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Nature of Residual Unsaturation during Cure of Dimethacrylates Examined by CPPEMAS ^{13}C NMR and Simulation Using a Kinetic Gelation Model

G. P. Simon,[†] P. E. M. Allen,* D. J. Bennett, D. R. G. Williams, and E. H. Williams[‡]

Departments of Physical and Inorganic Chemistry and Chemical Engineering, University of Adelaide, Box 498, G.P.O., Adelaide, S.A. 5001, Australia. *Received December 13, 1988*

ABSTRACT: Residual monomer, constrained and unconstrained, and pendant double bonds have been assayed by CPPEMAS ^{13}C NMR during the postgelation stages of the cure of ethylene glycol dimethacrylate. A simulation using a kinetic gelation model fitted the experimental values well and was extended to make predictions about the pregelation stage and the size and distribution of monomer pools. Estimations of cure by DSC did not correlate linearly with residual unsaturation, though they did so during the cure of tetrakis(ethylene glycol) dimethacrylate.

Introduction

We have reported on the application of CPPEMAS ^{13}C NMR to follow changes in the mobility of structural groups during the cure of poly[tetrakis(ethylene glycol) dimethacrylate] (PTetEGDMA)[1] and through the series of cured oligo(ethylene glycol) dimethacrylates from brittle glasses to soft gels.[2] In both cases our prime concern was the correlation of bulk properties with group mobility.

We are here concerned with the nature and organization of residual unsaturation in the dimethacrylate network. This is of particular importance in the first four homologues, the ones that form glassy networks, because these cannot be cured to a state where there is no residual unsaturation.

In the CPPEMAS ^{13}C NMR experiment ^{13}C nuclei are magnetized by cross-polarization from adjacent polarized protons (proton enhancement). It is a short-range, through-space interaction that only occurs if molecular tumbling of the groups is constrained. The CPPEMAS ^{13}C resonance is therefore only observed from groups where isotropic motion is constrained. Monomer in pools large enough to permit unconstrained molecular tumbling is not observed in the CPPEMAS ^{13}C NMR experiment. These unconstrained molecules are, however, directly observed in normal ^{13}C NMR experiments where ^{13}C nuclei are directly polarized, while resonances of constrained molecules and groups are so broadened as to be imperceptible. Thus it is possible to distinguish and follow the decay of monomer and unsaturated groups in constrained and unconstrained environments.

In order to support our interpretation of these results we performed computer simulations of network curing using a kinetic gelation model (KGM).[3-6] KGMs take note of the intrinsic tendency to inhomogeneity in radical polymerizations where diffusion control restricts the mobility of the reactive centers and leads to eventual isolation. Previous authors have been mainly concerned with the gelation point. Our concern is to follow the parameters of the system to full cure. We have added features to allow for variation in modes of initiation and range of mobilities for the reactive species.

A KGM for a divinyl system starts with a lattice where each point represents a monomer molecule (a tetrafunctional unit). Initiator radicals (monofunctional units) are introduced randomly in pairs, more than one unit apart to avoid geminate recombination. A radical chosen at random (functionality one or three) is allowed to attempt propagation in a random direction with a neighboring lattice site. The results of this test depend on the functionality of the unit sited there. If it is one or three, termination occurs; if two or four, propagation; and if zero, no reaction. At each termination or propagation event the functionality of each lattice point is reduced by one. Each attempted propagation step is treated as a unit of time. The program ends when all lattice points are reduced to zero functionality (complete reaction), all odd (radicals) or even functionalities (monomer) are consumed, or odd and even lattice points are isolated from each other by zero lattice points. This third event is the commonest way in which the program ends. In a two-dimensional model a square lattice is used and a radical has four possible directions to test for reaction. In the three-dimensional model, a cubic lattice and six test directions are used.

The main advantage of a KGM treatment is that it simulates the fundamental tendency to inhomogeneity arising from the independent growth of clusters. It can also simulate the persistence of pools of monomer to high states of cure and predict their size, number, and distribution.

Experimental Section

Details of the purification of TetEGDMA, curing procedures, assignment of ^{13}C NMR resonances, and differential scanning calorimetry have been reported previously.[1,2] EGDMA, from Fluka, was cured between plate glass into 3-mm sheet in an air-circulating oven at 388 K after displacement of dissolved oxygen by bubbling nitrogen and addition of 0.5 wt % *tert*-butyl 2-ethylperoxyhexanoate, from Interox (Australia).

CPPEMAS ^{13}C NMR spectra were obtained with a Bruker CXP300 spectrometer operating at 75.47 MHz with disks cut from cast sheet stacked in boron nitride Andrew-Beams rotors spun at 2.6 kHz at a probe temperature 298 ± 3 K. A proton decoupling field of 6 kHz, a carbon spin-lock field of 60 kHz, a recycle time of 5 s, and a $\pi/2$ carbon pulse of 4.2 μs were applied. Chemical shifts are cited relative to the CH_2O resonance of the Delrin rotor cap taken to be 88.5 ppm.

Percentage cure, defined as percentage of double bonds consumed, was estimated by two NMR spectrometric measurements. The integrated intensity of the polymer backbone quaternary carbon resonance was compared with that of all α-methyl resonances (polymer, monomer, and pendant unsaturated groups) and those of the carbonyl resonances of monomer and unsaturated pendant groups with the total intensity of the carbonyl region.

Programs simulating network formation were written for a VAX computer in Fortran using RANF, the VAX's random number generator, to simulate the diffusion of reaction centers. The program based on a KGM in three dimensions (MOD3DPLT) used

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* Address correspondence to this author at the Department of Physical and Inorganic Chemistry.

[†] Present address: Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia.

[‡] Present address: D298, Varian Associates Inc., P.O. Box 10800, Palo Alto, CA 94303.

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a 100 × 100 × 100 matrix, though for most purposes this was reduced to 30 × 30 × 30. The program plotted percent species of each functionality, percent cure, and number of live radicals as a function of number of iterations (simulating cure time). MOD2DPLT was a two-dimensional version of MOD3DPLT. Both models release a pair of radicals linearly after every predetermined number of iterations. Additional programs were written to simulate initiation by instantaneous release of radicals and by an initiator decaying exponentially. MOD3DSLOW simulated the case where a new radical was released once the previous one was trapped.

The standard initiation procedure for MOD3DPLT, releasing a radical pair every 100 iterations, was selected because it gave the best fit when tested against the time dependence of radical concentration and extent of cure of the data of O'Donnell and Sullivan,[7] on bis(allyl ethylene glycol) carbonate, when we simulated an initiator concentration of 3%. This initiator concentration was selected as standard for simulations because it gave conversions at ultimate cure in the range observed in our measurements of PEGDMA and PTetEGDMA.

The percent cure at ultimate conversion was not greatly dependent on procedures for simulating initiations. When 3% initiator was assumed, ultimate cure was 88% for MOD3DPLT when radical release was set at every 100 iterations; 92% when this was lengthened to 500 iterations, 94% for MOD3DSLOW, and 92% for a program releasing radicals according to an exponential decay law with an initiator decay constant of $1.7 \times 10^{-5}\ s^{-1}$, subject to standard deviation of ~1% in each case. In all programs the conversion at ultimate cure declined with decline of the assumed initiator concentration.

The programs included "folding over" of the matrix so that a radical reaching the side of the matrix was permitted a full coordination sphere of lattice points by including a required number from the opposite face. In this way radicals were kept within the field of the matrix.

The simple model permits a radical to react only with an unsaturated group in its first coordination sphere (CS1). To allow the possibility that network flexibility might bring the radical into contact with more remote unsaturated groups, the radical is permitted to solicit the second coordination sphere (CS2) if unsuccessful at the CS1 lattice point. If still unsuccessful it could be permitted to solicit CS3 and so on, if desired. The randomly selected direction of the initial test on the first coordination sphere is maintained in testing subsequent spheres and the whole series of tests are counted as one unit of time. By varying the number of coordination spheres permitted to be accessible, various degrees of network flexibility can be stimulated. The model has been adapted to allow for the presence of a solvent.[8] It counts cyclization but is not capable of distinguishing a ring-closing addition from an ordinary addition.

The POOL3D and its two-dimensional analogue POOL2D were developed to characterize heterogeneity in the curing network. The programs search the functionality matrix and count the number of units of a given functionality in clusters or pools. Our prime interest is in monomer pools and their size and size distribution. A unit was defined as being in a pool if it possessed a nearest neighbor in that pool.

Listings of programs MOD3DPLT and POOL3D are available.[8]

Results and Discussion

Nature of the Residual Unsaturation. We have reported previously that PTetEGDMA at limiting cure contained 2% residual unsaturation detectable by CPPEMAS ^{13}C NMR measurements even when DSC showed no further exothermic reaction on heating to 520 K.[1] Methacrylate esters of higher oligo(ethylene glycols) could be taken to full cure, but not PEGDMA and poly[bis- and tris(ethylene glycol) dimethacrylates].[2] Korolev et al.[9] predicted the short oligo(oxyethylene) chains would be insufficient to permit the degree of network flexibility at high cure to allow all vinyl groups to be accessible for reaction. Atsuta and Turner,[10] using infrared spectrometry, found residual unsaturation at ultimate cure in PEGDMA and PTriEGDMA.

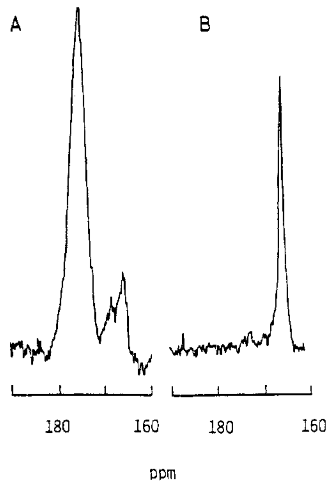

Figure 1. Carbonyl resonances of a PEGDMA network, which DSC measurement indicated was 98% cured, showing (A) CPPEMAS ^{13}C NMR spectrum of constrained groups, saturated ones at 176.3 ppm and unsaturated ones at 166.5 and 168.6 ppm and (B) ^{13}C NMR spectrum with unconstrained unsaturated groups at 167 ppm.

We measured the intensities of the resonances of a particular group in constrained environments, where the short-range ^{1}H–^{13}C cross-polarization interaction operates, as in the conventional CPPEMAS experiment, and in unconstrained environments where the interaction is nullified by isotropic molecular motion. With appropriate calibration the amounts of a particular group in each environment can be estimated.

During the cure of TetEGDMA, while unconstrained unsaturation declined monotonically to zero concentration, constrained unsaturation stayed in the 8–10% range from 40–70% cure and declined to a residual 2% at ultimate cure.[1] The carbonyl resonances of reacted and unreacted methacrylate groups were the basis of this estimation.

Unreacted monomer will be recorded as unconstrained saturation provided that it is an environment that permits molecules to tumble isotropically. Unreacted monomer *molecules* in liquid pools will appear as unconstrained unsaturation, but it is uncertain what minimum number of molecules a "pool" must contain to ensure that isotropic tumbling occurs. An unreacted methacrylate group attached to the network by a long flexible link might also appear as unconstrained unsaturation. This has been demonstrated in our laboratories.[11]

In the case of PTetEGDMA, the oxyethylene chain attaching an unreacted methacrylate group to the network is unlikely to be sufficiently long to permit free isotropic tumbling. We therefore assigned the unconstrained unsaturation resonance to monomer molecules.[1,2] In the absence of evidence to the contrary, we assigned the single constrained unsaturation resonance to unreacted methacrylate groups attached to the network (pendant double bonds).

The situation with PEGDMA was somewhat different. The constrained and unconstrained carbonyl resonances are shown in Figure 1. The sole carbonyl resonance in the spectrum of unconstrained groups appears at 167 ppm, which corresponds to that in the conventional high-resolution ^{13}C NMR spectrum of pure liquid monomer. The constrained-group pulse sequence shows a resonance at 176.3 ppm, which corresponds to a carbonyl in a saturated methacrylate group. We assign this to network backbone units.

There are also two resonances corresponding to carbonyls in constrained, unsaturated methacrylate groups, a

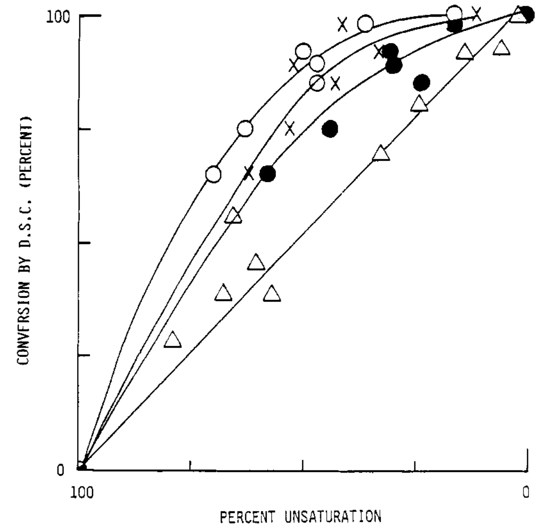

Figure 2. Percent cure estimated by DSC, assuming a linear relationship with the magnitude of the residual exotherm, plotted against percent residual unsaturation based on the polymer quaternary ^{13}C NMR intensity and that of all α-CH_3 resonances (×) and on CO resonances of saturated and unsaturated groups: total unsaturation (○) and unconstrained unsaturation (●) for EGDMA and total unsaturation for TetEGDMA (△).[1]

major peak at 166.5 ppm and a minor one at 168.6 ppm. It was assumed that these arose from pendant double bonds and constrained monomer. In order to make assignments, a model compound of an EGDMA unit incorporated in the network at one end only, $CH_2{=}C(CH_3)COOCH_2CH_2OCOCH(CH_3)_2$, was synthesized. Its ^{13}C NMR carbonyl resonances were at 165.8 and 175.4 ppm (referred to cyclohexane at 26.4 ppm).[12] EGDMA, using the same reference, showed a single carbonyl resonance at 165.8 ppm. This demonstration that an unsaturated group carbonyl resonance of EGDMA is not shifted when the other end is polymerized leads to the assignment of the 166.5 ppm resonance in the CPPEMAS ^{13}C NMR spectrum of cured resins (referred to Delrin[1]) to pendant double bonds. As a consequence the minor resonance at 168.6 ppm must be assigned to constrained monomer molecules. The significant chemical shift from the resonance of unconstrained monomer (167 ppm) must arise from monomer–network group interactions.

Changes in Unsaturation during Cure. Percent cure during the postvitrification stage estimated by DSC, the ratio of the integrated ^{13}C NMR resonances of the polymer quaternary carbon to that of all α-methyl carbons, and the ratio of carbonyl resonances of unreacted and reacted methacrylate groups are shown in Figure 2. The spectrometric estimations do not correlate linearly with that by DSC. Furthermore at the limiting attainable cure—set to 100% in the DSC assay—the NMR methods reveal 11 and 17% residual unsaturation.

The estimation by DSC exceeded spectrometric estimations by a significant amount. DSC assay estimates conversion relative to the limiting attainable conversion.

Unconstrained unsaturation (Figure 2) declines monotonically to vanish at limiting cure. Pools of monomer in liquidlike environments disappear by polymerization in the last quarter of the cure. Earlier experiments with EGDMA[2] used a lower curing temperature (55 °C) with postcure (150 °C). Unconstrained unsaturation persisted, so our current practice, cure at 65 °C without postcure, is more efficient.

Percent constrained unsaturation in curing EGDMA remains effectively constant at 18.8 ± (sd) 1.8% over the last five data points in Figure 2. Pendant unsaturated groups and constrained monomer remain at constant concentration. Whether these are steady states with polymerization of constrained groups balanced by unconstrained groups becoming constrained or they are groups trapped in a constrained environment earlier in the cure is uncertain. The more flexible PTetEGDMA network cured to higher conversion.[1] Percent constrained unsaturation remained reasonably constant (8.6 ± 0.8%) over the second and third quarters of the cure, declining to 2% in the final quarter. This is reminiscent of the slowly shifting steady states observed in many free radical reactions.

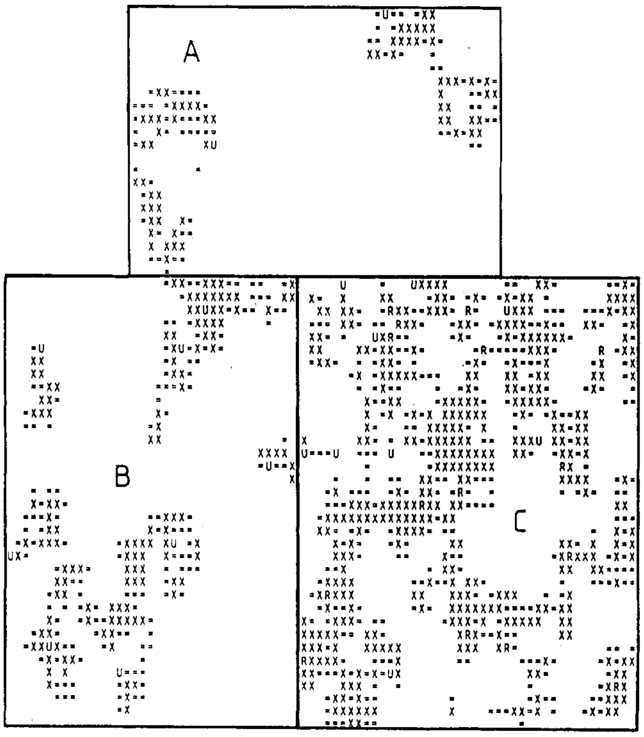

Figure 3. Printouts of representative sections of a standard MOD2DPLT simulation at (A) 3% cure, (B) 12%, and (C) 36%. Unreacted monomer is presented by blank lattice sites, fully polymerized units by X, incorporated units carrying pendant double bonds by =, unsaturated radicals by U, and saturated radicals incorporated in the network by R.

Simulation of Network Formation. The presence of both constrained and unconstrained monomer over the last 60–70% of the cure indicates heterogeneity. Simulations using a KGM strongly supported these indications and suggested further that the seeds of heterogeneity were sown very early in the cure. This is illustrated by the results obtained using MOD2DPLT on a 100 × 100 matrix, releasing a pair of radicals every 100 iterations. An initiator concentration of ca. 3% was assumed.

The inherent inhomogeneity is manifest very early in the cure (<0.2%) by the formation of isolated branched molecules carrying large numbers of pendant double bonds. These are the precursors of the highly branched molecules shown in Figure 3A, which is a section of the matrix at a simulation corresponding to 3% cure. These highly unsaturated, highly branched, compact molecules correspond very closely to the concept of the β-polymer postulated 40 years ago by Berlin (cited in ref 13).

Beyond 3% cure the reactive centers propagate within and around the β-polymer particles formed initially. As Malinský[14] proposed, there is an enhanced concentration of pendant unsaturated groups (=) in the vicinity of growing radicals (R/U) at low conversion, which leads to polymerization in these local regions going largely to

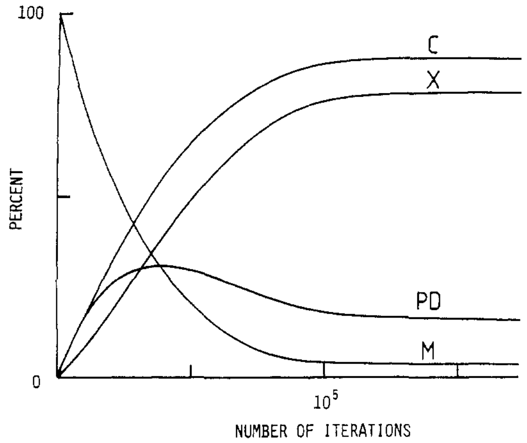

Figure 4. Percent cure (C), residual monomer molecules (M), pendant double bonds (PD), and fully polymerized units (X) as a function of reaction time simulated by the number of iterations, using the standard MOD3DPLT program.

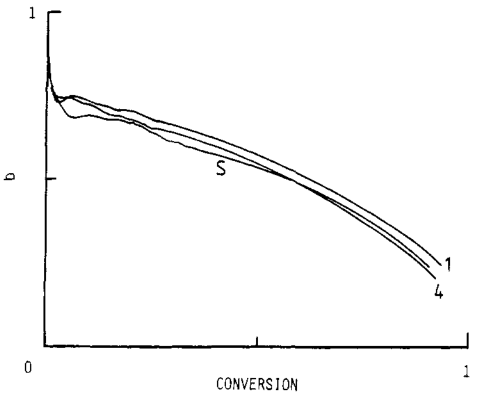

Figure 5. Fraction of units incorporated in the network carrying pendant double bonds (*b*) as a function of cure simulated by MOD3DPLT with standard parameters, with radicals permitted to solicit their first coordination shell (1), up to the fourth coordination shell (2), and by MOD3DSLOW (S).

completion. This is apparent at 6 and 12% cure (Figure 3B).

The pendant double bonds congregate at the interface between particles of network polymer (clusters of X units) and the sea of unreacted monomer molecules (blank). A KGM simulation by Boots and Pandey[15] yielded a similar picture. At 24% cure the particles are beginning to grow together. Their fringes of pendant double bonds play an important part in linking them together. At 36% (Figure 3C) the system has undergone phase inversion from particles in monomer to monomer pools within a continuous, though inhomogeneous, network polymer. It is at this stage that monomer and radical became trapped among network units and immobilized.

The MOD2DPLT simulation reproduces a major feature of experimental conversion curves of dimethacrylate and analogous monomers: a decline in rate to a limiting cure short of complete cure.[7,9,13,16,17]

The standard parameters adopted for simulations using MOD3DPLT were a 30 × 30 × 30 matrix, 3% initiator, and release of a radical pair after every 100 iteration steps. Figure 4 shows MOD3DPLT cure profiles obtained with standard parameters. While percent fully reacted and percent unreacted monomer units rises and falls, respectively, to steady values, that of pendant unsaturated groups rises to a maximum early in the cure before falling to a steady value. In subsequent correlations comparison is made with percentage cure.

The rate of formation of fully saturated units shows a slight acceleration in the early stages. MOD3DPLT and MOD2DPLT do not simulate the kinetic gel effect, so this acceleration arises from the statistics of the simulated propagation steps. The printouts of MOD2DPLT (Figure 3) give a good qualitative analogue of the organization of the various structural units during cure, cf. limiting contents of monomer and pendant double bonds 9 and 19% (2D) and 3 and 16% (3D), maximum content of pendant double bonds 26% (2D) and 30% (3D), but do not give as accurate a prediction as MOD3DPLT of the extent of cure at which organizational changes occur.

The *percentage* of *reacted monomer units* incorporated in the network *which carry pendant double bonds*, *b*, was simulated by the MOD3DPLT. the cure profiles (Figure 4) show that up to 30% cure, most reacted monomer units carry pendant double bonds and then fully reacted units become dominant. Figure 5 shows the parameter *b* as a function of percent cure simulated by the standard MOD3DPLT program modified to permit radicals to solicit coordination shells up to CS4 and by MOD3DSLOW. All predict a rapid early decline in *b*, which is over by 5% cure, followed by a steady state, which slowly declines at a slowly accelerating rate to ultimate cure. The steady-state values of *b* predicted lie in the range 68–75%, and are attained within 3–6% cure. In standard MOD3DPLT simulation, *rate of increase* in *number* of pendant double bonds begins to decelerate at ca. 20% cure while the decline in their actual number set in ca. 30% (Figure 4).

Galina et al. report that 70% of reacted ethylene dimethacrylate groups carried pendant double bonds in the pregelation state.[18] This corresponds with the range of values of *b* predicted by our models in the steady-state domain. Their results were, however, obtained in diluted monomer.

Kloosterboer et al.[19] investigated the inhomogeneity of diacrylate and dimethacrylate photosensitized polymerization beyond the gelation point using DSC and solvent extraction of unreacted monomer as experimental techniques and a simulation based on a KGM model.[15,19] The simulation of the dependence of *b* on state of cure has a very similar profile to our simulations (Figure 5); however, the experimental values differ significantly, showing a prolonged steady state and a late decline. Experimental origins of the misfit have been discussed.[15,19]

The parameter *b* is a valuable adjunct to the overall percentages of various unsaturated groups, since the bulk of pendant double bonds reside in the polymer clusters and they constitute the bulk of the unsaturation within these clusters. When they react the network tightens and radicals and monomer molecules become trapped.

The prime reason for permitting radicals to solicit lattice sites beyond the first coordination shell was to simulate the increasing flexibility of the networks in the higher homologues of PEGDMA. In the standard MOD3DPLT simulation the ultimate cure increased from 87% to 94, 96, and 97% as CS2, CS3, and CS4 were made successively accessible. The corresponding decreases in limiting monomer and pendant double bonds were 4% to 1, 0.7, and 0.5% and 16% to 9, 6, and 4% respectively. However, the cure profiles did not diverge until 30% conversion, so only beyond this conversion does the probability of finding unsaturation in the first coordination shell begin to decline significantly. Within polymer clusters, pendant groups will be the predominant unsaturated species at this conversion. The overall number of pendant unsaturated groups begins to decline at 30% conversion (Figure 4).

Examination of Polymer Cluster Growth. POOL2D and POOL3D can be used to detect polymer clusters (con-

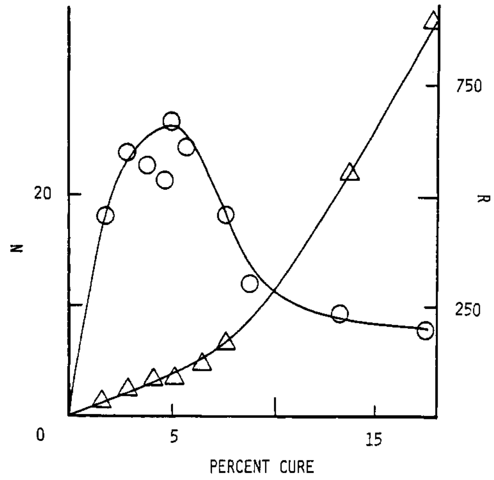

Figure 6. Number of polymer particles N (○), their average size R, and the number of lattice points occupied (△), as a function of cure simulated by the standard POOL3D program.

sisting of units of functionality 0, 1, 2 and 3) in simulated cures, count them (N), and estimate their size (R the average number of lattice sites occupied by a cluster). POOL2D showed a sudden and substantial increase in particle size and a concomitant decrease in number between 18 and 36% percent cure in accordance with the MOD2DPLT printouts. Jan et al.[6] found that modeling in three dimensions predicted an earlier gel point than simulation in two dimensions and a much earlier coalescence of clusters. POOL3D also predicts that events occur much earlier (Figure 6). Prior to 5% conversion the number of clusters rises rapidly while their mean radius rises slowly (Figure 6). Thereafter the rate of coalescence of clusters overtakes the rate of initiation and a sharp decline to a lower number sets in. The mean radius rises at an accelerating rate during the sharp decline in N. Extending the range of accessible lattices from CS1 to CS4 led to an earlier coalescence (at ca. 4% cure) but little change in the cluster growth profile (R).

Roschupkin et al.[20] have estimated the increase in size of particles in the polymerization of tris(ethylene glycol) dimethacrylate. They found that the most rapid increase in mean radius occurred concomitantly with a sharp decrease in number of particles, but they did not pick up the earlier increase in number of particles. Their estimations of size and number depend on many approximations, but the qualitative agreement of their results with our simulation increases the confidence that can be placed in both.

Comparison of Simulated Networks with the Structure of Real Networks Determined by CPPEMAS ^{13}C NMR Spectrometry. The simulated parameters were generated by running standard MOD3DPLT set to terminate at various extents of cure. Pendant double bonds were assumed to be constrained from tumbling isotropically. POOL3D was then set to analyze the size and number of pools of monomer. It was assumed that all monomer molecules in pools in which all molecules were in contact with polymer units were also constrained, that is all molecules in pools of six or less. All members of pools of seven or more molecules were unconstrained. Figure 7 shows that there was an excellent fit of the simulated cure profile of unconstrained unsaturation to that determined experimentally for PEGDMA. The simulation underestimated the unconstrained unsaturation of PTetEGDMA in the latter stages of the cure. The experimental values of percentage and unsaturation were estimated from NMR of the carbonyl groups. The simulation predicts an ultimate cure of 87% compared with 83% observed with PEGDMA and the observed 98% with PTetEGDMA. In both cases the residual unsaturation was constrained.

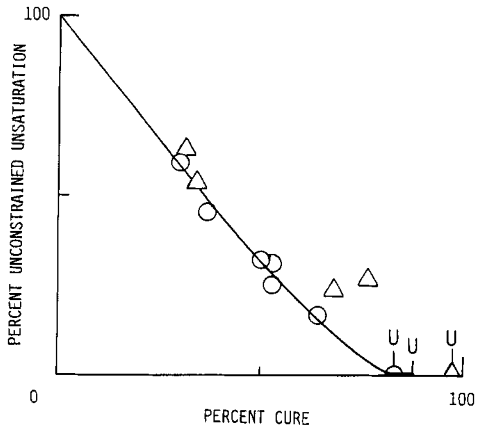

Figure 7. Cure profiles of unconstrained unsaturation estimated by ^{13}C NMR spectrometry for EGDMA (○) and TetEGDMA[1] (△). The curve is the cure profile generated by standard MOD3DPLT and POOL3D simulations, assuming that monomer molecules in pools of seven or more members are unconstrained. U indicates observed and simulated values at ultimate conversion.

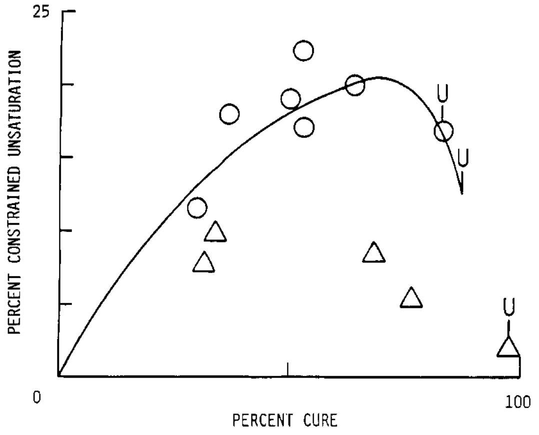

Figure 8. Cure profiles of constrained unsaturation estimated by CPPEMAS ^{13}C NMR for EGDMA (○) and TetEGDMA[1] (△) and by simulation (line). U represents values at ultimate conversion.

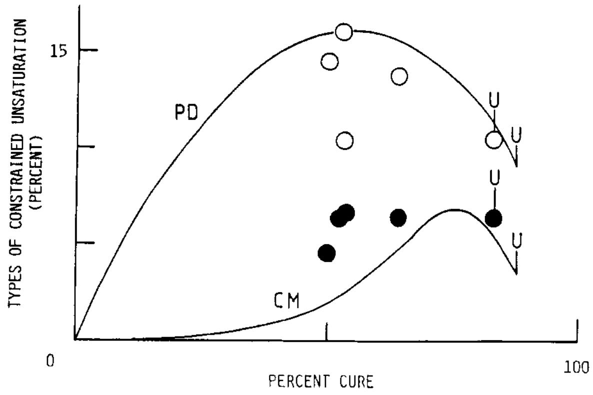

Figure 9. Simulated cure profiles of pendant double bonds (PD) and constrained monomer molecules (CM), with spectrometric estimations from the 166.5 (○) and the 168.6 ppm (●) resonances.

Figure 8 shows the simulated cure profile for constrained unsaturation, a reasonable fit to the experimental data for PEGDMA but not for PTetEGDMA. PEGDMA is a highly rigid network and the standard parameters of MOD3DPLT, appropriately, permit reaction only between radicals and unsaturated groups on adjacent sites. We attempted to allow for the greater flexibility of the

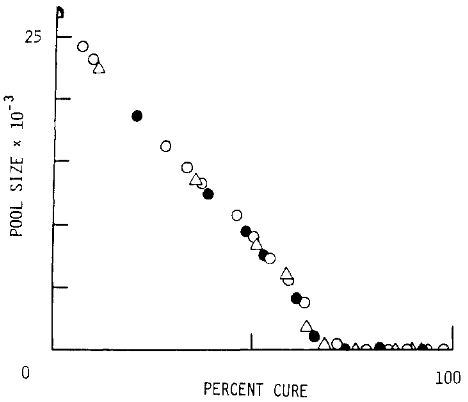

Figure 10. Mean size of monomer pools simulated by standard POOL3D on a 30 × 30 × 30 matrix with radicals permitted to solicit their first coordination shell (○) and out to the second (△) and fourth (●) shells.

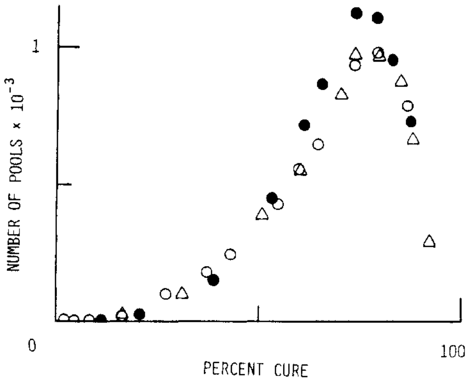

Figure 11. Number of monomer pools simulated by POOL3D with different initiation procedures: radical pair release every 100 iterations (●) and every 500 iterations (△) and by MOD3SLOW, with all other parameters standard.

PTetEGDMA network by permitting reaction with groups in CS4. The maximum of constrained unsaturation was reduced to 17%, a poor fit to the observed maximum for PTetEGDMA of 9%. Adjustment of the radical release rate and use of MOD3SLOW also failed to fit to the PTetEGDMA cure profile. Figure 9 shows the simulated cure profiles of double bonds and monomer in pools of six or less molecules and of the constrained unsaturated groups responsible for the 166.5 and 168.6 ppm resonances. Comparison of the simulated and experimental data would indicate that the major resonance, 166.5 ppm, arises from pendant double bonds. This is consistent with the assignment on the basis of the spectrum of a model compound. The chemical shift of constrained monomer from liquid monomer arises from molecule–network group interactions. This supports what was an entirely arbitrary distinction for the purpose of modeling that constrained monomers were those in pools where all were in nearest-neighbor contact with network groups.

Figures 10 and 11 show the results of POOL3D simulation of the size and number of pools. The cure profile of mean size (number of lattice points occupied by a pool) is very similar to that of the simulated and experimental profiles of unconstrained unsaturation for PEGDMA (Figure 7). The only difference is that the steady decline to very small values extrapolates to the base-line at 80% cure in Figure 7 but 70% in Figure 10. The reason is that monomer molecules in larger than average sized pools will still contribute to unconstrained unsaturation after the mean size has declined below the minimum value. The profile in Figure 10 represents data points simulated using CS1, CS2, and CS4. There was no distinction between them. The number of monomer pools reached its maximum value at 80% cure (Figure 11). The number profile was independent of variation of coordination spheres accessible but slightly dependent on the radical release program used.

Conclusions

Our CPPEMAS ^{13}C NMR spectrometric measurements provide direct evidence of the type and distribution of residual unsaturation at high cure in glassy glycol dimethacrylate networks. This is most relevant to the chemical aging of the resin: pendant unsaturated groups are not susceptible to leaching out; constrained monomer will be less susceptible than unconstrained. The distribution of residual monomer will affect physical and mechanical properties, both through plasticizer action and microheterogeneity. It is now possible to monitor and select cure cycles with the least unsatisfactory distribution of residual unsaturation at ultimate cure.

The lack of linear correlation between cure estimated by DSC and residual unsaturation by either spectrometric method (Figure 2) is unusual—particularly as cure by DSC and residual unsaturation of TetEGDMA regress linearly.[1] It implies that the enthalpy of polymerization of EGDMA is cure dependent. Whether it is the result of the tightness of the network or heterogeneity or both, it is an important result if only because a linear relationship between the magnitude of the residual exotherm in DSC and residual unsaturation is sometimes taken as axiomatic.

Much of the structural and organizational detail during cure still remains inaccessible to direct observation, in particular the size and distribution of monomer- and network-rich regions. KGM simulations are the obvious way of bridging this gap in experimental observation. Models can now be tested against those predictions, which are accessible to spectrometric determination. In the case of EGDMA a model gave confirmable predictions and it was extended to examine the development of polymer clusters and monomer pools. The simulations coincided closely with the theories of earlier Soviet workers that polymer clusters developed from small highly branched, highly unsaturated polymer molecules formed early in the cure. The polymer clusters then grow together and enclose monomer pools. We were not successful in developing a realistic model for the formation of the more flexible PTetEGDMA network.

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Registry No. TetEGMA (homopolymer), 25101-32-0; EGDMA (homopolymer), 25721-76-0.

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Line Broadening in the Carbon-13 NMR Spectra of Cross-Linked Polymers

A. D. Bain, D. R. Eaton,* A. E. Hamielec, M. Mlekuz, and B. G. Sayer

Department of Chemistry and Institute for Polymer Production Technology, McMaster University, Hamilton, Ontario, L8S 4M1, Canada.

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ABSTRACT: The ^{13}C NMR spectra of cross-linked poly(sodium acrylate) in a swollen gel have been examined. As has been reported by other investigators, the line widths of the resonances increase with the degree of cross-linking. The origin of the broadening has been examined in some detail. Spectra have been obtained at six different field strengths, and a number of relaxation and "hole burning" experiments have been performed. All of the results are consistent with the proposition that the increased width is due to unresolved chemical shift structure arising from the presence of the cross-links rather than from shorter relaxation times associated with decreased polymer mobility.

Introduction

NMR has become one of the more versatile techniques for investigating polymer structure. High-resolution NMR has revealed many details regarding the microstructure of polymer molecules. The advent of two-dimensional methods promises further applications.[1] There are however some limitations particularly in the case of cross-linked polymers. These arise from the low solubility of such compounds. To some extent, that has been overcome by the use of the CPMAS (cross-polarization/magic angle spinning) technique for obtaining well-resolved spectra of solid samples.[2] However, the resolution obtained is still less than that normal for solution spectra and the finer structural details such as information on tacticity are usually lost. An alternative, which is available at relatively low levels of cross-linking, is to obtain the NMR spectra of solvent-swollen samples on a high-resolution instrument. The spectra obtained are usually significantly broader than solution spectra but can provide valuable information.[3-7] We have previously used the line widths in such spectra to provide an empirical measure of the degree of cross-linking.[8]

The origin of the line broadening of cross-linked polymers compared to their straight-chain analogues is not unambiguously known. Two different causes have been suggested. One possibility is that the cross-linking reduces the mobility of the polymer, leading to longer correlation times and hence shorter relaxation times and broader lines. A recent study by Errede et al.[9] on the swelling of styrene/divinyl benzene cross-linked polymers in chloroform reported that the line broadening increased exponentially with cross-linking and concluded that the increase was caused by a relaxation effect. Chemical shift anisotropy relaxation was suggested as the most likely mechanism. The alternative explanation is that the increased line width arises from unresolved structure due to the greater multiplicity of chemical environments introduced by the cross-linking. Mohanraj and Ford[10] studied cross-linking in poly[(chloromethyl)styrene]/divinyl benzene and favored this explanation on the basis that the apparent line width increased by approximately a factor of 3 on changing the resonance frequency from 25 to 75 MHz. If the origin of the broadening is chemical shift dispersion, the widths should be proportional to frequency whereas relaxation due to chemical shift anisotropy increases with the square of the frequency. There is, of course, no reason why there should be a single cause of the line broadening, and Mohanraj and Ford do indeed suggest that dipolar coupling effects become significant at high cross-linking ratios.

It is of some interest and of practical value to establish the nature of this broadening. If it originates in a relaxation effect due to changes in polymer mobility, it might be anticipated that similar results would be obtained for a wide range of cross-linked polymers and that a general empirical correlation with the degree of cross-linking might be established. If, on the other hand, the origin lies in chemical shift effects, these are likely to be different for each different polymer, and no general correlation would be anticipated. In the present paper the question of the origin of the line broadening observed in gels containing cross-linked polymers has been investigated.

Experimental Section

Cross-linked sodium acrylate polymers were prepared as described previously.[8] *N,N′*-Methylenebis(acrylamide) was used as the cross-linking monomer. The details of the preparation of these polymer samples will be described elsewhere.[13]

Gel samples were prepared directly in 10-mm NMR tubes. The spectra of the gels were recorded 24 h after preparation to allow time for complete swelling. A constant concentration of 10% polymer by weight with D_2O or H_2O was used for all the poly(sodium acrylate) spectra discussed in the present paper. The use of D_2O rather than H_2O has no observable effect on the spectra. A number of samples were also run at 2, 4, 6, and 8 wt

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* Author to whom correspondence should be addressed.

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