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Application of NMR Spectroscopy and Multidimensional Imaging to the Gelcasting Process and In-Situ Real-Time Monitoring of Cross-Linking Polyacrylamide Gels

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by

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Abstract

In the gelcasting process, a slurry of ceramic powder in a solution of organic monomers is cast in a mold. The process is different from injection molding in that it separates mold-filling from setting during conversion of the ceramic slurry to a formed green part. In this work, NMR spectroscopy and imaging have been conducted for in-situ monitoring of the gelation process and for mapping the polymerization. ^1H nuclear magnetic resonance spectra have been obtained during polymerization of a premix of soluble reactive methacrylamide (monomer) and N, N'-methylene bisacrylamide (cross-linking molecules). The premix was polymerized by adding ammonium persulfate (initiator) and tetramethyl-ethylene-diamine (accelerator) to form long-chain, cross-linked polymers. The time-varying spin-lattice relaxation times T_1 during polymerization have been studied at 25 and 35°C, and the variation of spectra and T_1 with respect to extent of polymerization has been determined. To verify homogeneous polymerization, multidimensional NMR imaging was utilized for in-situ monitoring of the process. The intensities from the images are modeled and the correspondence shows a direct extraction of T_1 data from the images.

Introduction

Copolymerization of methacrylamide (MAA) and N,N'-methylene bisacrylamide (MBAA) has been of interest in making strong, machinable polymeric parts.¹ Both aqueous (water-based), as in traditional ceramic processing, and nonaqueous (organic-solvent-based) versions of MAA-MBAA copolymerization have been studied. The gelcasting slurries are prepared with premixed MAA-MBAA, alumina powder, and the dispersant Darvan C. Ammonium persulfate (AP) is used as an initiator and tetramethyl-ethylene-diamine (TEMED) acts as an accelerator. The slurry is poured into a preheated mold, allowed to solidify into a formed part, and then dried to remove the solvent (water).^{1,2} In the aqueous process, polymerization begins only by the addition of AP and TEMED and the shelf life of the raw premix is longer than its nonaqueous counterpart.

Study of the relaxation effects in the polymeric network directly correlates with the polymerization process. This report is concerned with the process of aqueous polymerization because the use of water as a solvent facilitates drying and disposal while reducing overall viscosity. In this work, multidimensional nuclear magnetic resonance (NMR) imaging was conducted to characterize polymerization homogeneity and because in-situ study of the polymerization process was necessary. The varying relaxation effects, especially the spin-lattice relaxation time, T_1 , in the premix have been determined by NMR spectroscopy.

In the past, high-resolution ^1H NMR spectroscopy has been used to study the cross-linking polymerization of acrylamide (AA) and MBAA to measure the composition of a residual comonomer mixture during and after polymerization.³ Heterogeneity of solidified acrylic monomer films and their molecular dynamics have also been investigated.⁴ TEMED has been used as a probe to study diffusion and electrophoresis in polyacrylamide (PA) gels⁵ and AP has been extensively used as an initiator.⁶ Separately, MBAA has been used as the cross-linking monomer.⁷ Cross-linking polymers and polymeric gels have been used extensively because of their chemical and physical properties. The physical properties of polymeric gels have been determined by applying NMR to study the motional state of water and the polymer network.⁸ Low-temperature studies of aqueous solutions of AA and MBAA with AP and TEMED have shown that polymerization of cross-linked PA to form cryogels is complex and involves intricate chemical and physical phenomena. Furthermore, the dynamics of polymerization depend on the thermal history of the sample.⁹

NMR imaging techniques can provide information about chemical composition, molecular structure; bonding; molecular interactions; diffusion, and mobility; chemical kinetics; flow; etc. and have been employed on many materials, including polymers, rubbers, rocket propellants, porous media, coal, wood, and ceramics.¹⁰⁻¹² The first application of three-dimensional (3-D) ^1H NMR to obtain spatially resolved images of a rigid polymer has shown that imaging can help in mapping the proton content within a specimen to a good spatial resolution.¹³ Polymer microstructure can be studied by relaxation techniques¹⁴ to obtain information about the crosslink density, blend homogeneity, and crystallinity.

NMR studies have been conducted with an electron beam rather than the combined use of initiators and accelerators to induce polymerization,¹⁵ and various techniques, e.g., two-dimensional (2-D) back projection imaging, have been used successfully to analyze the variations in the concentration of organics in injection-molded specimens.¹⁶ NMR imaging can also be used to obtain spatial variations in the physical and chemical properties of materials. In this work, we obtained 2-D NMR images, in-situ, of polymerizing gels, theoretically related the relaxation times to intensity, and compared our experimental results of image intensities with theoretical values obtained with experimental relaxation times obtained by an inversion recovery sequence.

Fundamental Concepts

Development of the ability to control and design the physical and chemical properties of polymeric materials continues to be an active area of technology. Advancement in this field depends, in part, on an increased understanding of the molecular origins of macroscopic behavior. Relaxation of the nuclear-spin system as it gives up energy to its environment typically takes place on a time scale of 0.1 ms to tens of seconds. This time scale can easily be measured via NMR techniques, thus providing the opportunity to externally probe a spin system in various useful ways. Using NMR, investigators have been successful in devising means to manipulate the spin system under study by imposing external forces. This success derives chiefly from the fact that it is possible to apply both static and dynamic magnetic fields that interact strongly with the nuclear magnetic dipoles. External forces are frequently used to control the dynamics of spin systems in multiple-pulse experiments, during which the importance and utility of exploiting these forces to dominate the natural motions of the spin system in a controlled way is particularly evident.¹⁷

Basic NMR theory can be found in many books.¹⁸⁻²² A nucleus may contain many particles that are coupled together so that it may possess a total magnetic moment $\bar{\mu}$ and a total angular momentum $\bar{J}$ related by

$$\bar{\mu} = \gamma \bar{J}, \quad (1)$$

where γ is the magnetogyric ratio. All nuclei with odd mass number possess the property of spin, and the spin angular momentum is given by $\hbar \bar{I}$. The component m of the nuclear spin vector, in any given direction, can take a set of discrete values given by $I, I-1, \dots, -I$. If the eigenvalues of I^2 and I_z are, respectively, I and m , then Eq. 1 implies

$$\langle I m | \mu_z | I m' \rangle = \gamma \hbar \langle I m | I_z | I m' \rangle, \quad (2)$$

where the matrix elements vanish unless $\Delta m = m' - m = \pm 1$. When a magnetic field $\bar{H}$ is applied, the interaction energy is given by the Hamiltonian

$$\bar{H} = -\bar{\mu} \bar{H}. \quad (3)$$

If $\bar{H}_0$ is along the z -direction,

$$\tilde{H} = -\gamma \hbar H_o I_z. \quad (4)$$

The allowed energies are, therefore,

$$E = -\gamma \hbar H_o m \quad (5)$$

and the separation between two adjacent Zeeman energies is

$$\Delta E = |E_{m+1} - E_m| = \gamma \hbar H_o. \quad (6)$$

To induce transitions between two nuclear levels, an oscillating electromagnetic field should be applied to the system. Energy is absorbed only if the magnetic vector of the oscillating field is perpendicular to the steady field $\tilde{H}_o$ and if the frequency ω of the oscillating field satisfies the resonance condition

$$\hbar \omega = \Delta E = \gamma \hbar H_o,$$

or

$$\omega = \gamma \hbar. \quad (7)$$

Eq. 7 is void of Planck's constant, $\hbar$; classically, one obtains the same result. If the properties that determine γ are known, Eq. 7 can be used to find the frequency required to observe resonance. It is expected that γ is lower by a factor of $\approx 1,000$ for nuclei than for electrons. It is easy to change ω by altering H_o , but to obtain a stronger signal, the magnetic field must as large as possible.

Thermal Equilibrium and Spin Relaxation

Consider a system whose nuclei possess spin $1/2$. In an assembly of protons subjected to an external field $\tilde{H}$, one expects to find some protons with spin $m = 1/2 = \alpha$ and some with spin $m = -1/2 = \beta$. Assume that a sample containing N spins has been placed in a steady magnetic field and that there are N_α spins in the lower state and N_β spins in the upper state. The ratio of α to β spins is given by Boltzmann's law,

$$\frac{N_\alpha}{N_\beta} = e^{-\gamma H_0 / kT}. \quad (8)$$

The total number of spins, $N = N_\alpha + N_\beta$, is a constant, but N_α or N_β will change as a result of the transition induced by the application of an oscillating magnetic field to the spin system. Let us consider such an application.

If a time-dependent perturbation, $V(t)$, which in our case is the radio frequency (RF) field, is applied to any system with discrete energy levels, the probability per second that the system will transit from level a to level b is

$$P_{ab} = \frac{2\pi}{\hbar} |\langle b|V|a \rangle|^2 \delta(E_b - E_a - \hbar\omega), \quad (9)$$

the probabilities of upward and downward transitions being equal. The transitions due to the oscillating field are called stimulated transitions. For the spin-1/2 case, if the stimulated transition probabilities $P_{\alpha\beta}$ and $P_{\beta\alpha}$ are denoted by P , the rate of change of population of the $|\alpha\rangle$ state is given by

$$\frac{dN_\alpha}{dt} = N_\beta P_{\alpha\beta} - N_\alpha P_{\beta\alpha} = P(N_\beta - N_\alpha). \quad (10)$$

Taking the population difference as $n = N_\alpha - N_\beta$ and expressing N_α and N_β in terms of N and n , we finally obtain

$$\frac{dn}{dt} = -2Pn, \quad (11)$$

the solution of which is

$$n = n(0)e^{-2Pt}, \quad (12)$$

where $n(0)$ is the difference in population at time $t = 0$. Equation 12 implies that even though we start with a population difference $n(0)$, applying the RF field results in an exponential decay of the population difference and leads to equally populated levels.

This situation is called saturation. Now, our interest lies in the rate of absorption of energy, dE/dt , given by

$$\frac{dE}{dt} = N_{\alpha} P_{\alpha\beta} (E_{\beta} - E_{\alpha}) + N_{\beta} P_{\beta\alpha} (E_{\alpha} - E_{\beta}). \quad (13)$$

Equation 13 implies that if absorption of energy from the radiation field is to occur, n should be finite. Therefore Eqs. 12 and 13 state that the resonance absorption line would ultimately disappear. The argument lies in the unjustified assumption that $N_{\alpha} > N_{\beta}$. $N_{\alpha} = N_{\beta}$ in the absence of any external magnetic field.

To establish thermal equilibrium between the two states after the application of the field $\vec{H}$, interactions must occur among the nuclei and between the nuclei and their environment, which cause the orientation of the spins to change. The excess magnetic energy would be transferred to other degrees of freedom. This process of nonradiating transitions between the two states $|\alpha\rangle$ and $|\beta\rangle$ is known as spin-lattice relaxation. There are two types of spin-relaxation processes: longitudinal (T_1) and transverse (T_2). The term "spin-lattice relaxation" evolved from the fact that nuclear spins transfer energy ΔE to other degrees of freedom, including the vibrations of the crystal lattice, each time a spin flips over.

Spin relaxation is possible because the spin system is coupled to the thermal motions of the "lattice." The important point is that because the lattice is at thermal equilibrium, the probabilities of spontaneous up and down spin transitions are not equal, as they were for RF-induced transitions, because of the effect of spin-lattice relaxation on the two-level system. On an average, a nucleus remains in an energy level for a time T_1 . If ΔE and Δt are the uncertainties in measurement of energy and time, the minimum width of the NMR line can be obtained from Heisenberg's uncertainty principle,

$$\Delta E \Delta t \geq h. \quad (14)$$

If $\nu_{1/2}$ is the full width at half-maximum intensity, then

$$(h\nu_{1/2})T_1 \geq h, \quad \nu_{1/2} \geq 1/T_1. \quad (15)$$

The spin-spin relaxation time, defined as

$$v_{1/2} \approx 1/T_2,$$

accounts for processes that cause the nuclear spins to come to equilibrium with each other. The relationship of the observed line width, $1/T_2^*$, to the natural line width, $1/T_2$, and the line width due to magnetic field inhomogeneity, $\gamma(\Delta H_0)/2$, is expressed by the equation

$$1/T_2^* = 1/T_2 + \gamma(\Delta H_0)/2. \quad (16)$$

Let $W_{\alpha\beta}$ and $W_{\beta\alpha}$ be, respectively, the upward and downward relaxation probabilities. Analogous to Eq. 10, the rate of change of N_α is

$$\frac{dN_\alpha}{dt} = N_\beta W_{\beta\alpha} - N_\alpha W_{\alpha\beta}. \quad (17)$$

At thermal equilibrium, $dN_\alpha/dt = 0$. If N_α^o and N_β^o denote the equilibrium populations, the populations follow Boltzmann's law, Eq. 8, and we have

$$\frac{N_\alpha^o}{N_\beta^o} = \frac{W_{\alpha\beta}}{W_{\beta\alpha}} = e^{-\gamma H_0 / kT}, \quad (18)$$

which shows that $W_{\alpha\beta} = W_{\beta\alpha}$ if $T = \infty$. Rewriting, for N_β , a relation similar to Eq. 17, and expressing N_α and N_β in terms of N and n as before, we get

$$\frac{dn}{dt} = -\frac{(n - n_o)}{T_1}, \quad (19)$$

where

$$n_o = N \frac{(W_{\beta\alpha} - W_{\alpha\beta})}{(W_{\beta\alpha} + W_{\alpha\beta})}, \quad \text{and} \quad \frac{1}{T_1} = W_{\beta\alpha} + W_{\alpha\beta}. \quad (20)$$

Thus, T_1 exhibits the dimensions of time and is called the spin-lattice relaxation time. T_1 is a measure of the time taken for the transfer of energy to or from the lattice; that is, for the spin system to approach thermal equilibrium. Large values of T_1 indicate very slow relaxation. Now, including the effect of the perturbation field, we find

$$\frac{dn}{dt} = -2Pn - (n - n_o)/T_1, \quad (21)$$

which, at equilibrium ($dn/dt = 0$) and in the presence of an RF field, gives the population difference n as

$$n = \frac{n_o}{1 + 2PT_1}. \quad (22)$$

Thus, saturation can be avoided provided $2PT_1 \ll 1$. If H_1 is the amplitude of the RF field, P is proportional to the square of H_1 and the power of the field must be kept low to allow the spins to relax.

Relaxation Times

Very early in NMR history, Bloch²² suggested that the phenomenon of NMR may be observed in many ways. One way was to sweep the static external field H_0 while keeping the radio frequency, ω , constant, or alternatively, to sweep ω while keeping H_0 constant. The sweep experiment may contain two limits. First, there is the slow-passage limit where, on the nuclear-spin time scale, the sweep rate is sufficiently slow that the experiment represents equilibrium conditions. Second, there is a limit of the very-rapid-passage experiment, where adiabatic conditions exist. High-resolution spectra are obtained under conditions that approximate the slow-passage limit. The adiabatic rapid-passage technique is now used mainly for rapid location of weak signals. The slow- and rapid- passage limits constitute the continuous-wave (CW) approach to recording an NMR spectrum.

Another approach to studying NMR, also suggested by Bloch²² and put into practice by Hahn,²³ involved subjecting the spin system to a short intense pulse of RF power and observing its subsequent behavior. This is known as the pulse or free-precession approach. The pulse- or free-precession technique can be applied to the study of time domain phenomena, that is, relaxation times.

Pulsed experiments are more efficient than sweep experiments because all of the nuclei are simultaneously and not sequentially studied. The continuous wave approach

developed into what is now called high-resolution NMR. The spectra resulting from such an experiment have found many applications in chemistry, one application being the determination of the structure of organic compounds. In a frame rotating at the frequency $\bar{\omega}_o = -\gamma\bar{H}_o$, $\bar{H}_{eff} = \bar{H}_1$, which is constant in direction and magnitude.

Fig. 1. Determination of T_1 by 180° - τ - 90° sequences: (a) at $t = 0$, $\bar{M}$ is inverted by a 180° pulse; (b) after $t = \tau$, a 90° pulse rotates $\bar{M}$ to the y' (or $-y'$) axis; (c) initial FID amplitude after the 90° pulse, proportional to the value of $\bar{M}$ at time τ , is plotted as a function of τ . Each point results from a separate 180° , τ , 90° sequence.

Therefore, we can consider relaxation experiments in the rotating frame analogous to those in the laboratory frame, with $\bar{H}_o$ replaced by $\bar{H}_1$. Because $H_o \ll H_1$, the precession frequencies found in the rotating-frame experiments are much lower than those obtained in the laboratory-frame experiments. By conducting experiments in the rotating frame, we can acquire information about molecular processes in a frequency range much lower than that found in ordinary pulse or CW experiments.

Spin-lattice relaxation time, T_1 , can be measured over a wide range of values by pulse methods. The 180° - τ - 90° sequence that is often applied is shown in Fig. 1. Initially, the magnetization along the z' axis is inverted by a 180° pulse. This results in longitudinal relaxation which causes M_z to take negative through positive M_0 values. If a 90° pulse is also applied along the x' axis at a time τ after the 180° pulse, then $\bar{M}$ is rotated to the y' axis. The result is a free induction signal the initial height of which is proportional to the magnitude of $\bar{M}$ and hence to the value of M_z at the time τ . The decay rate of M_z can be established if the system is allowed to attain equilibrium by waiting at least for a time of $5T_1$ and then repeating the 180° - τ - 90° sequence for a different length of time τ . Since M_z is proportional to n , an analogous expression to Eq. 19 can be written as:

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1} \quad (23)$$

Integrating Eq. 23 and assuming M_z equals M_0 at $t = 0$, we obtain

$$M_z = M_0(1 - 2e^{-t/T_1}) \quad (24)$$

which is plotted in Fig. 1. We rewrite Eq. 24 as

$$\ln(A_0 - A_\tau) = \ln 2A_0 - t/T_1, \quad (25)$$

where A_τ is the initial amplitude of the FID following the 90° pulse at time t , and A_0 is the limiting value of A_τ after a long time between the 180° and 90° pulses. Eq. 25 implies that $A_\tau = 0$ for $\tau = T_1 \ln 2$. Thus, T_1 can be found from the pulse spacing τ that results in no free induction signal following the 90° pulse. This method gives only a rough estimate of T_1 . Provided $T_2 \ll T_1$, T_1 can also be determined with the 90° - τ - 90° sequence. In this case, following the 90° pulse, M_z attains its equilibrium value due to the free induction signal decaying rapidly to zero. Thus, as in the 180° - τ - 90° sequence, a second 90° pulse permits a check on the value of M_z at time τ . If a series of 90° pulses is repeated several times with a common interval τ , $\bar{M}$ rapidly decreases to a steady-state value, depending on τ and T_1 . The steady-state value of the signal is noted, and the 90° , τ , 90° , τ , sequence repeated for a different value of t .

A Gaussian function exhibits the property that its Fourier transform is also a Gaussian function. For instance, the function

$$f(\omega) = \exp(-\omega^2 / 2\sigma^2) \quad (26)$$

exhibits a Fourier transform

$$F(t) \propto \exp(-\sigma^2 t^2 / 2). \quad (27)$$

In the frequency domain, the full width at half height is 2.36σ . We can define a characteristic decay time for $F(t)$ as the time T_2 required for $F(t)$ to decay to $1/e$ of its original value. Then $T_2 = \sqrt{2}/\sigma$ and the full width at one-half height in the frequency domain is $3.34/T_2$.

Spin-spin relaxation, also known as transverse relaxation, is a process where the magnetization in the x-y plane, perpendicular to the static laboratory field, decays. Depending on the magnitude of T_2 , different problems are encountered while measuring T_2 . For example, if it is too long, say, more than 10 s, then the inhomogeneity of the magnet will make the spins dephase faster than the real T_2 and one must use the Carr-Purcell-Meiboom-Gill sequence to measure T_2 . For the correct operation of the sequence, as with all multiple-pulse sequences, adjustments, such as tip angle, RF phase, and resonance condition, are quite critical. If T_2 is too short, the FID decays before the instrumental dead time and it is difficult to observe the signal. One way to solve this problem is to form an echo that occurs later than the end of the dead time.

Ceramic Forming Process: Gelcasting

Gelcasting is a ceramic forming process in which a slurry of ceramic powder is mixed in a solution of organic monomers and the mixture is cast into a mold.¹⁻² A flow-chart of the process is shown in Fig. 2. The ceramic powder, organic monomers (binders), a solvent, and a dispersant are mixed to form a slurry. The initiator is added to the slurry to begin the polymerization and the mixture is transferred into a mold for casting. After the mixture is cast, the slurry is converted into a gel, which holds the ceramic particles in shape. The mold is removed and the specimen is dried in a controlled atmosphere to remove the solvent. The organic monomers (binders) are then burned off and the specimen is sintered to form a dense part. Organic solvents are used in nonaqueous gelcasting. If water is employed as the solvent, the process is termed aqueous gelcasting. As mentioned earlier, aqueous gelcasting has a number of advantages over nonaqueous gelcasting processes. In the aqueous gelcasting process, monofunctional monomers MAA and difunctional MBAA are premixed using the solvent water, AP is added to the premix to initiate the polymerization and the catalyst TEMED is used to accelerate the polymerization process. The gelation process is usually exothermic and the gels formed are transparent and form homogeneously in the

solution without a gelation front and without phase separation. To make ceramic parts, alumina powder is added to the premix and Darvan C is added as a dispersant prior to adding the initiator and the accelerator. The mixture is then poured into a preheated plastic, metal, wax, or glass mold. In this case, the slurry gels into a green part with no noticeable defects or porosities, even when complex molds are employed. The difference between traditional ceramic processing and the acrylamide gelcasting technique is that the MAA and MBAA monomers replace the poly(vinyl alcohol) used as a binder.

Fig. 2. Flowchart for gelcasting process (Adapted from Ref. 1)

Nuclear Magnetic Resonance Imaging

Imaging techniques provide good sensitivity to the chemical and physical properties of the specimen. In general, the NMR image of a sample can be thought of

as representing the actual physical, chemical, and morphological properties of the specimen as observed through a selective filter or tomographic window.²⁴ The tomographic window is a direct result of the overall combined response of the three main experimental components: (1) intrinsic or induced image contrast mechanisms; (2) experimental imaging parameters and protocols, and pulse sequences; and (3) data reconstruction and image processing techniques and parameters. A partial list of the item that contribute to the response of the three experimental components are indicated within the corresponding blocks in Fig. 3.

Fig. 3. Schematic representation of NMR imaging of specimen viewed through tomographic window resulting from intrinsic or induced image contrast mechanisms, experimental imaging parameters, pulse sequences and imaging protocols, and data reconstruction and image processing techniques and parameters²⁴

The contribution of each of the items to the overall response of the system can be influenced by the experimental techniques and parameters used during the analysis. By appropriate choice of experimental conditions, the analyst is provided a mechanism that will maximize the overall response of the system to the physical, chemical and morphological properties of interest. This ability to control the response of the system is the basis of the power and versatility of NMR imaging, as well as its complexities.

In NMR imaging, as in other nondestructive testing methods, contrast and sensitivity are the variables that ultimately determine the feasibility of monitoring sample properties of interest. NMR imaging is responsive to many nuclear-spin properties that may be used to provide sample contrast and sensitivity, and the analyst is provided many mechanisms to modify the response of the experiment to these properties. The properties that provide contrast and sensitivity may be either intrinsic to the specimen or induced by the analyst. Intrinsic properties may include one or more of the following: the nuclear isotope, the spin density or number of nuclei per volume element (voxel), the nuclear relaxation times T_1 and T_2 , the chemical shift, and the intramolecular and intermolecular couplings.

Properties that may be induced by the analyst include physical changes within the specimen caused by variation of externally applied stress, temperature gradients, or specimen aging; induced materials such as filler fluids and relaxation agents, and induced diffusion and flow within the specimen. Although it is not always possible to induce these mechanisms in a nondestructive manner, NMR imaging is a powerful tool for the analyst. In general, the sensitivity of the technique is directly related to the concentration of the nuclei, the intrinsic sensitivity of the nuclei, and parameters such as relaxation times. It may be noted that several abundant nuclei, such as ^{16}O and ^{12}C , lack a magnetic moment and therefore are not observable with NMR imaging techniques.

Experimental Aspects

The NMR and imaging system in the Energy Technology Division, Argonne National Laboratory, shown pictorially in Fig. 4, is a three-channel broadband spectrometer system for solutions/solid-state NMR spectroscopy and NMR imaging. The system includes an integrated Bruker Avance DMX/300 spectrometer console and two superconducting magnet systems. The horizontal NMR imaging magnet has the potential of being used in many material applications including studies on the MAA-MBAA system as a function of reaction extent and temperature, and as a function of the concentration of individual reactants.

High-resolution NMR spectrometry of an MAA-MBAA copolymer mix was performed on a Bruker AP-300 Spectrometer with a commercial probe at a magnetic

field strength of 7.1 T. Low-resolution NMR spectroscopy and imaging studies were conducted on a Tecmag NMR Kit II and Libra data acquisition system interacting with a CXP-100 Spectrometer and a Macintosh Quadra 950 computer. Spectra and images at a magnetic field strength of 35 T were obtained by an in-house-built imaging accessory²⁵ tuned to the proton resonance frequency of 100.13 MHz. Orthogonal linear magnetic field gradients across the specimen were driven by three 1000-W Techtron audio amplifiers. A sequence of spectra was acquired with varying interpulse delay times, τ . Delay times of 2, 5, 20, 50, 200, and 500 ms, and 2, 5, 10 and 20 s were used in the sequence to obtain 2-D images. For each time delay, the time domain data matrix of 128 x 128 was obtained by accumulating eight transients. The total time for data acquisition was 139 min. Room-temperature shims were used to acquire a good free induction decay (FID) on a water sample and the acceptable line width was 28 Hz. The data matrix was made symmetrical by adjusting the gradients, thus evolving a central image of a slice of a sample cross section.

Fig. 4. NMR spectroscopy and imaging system in the Energy Technology Division

The samples were prepared from soluble reactive AA (monomer) and MBAA (cross-linking molecules), and the premix was made with water as solvent.¹ The initiator, 10% AP, and the accelerator TEMED were then added to begin the polymerization of the monomers, which formed long-chain, cross-linked polymers. For high resolution, 5-mm NMR sample tubes were used; for low resolution, the solution was transferred to a 15-mm, cylindrical, flat-bottomed tube and rapidly placed in the probe for spectroscopy experiments.

For low-resolution imaging experiments, it was necessary to obtain a corresponding contrast between the polymerized and nonpolymerized specimens. For this reason, the sample geometry shown in Fig. 5 was such that MAA-MBAA without the initiator was placed in a small-diameter inner tube (5 mm) immersed in a larger diameter (15-mm) tube that contained polymerizing MAA-MBAA and the initiator. The time of the initial measurement was recorded and careful monitoring of the polymerization was conducted with respect to time. Times were subsequently recorded at the end of an experiment and at the beginning of the next computer-controlled experiment.

Fig. 5. Sample configuration and probe assembly used in imaging experiments

Figure 6 shows a 2-D data matrix acquired in time domain for water. A 2-D surface plot of the data matrix shown in Fig. 7 indicates the intensity variation of the water peak with respect to the base line. The concentric intensity peaks relate directly to the concentric circles in the time domain data matrix. The Fourier transform of the time domain matrix that evolves the frequency domain image of the water specimen is shown in Fig. 8. The image shows the variation in intensity due to the existence of a meniscus on the specimen surface. Thus, the intensity at the periphery is higher than the intensity at the specimen center.

Fig. 6. 2-D time domain data matrix for water

Fig. 7. 2-D surface plot of time domain data matrix for water shown in Fig. 5

Fig. 8. Fourier transform image of water, evolved from time domain data matrix

Discussion

NMR spectra were studied as a function of the extent of MAA-MBAA polymerization. The ^1H NMR spectra were acquired on individual standard MAA-MBAA reagents and on composite copolymer premix reagents. Spectra were acquired with H_2O (as solvent) at ambient temperature and at 35°C . The composite spectrum of the copolymer premix is given in Fig. 9, where structural identification of the resultant peaks is indicated. The standard inversion recovery NMR pulse technique, employed for the measurement of T_1 , utilized a 180° pulse, followed by a time delay, τ , then another 90° pulse (180° - τ - 90° -acquire). In these studies, real-time ^1H NMR spectra of the copolymerization reaction were acquired as a function of reaction time; see Fig. 10. The spectra demonstrate a reduction in methylene and methyl resonances as the polymerization reaction progresses.

A variation of the spin-lattice relaxation rates of the components as a function of reaction extent is also expected. ^1H NMR studies of spin-lattice relaxation time, T_1 were conducted on the individual standard MAA-MBAA copolymer premix at a magnetic field strength of 7.1 T. Spectra were acquired with D_2O as the solvent at 35°C to suppress the observable solvent resonance. The standard inversion recovery NMR pulse technique was employed for these studies. A stack plot of the resultant spectra for the copolymer premix is presented in Fig. 11. Variations in relaxation times are indicated by the rate of recovery from the inversion pulse. Studies suggest that as the reaction occurs, spin-lattice times are longer.

Fig. 9. ^1H NMR spectra of composite spectrum of copolymer MAA-MBAA premix. Spectra acquired at 7.1 T; off-scale peak is from solvent (water).

Fig. 10. ^1H NMR spectra of composite spectrum of MAA-MBAA copolymer reaction as a function of reaction time (min). Spectra acquired at 7.1 T and 35°C .

Fig. 11. In-situ 2-D stack plot of ^1H NMR T_1 inversion recovery sequence of MAA-MBAA copolymer premix. Spectra acquired at 35°C at onset of polymerization reaction with respect to varying interpulse delays.

NMR spectroscopy and imaging procedures were performed at 25 and 35°C to determine the variation in T_1 and whether the polymerization is homogeneous. Figure 12, obtained by low-resolution NMR spectrometry, shows the effect of polymerization on the intensity of the peaks with respect to time at the end of an inversion recovery sequence. The unchanged peak is that of the solvent, water, although T_1 of the solvent varied as the polymerization evolved. Also, the polymerizing peak encompasses several peaks that are not visible because of low-resolution analysis.

Figure 13 indicates the variation of relaxation time during polymerization, derived from inversion recovery sequence results for the two peaks recorded at 25 and 35°C . T_1 is a measure of the time taken for transfer of energy to or from the lattice; i.e., for the spin system to approach thermal equilibrium. Large values of T_1 , existing at the onset of polymerization in Fig. 13, indicate very slow relaxation. The measurements of T_1 reveal the effect of polymerization on the motion of the methyl group, and the side and main chains.²⁶ T_1 measurements can be used to determine changes in molecular motion caused by polymerization.²⁷⁻²⁹ In Fig. 13, the value of T_1 decreases, depending upon the correlation time of the local motions that contribute to the relaxation. T_1

increases with temperature and decreases during polymerization. This indicates that the polymerization of MAA-MBAA with AP as the initiator and TEMED as the accelerator, was more rapid at higher than at lower temperature.

Fig. 12. Low-resolution ^1H NMR spectra evolved with time (min) during polymerization process of MAA-MBAA due to AP and TEMED at 35°C

Fig. 13. Variation of spin-lattice relaxation time T_1 with time during polymerization of MAA-MBAA at 25 and 35°C

NMR imaging was conducted on MAA-MBAA prepared in water. During imaging, the obtained NMR signal was largely due to water in the premix and overwhelmed the signal due to other constituents in the premix. A T_1 inversion recovery sequence 90° - τ -composite 180° , given in Fig. 14, indicates delays and gradient activation at specific intervals. Figure 15 shows a sequence of 2-D ^1H NMR images of the MAA-MBAA polymerization reaction with time in the frequency domain. These were obtained by Fourier transforming 2-D spectra initially acquired in the time domain. All of the images show the concentration gradient in the specimen.

Figure 15a shows a 2-D ^1H NMR image of the MAA-MBAA copolymer premix at 0.0 s. Here, the polymerization has not begun because the initiator and the accelerator have not begun to react with the copolymer premix. During the process, at any temperature, no polymerizing front was observed with imaging techniques, and polymer gels formed homogeneously throughout the solution, as seen in Fig. 15. It may be noted that the distortion at the periphery of the sample is an artifact of the imaging experiment and relates to the limitation of tuning of the gradient coils in the probe assembly. The sequence of images shows that because of the polymerization, relaxation occurred more rapidly in the polymerizing MAA-MBAA (i.e., in the outer tube) than in the inner tube where the relaxation remained constant.

Because the images are individually scaled in intensity, it appears that the image intensity of the inner tube decreases. The images also demonstrate the actual time of polymerization. At time 0.0 s, the concentration of the polymerizing specimen in the outer tube was essentially the same as the concentration of the raw specimen without initiator in the inner tube, as seen in Fig. 15a. As the polymerization continues, the specimen in the outer tube becomes more viscous, which leads to the intermediate intensity shown in Fig. 15e at 83 min.

Complete polymerization takes place at 139 min, as shown in Fig. 15h. The intensities of the images did not vary with further acquisition of images. The magnitude of the intensity of the sample at 0 s is shown in Fig. 16. The surface plot also shows the intensity of the glass wall of the inner tube concentric to the intensity of the inner specimen. Figure 17 indicates a decreased intensity due to the nonpolymerized specimen at time 139 min and is consistent with Fig. 15f. The variation of intensity has been indicated in Fig. 18, by a plot (intact line) of the intensity ratio (outside intensity/inside intensity, I_1/I_0) vs. time as the polymerization occurred.

The variation in intensity corresponds to that from a simple spherical domain with an exterior sink. If the material is inhomogeneous, the magnetization or intensity decay can be expected to be a composite sum of two exponentials.³⁰ The curvature in the intensity-vs-time plot for the MAA-MBAA system strongly indicates that the system is inhomogeneous. Inasmuch as the applied field M_0 is larger than the dipolar field, the shape of the decay of this spin-lattice relaxation depends on the small-scale morphology of the inhomogeneities:

Fig. 14. T_1 inversion recovery 90° - τ -composite 180° sequence for acquisition of time domain data matrix

$$M(t) = I(t) = \frac{2a^3}{\pi} \sum_{n=1}^{\infty} \frac{1}{2} \exp \left\{ - \left[K \left(\frac{n\pi}{a} \right)^2 + \frac{1}{T_1} \right] t \right\}, \quad (28)$$

where a is the atomic radius and K is a normalization constant.

Magnetization is directly related to the spin-echo intensity; therefore, it is possible to correlate the intensity obtained from the images with the magnetization. Because the fast inversion recovery pulse sequence was employed to determine T_1 , the peak intensity as a function of time, t , can be written as³¹

$$M(t) = M_0 \left\{ 1 + e^{-\Delta/T_1} \right\} e^{-t/T_1}, \quad (29)$$

where M_0 is a normalization constant, Δ is the delay time, T_1 is the spin-lattice relaxation time, and the total delay time is the sum of the individual delays. More accurately, the intensity variation can be verified by using the inversion recovery sequence, the variation in the spin-lattice, and the spin-spin relaxation times as a basis for calculating the image intensities in each voxel. For the standard inversion recovery NMR pulse technique employed to measure T_1 , the images were analyzed to relate the signal intensity to T_1 and the spin-spin relaxation time T_2 . The signal intensity is

$$S \propto \rho e^{-\tau/T_2} \left[1 - \left(1 + e^{\tau/2T_2} \right) \right] \left(2e^{\tau/2T_1} - 1 \right) e^{-T_1/T_1} + e^{-\tau/T_2} \left(2e^{\tau/2T_1} - 1 \right) e^{-\tau_{inv}/T_1}, \quad (30)$$

(a)

(b)

(c)

(d)

Fig. 15. 2-D ^1H NMR images at (a) 0 min, (b) 26 min, (c) 45 min, (d) 64 min, (e) 83 min, (f) 102 min, (g) 120 min, and (h) 138 min of standard MAA-MBAA polymerization reaction with initiator.

(e)

(f)

(g)

(h)

Fig. 15 (cont'd)

Fig. 16. Surface plot of frequency domain image of Fig. 15a at 0 min

Fig. 17. Surface plot of frequency domain image of Fig. 15f at 139 min

Fig. 18. Ratio of intensities of polymerizing MAA-MBAA (I_1) to uninitiated MAA-MBAA (I_0) vs. time; solid line, experimental plot derived from images in Fig. 15; dashed line, theoretical plot of image intensity according to Eq. 31

where the recovery process is inspected with a 90° pulse applied at time T_1 following the inversion, and τ_{tot} is the total recovery time. Taking $T_2 \gg \tau$,

$$S \propto (2e^{\tau/2T_1} - 1)(\rho e^{-T_1/T_1} + e^{-\tau_{\text{tot}}/T_1}) \quad (31)$$

The relationship in Eq. 31 shows the codependency of T_1 with the intensity of the obtained images. Figure 18 (dashed line) shows a plot of the intensity vs. time according to Eq. 31 for corresponding values of T_1 . The decrease in intensity corresponds to the images shown in Fig. 15 and the intensity variation (solid line) shown in Fig. 18. The theoretical fit according to Eq. 31 breaks down with further passage of time because of the assumption that $T_2 \gg \tau$. Because this assumption is valid only for large values of T_2 , and therefore large values of T_1 , a better fit can be obtained if T_2 is considered in the fitting analysis. Inasmuch as this report is restricted to variation of T_1 , T_2 values were not experimentally determined. Nevertheless, the above analysis demonstrates the capabilities and varying information that can be obtained with NMR imaging techniques. Equation 30 can be used to separately verify the spin-spin relaxation times T_2 if the intensities of the images and T_1 are known.

In future work, we will analyze nonaqueous gel systems that involve alumina solid loading and composites, as well as the concentration differences between the raw

specimen and the polymerizing specimen, to understand how the main quantity of comonomers becomes involved in the polymerization process. T_2 values will be determined and the fitting analysis recomputed to understand the differences between Eqs. 30 and 31.

Additional studies are being conducted on the MAA-MBAA system as a function of reaction extent and temperature, and as a function of the concentration of individual reactants. This information is expected to provide details on molecular correlation times, sample viscosity, and reaction kinetics. Also, the nonaqueous organic gel systems that involve the addition of solid particles to the copolymer premix of MAA-MBAA will be imaged and concentration differences will be analyzed to understand how the main quantity of comonomers becomes involved in the polymerization process. Effort is underway to evaluate the potential of NMR imaging to affect development and process control of near-net-shape gel-cast parts. Some of the objectives of the work are to determine the utility of NMR imaging for nondestructive evaluation of voids and flaws in components and for measurement of physical properties, such as the degree of polymerization, viscosity, and specimen strength by correlating these properties with measurable NMR parameters (T_1 , $T_{1\rho}$, and T_2).

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