different. The Hounsfield and short-cylinder test parameters peaked at the last of the glassy samples (PTetEGDMA; T_g, 115 °C), whereas the energy-to-fracture peaked at P400- and P600EGDMA (T_g, −5 and −35 °C). The inversion of the proportions of this energy dissipated in initiation and propagation occurred between these two samples. The crystallites present in P1000EGDMA did not significantly impede crack propagation.

PE/MAS ^{13}C NMR Time Constants: T_{SL}, $T_{1\rho}(C)$. These are shown in Figures 7 and 8 as a function of the number of oxyethylene groups ($\bar{x}$) in the soft link of the

network. The increasing flexibility of this link, as $\bar{x}$ increased, had an indirect consequence, residual unsaturation at ultimate cure decreased to an insignificant 2% (none of it free monomer) by $\bar{x} = 4$, and two direct consequences, T_g dropped below the probe temperature (25 ± 2 °C) between $\bar{x} = 4$ and 9 and crystallinity appeared at $\bar{x} = 22$. The latter two were clearly reflected in the T_{SL} values of the CH_2O groups (Figure 7) but not in $T_{1\rho}(C)$ of these groups (Figure 8). The effect on T_{SL} is particularly strong at the resonance due to all the inner CH_2O groups of the $-OCH_2(CH_2OCH_2)_{x-1}CH_2O-$ links. The increase in mobility (as indicated by a lengthening of T_{SL}) was only slight with the first of the rubbery samples P400EGDMA (T_g = −11 °C) but then increased by an order of magnitude with P600EGDMA. This is consistent with our observation of changes in T_{SL} during cure of PTetEGDMA,[4] which showed that the decline in components of group motion which destroy the cross-polarization interaction was complete well before the vitrification point indicated by DSC or 1-Hz torsion pendulum measurements. With the onset of crystallinity (P1000EGDMA), T_{SL} of the inner CH_2O groups shortened by an order of magnitude as these groups became involved in crystalline domains.

The acrylate quaternary C showed a very similar pattern of behavior to the inner CH_2O groups. This may not be a coincidence. Lacking nearest-neighbour protons this group has longer T_{SL} values than CH_3, CH_2, and CH_2O groups. The cross-polarization of quaternary ^{13}C groups depends on protons of other groups.[16,36,37] The similarity of T_{SL} for quaternary C and the inner CH_2O groups in P600- and P1000EGDMA suggested that the cross-polarization of C depended on the latter group rather than the CH_2 or outer CH_2O groups. The interaction falls off in the inverse sixth power of the separation,[16] which implies that chain conformations bring the inner CH_2O protons close, through space, to the quaternary C. T_{SL} declined from PEGDMA to PTetEGDMA at both quaternary and α-methyl carbons. This can be attributed to a restriction of low-frequency components of the α-methyl rotation leading to an increased efficiency in the cross-polarization of both carbons by the methyl protons as the plasticization effects of residual monomer declined. Residual monomer had little effect on T_{SL} of other groups, in contrast to its strong influence on $T_{1\rho}(C)$. The α-methyl peak was complex, showing an incompletely resolved triad structure. We used the sharp peak in the middle of the resonance range,[4] which is usually taken as that of the heterotactic triad, but results could not be as accurate as those for the better resolved groups.

The acrylate backbone CH_2 showed no significant change in T_{SL}. The end CH_2O of the oxyethylene link echoed changes in T_{SL} of the inner groups at a much reduced level. $T_{SL}(CO)$ was between 0.2 and 0.3 ms for the four glasses and declined to 0.02 ± 0.01 ms for the partially crystalline P1000EGDMA. We could not obtain reliable values for the two rubbery samples.

The lengthening of T_{SL} with extent of cure[4] was attributed to the loss of isotropic group motion in the low-frequency range.[16] We are still inclined to follow this interpretation but note that Lauprêtre et al.[38] have suggested that fast motions (>10^5 Hz) may average out the dipolar interactions responsible for cross-polarization of ^{13}C during the *initial* spin–lock contact.

In the 60-kHz range CH_2O motions showed no significant change throughout the series (Figure 8). The changes came at the acrylate group; $T_{1\rho}(C)$ for quaternary C, CO, acrylate CH_2, and CH_3 lengthened as $\bar{x}$ increased through the four glasses and shortened through the rubbery samples. In this frequency domain there was no evidence that components of group motion were constrained by the onset of crystallinity.

The retardation of the $T_{1\rho}(C)$ relaxation through the first four members of the series (the glassy ones) can be attributed to the decrease in residual monomer concentration, the first three being undercured at ultimate conversion. It was observed most strongly at the quaternary and CO groups. The dampening of the group motions involved in the $T_{1\rho}(C)$ relaxation only occurs during the last 20% of the cure of TetEGDMA and is particularly strong at these two groups.[4]

In the samples that contained no residual monomer, PTet- to P1000EGDMA, the major shortening of $T_{1\rho}(C)$ of the acrylate groups, quaternary and CO in particular, occurred between PTet- and P400EGDMA, the point at which T_g drops below probe temperature. Acrylate motions in the 60-kHz domain are, in contrast to those of oxyethylene groups, of considerable importance in the activation of lower frequency, cooperative motions at the glass-transitions observed in the tests we applied. There would seem to be a significant damping of 60-kHz components at the α-methyl group at this point.

The small increase in $T_{1\rho}(C)$ of the α-methyl group in the postvitrification curing of TetEGDMA[4] was proportionally much less significant than those at other groups. Similarly, in the present work, $T_{1\rho}(C)$ of α-methyl echoed in diminution the changes at quaternary and carbonyl carbons. This is interesting because it is widely believed[39,40] that the rotation of α-methyl in poly(methyl methacrylate) dominates the relaxation of the other groups. The explanation is that we were observing *changes* in group mobility in the 60-kHz range as network rigidity decreased with increasing length of the oxyethylene links, or, in the curing experiments, rigidity increased as plasticization by monomer vanished. $T_{1\rho}(C)$ and its frequency domain are particularly sensitive to plasticization.[41] The α-methyl rotation is not greatly affected by changes in network mobility in this frequency range and so cannot be responsible for the changes at other groups. The importance of network rigidity is demonstrated by the $T_{1\rho}(C)$ values for PTetEGDA which were shorter at all comparable groups than those of PTetEGDMA. The effect of the presence, or absence, of α-methyl on network flexibility was manifest—direct group-to-group relaxation mechanisms were not.

There remains the question of the role of α-methyl transitions in PMMA. An answer can be obtained by comparing recent 50-MHz $T_1(C)$ measurements by Gabrys, Horii, and Kitamura[42] with the 37-kHz $T_{1\rho}(C)$ (supported by $T_2(C)$) measurements of Wobst.[43] Comparing values for typical stereorandom, syndiotactic-rich PMMA, prepared seemingly by radical polymerization, $T_1(C)$ for the α-methyl resonance showed a broad minimum centred at 2 °C, while $T_{1\rho}(C)$ showed well-defined minima at −85 and −136 °C (supported by corresponding steps in the $T_2(C)$–temperature plot). If we accept Wobst's assignment of the lower $T_{1\rho}(C)$ transition to the syndiotactic *triad* and compare it with the broad 50-MHz transition for syndiotactic-rich polymer, an Arrhenius energy of activation of ~35 kJ mol^{-1} is obtained. In a 1-Hz measurement this transition would then appear around −146 °C. The uncertainty of these values must be wide—there is reason to believe (see references cited by Gabrys[42]) that the energy of activation is lower, which would place the transition well below the range of reported 1-Hz measurements.[33]

The dependence of $T_{1\rho}(C)$ on network rigidity and plasticization by monomer have bearing on another in-

teresting problem: the extent to which the $T_{1\rho}$(C) measurement reflects spin–lattice and spin–spin relaxations.[16,38,40,44,45,46] Whatever the relative contributions of the two, the spin–lattice term is sufficiently prominent for $T_{1\rho}$(C) to be a sensitive monitor of group mobility.

Correlations between Group Motions and Bulk Properties. The prime influence on group mobility is the increase in network flexibility as M_c is increased. This simple pattern is modified by two other effects: plasticization by residual monomer augments group mobility and crystallization constrains low-frequency components of groups whose cross-polarization depends on the oxyethylene groups. Despite these complications it can be seen that the constraints on 60-kHz and low-frequency components of group motion are relaxed over different ranges of M_c and different groups relax at different points in the series. Precise, simple, general correlation of bulk properties to group mobility is unlikely. However, it is possible to discern the effects of some components of group motion on some properties. The decline in T_g and storage modulus, G', with increasing M_c corresponds with increasing activity of the 60-kHz components of acrylate backbone units and with low-frequency components of the oxyethylene links, *except* where the trend is overridden by the sensitivity of $T_{1\rho}$(C) to plasticization by residual monomer and T_{SL} to crystallization. Neither of these effects shows its influence on T_g or G'. The loss modulus, G'', and tan δ at T_g are influenced by the onset of crystallinity in P1000EGDMA, and this is associated with constraints on low-frequency components of the CH_2O group motion due to crystallization.

The properties defined to express the results of impact and fracture tests are complex in terms of macroscopic mechanics. This must also be true in terms of segmental and group dynamics. Nevertheless one correlation has been reported; Schaefer[16] found a bilinear positive correlation between $T_{SL}/T_{1\rho}$(C) of main-chain groups and the notched-sample impact strength for seven linear glassy polymers having very different chemical structures. We were only able carry out impact tests on two glassy polymers. The values of $T_{SL}/T_{1\rho}$(C) for PEGDMA and PDEGDMA exceeded those for PTetEGDMA at all groups. Since the former pair were so brittle that coherent test samples could not be cast, it seems likely that the correlation with impact strength observed with linear glassy polymers does not apply to tight, rigid network polymers. Schaefer et al.[16] believed that $T_{SL}/T_{1\rho}$(C) would not be very relevant to fracture in rubbery polymers. Our results confirm that finding.

Conclusions

It is axiomatic that differences in the bulk properties of structurally similar polymers arise from differences in the mobilities of particular structural groups. The measurement of PE/MAS ^{13}C NMR time constants, described in this and the previous paper,[4] shows that in favorable circumstances it is possible to be specific about the contributions of certain groups. Changes in the bulk properties through the poly[oligo(glycol) dimethacrylate] series coincide with significant changes in the 60-kHz components of the motion of the acrylate backbone groups. On the other hand, 60-kHz motions in the oxyethylene do not change significantly and are not relevant to the changes in bulk properties. In the low-frequency domain (if Schaefer's interpretation of the T_{SL} magnitude[16] is followed), the mobility of the oxyethylene links is most important. During cure[4] low-frequency components dampen well before vitrification and change little thereafter; 60-kHz components remain unaffected through vitrification and are dampened very late in the cure, coincidental with the rise in bulk modulus. The dampening of low-frequency group components corresponded to a sharp rise in T_g early in the cure; that of the 60-kHz components corresponded to the final sharp rise in T_g.

The PE/MAS time constants in revealing changes in some components of group motion indicate the contribution of these groups to the gross macroscopic behavior. They reveal the dampening of components and groups responsible for the stiffening of the network as M_c is decreased and that, in the 60-kHz domain, it is the acrylate group motions which are dampened not those of the shortening oxyethylene links. When the oxyethylene links are sufficiently long to crystallize, it is their low-frequency components which are dampened not the 60-kHz component. The effects of crystallinity are more strongly evident in T_{SL} than in any other dynamic property. Of the bulk dynamic properties, only the loss modulus and tan δ at T_g are obviously affected.

Changes in bulk properties can be seen to be associated with changes in the mobility of particular groups in particular frequency ranges. What is lacking is precise correlation of the defined parameters of dynamic-mechanical analysis, fracture mechanics, and impact testing with specific components of group motion. Correlations between T_g and the 25 °C values of $T_{1\rho}$(C) and T_{SL} do not meet this specification; T_g is only the vaguest of indicators of network mobility at ambient temperature. While disappointing, the absence of correlation is not altogether surprising. The response to a macroscopic deformation depends on cooperative segmental motion to which the group motions contribute. We may have seen this in the coincidental sharp rise of T_g (1 Hz) and $T_{1\rho}$(C) late in the cure of TetEGDMA[4]—a loss of 60-kHz group motions which contribute to cooperative segmental response at lower frequency. However, we would not expect such effects to be manifest in general, particularly when the macroscopic deformation is mechanically complex. Furthermore, $T_{1\rho}$(C) and T_{SL} measurements at one temperature sample only two frequency ranges. To fill the gaps by variable-temperature measurements involves an order-of-magnitude extension of observation and processing time.

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Registry No. PEGDMA (homopolymer), 25721-76-0; PTriEGDMA, 25101-31-9; PTetEGDA, 57619-91-7; PTetEGDMA, 25101-32-0; PDEGDMA, 25101-18-2; PPEGDMA (SRU), 9051-34-7.

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Quasi-Elastic Light Scattering from Ternary Mixtures of Polystyrene/Poly(dimethylsiloxane)/Solvents

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ABSTRACT: Ternary mixtures of polystyrene/poly(dimethylsiloxane)/tetrahydrofuran (PS/PDMS/THF) and PS/PDMS/toluene were investigated by quasi-elastic light scattering experiments. In THF, the increment of refractive index of PDMS is practically zero, and one "sees" only the PS. One obtains two relaxation modes which are characterized unambiguously for concentration around c^*. In toluene, which is a solvent with "zero average contrast", only one relaxation mode has been observed. This is in perfect agreement with theoretical predictions published earlier. It shows that in many cases the presence of two modes is normal, and artifacts or special dynamical features do not have to be invoked.

I. Introduction

In recent years, there has been a growing interest on the dynamic properties of polymer mixtures in bulk and in solution.[1-7] Most of the works published in the literature dealt with compatible (such as polystyrene/poly(vinyl methyl ether) (PS/PVME))[8-11] or slightly incompatible (such as polystyrene/poly(methyl methacrylate) (PS/PMMA))[12-15] mixtures in solvents presenting no contrast with one of the polymers. The idea is that, when one polymer is not "visible", the dynamics of the only visible polymer is observed and the interpretation is easier. At infinite dilution of the visible polymer, one observes its self-diffusion coefficient at a finite concentration of the other polymer, i.e., in a matrix which is a solution of the invisible polymer. These studies were limited to the determination of the scaling laws of the self-diffusion coefficient as a function of the molecular weight of the visible polymer and the concentration of the matrix. All the reported experiments dealt with a system far from the "cloud point" or the phase separation concentration.

In this work, since we have at our disposal a theory[4] which allows us to envisage all the experimentally possible cases, we have focused our attention on the following points:

(i) In ternary systems, two modes characterize the time evolution of the intermediate scattering function, $S(q,t)$, given by

$$S(q,t) = A_c e^{-\Gamma_c t} + A_I e^{-\Gamma_I t} \quad (1)$$

q is the scattering wavevector ($q = (4\pi/\lambda_0)n_0 \sin(\theta/2)$), λ_0 is the wavelength of the incident radiation, θ is the

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