Pulsed NMR Study of Network Formation in the Course of Bulk Polymerization of Methyl Acrylate

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The proton spin-spin relaxation time (T_2) during the bulk polymerization of methyl acrylate was measured as a function of the reaction time at various temperatures. Three kinds of T_2 (T_{2L} (long), T_{2S} (short) and T_{2M} (intermediate)) were obtained as the polymerization proceeded. The fraction of T_{2S} (F_S) increased sigmoidally at a certain reaction time, while that of T_{2L} (F_L) decreased reciprocally. The former corresponded to the amount of a polymer whose molecular weight was sufficiently high enough to cause a tight entanglement that produced a transient network structure; the latter reflected a decrease in the mixture of the monomer and the low molecular weight of the polymer. T_{2M} is considered to arise from a relatively mobile region of the entanglement. The relationship between the fractions of $T_{2S} + T_{2M}$ and the polymer yield was found to be linear, which led us to monitor the polymer yield in real time during the polymerization in a non-distractive manner. ^{13}C DD (dipolar decoupling)/MAS (magic angle spinning) NMR spectra were also measured to monitor the polymerization process in terms of the molecular motions between the main chain and the side chain in the formation of a network structure. The ^{13}C DD/MAS NMR spectra show that the side chain motion became restricted as well as the main chain when the "Trommsdorff effect" (gel effect) was observed, and a part of the monomers were trapped in the network structure.

(Received September 29, 2004; Accepted January 6, 2005)

Introduction

Pulsed NMR can be used to elucidate certain aspects of the polymer structure and those properties that are affected by the molecular mobility. The spin-spin relaxation time (T_2), which is primarily determined by the relatively slow motion of the polymer chain in the fluid state, was found to be useful for investigating the polymer structural order, chain entanglement and their presence as permanent cross-links.¹⁻³ Short polymer chains in a liquid state or at high temperature in the molten state will give rise to a single exponential T_2 decay. When the molecular weight exceeds a critical value, the spin-spin relaxation deviates from the single exponential behavior. This is explained by the presence of higher molecular weights of molecular entanglements sufficient in number to provide a three dimensional network.⁴ The entanglement of a polymer chain restricts the chain mobility. Since this long-range chain motion affects the NMR relaxation times, the studying T_2 can provide a sensitive probe with which to investigate the effect of intermolecular coupling on the mobility.

Most of molecular motion studies, however, have focused on polymers in a static state, such as cross-linked rubbers,⁵ polymer melts with non-disperse molecular weight.³ From a molecular motional point of view, bulk polymerization is also one of the most interesting targets for pulsed NMR spectroscopy. The reaction is followed by a liquid-to-solid transition accompanied by a change in the polymer structure, the molecular weight distribution and the density. The molecular motion during the

course of the reaction is, therefore, continuously influenced particularly by the propagation process, where the entanglement occurs along with a rapid increase in the degree of polymerization. Under such circumstances, samples consist of a mixture of high-polymer, low-molecular weight polymer, oligomers, and a residual monomer where high molecular weight entangled (network structure) molecules co-exist with low molecular weight "free molecules". The constituents' fractions also continuously change during the reaction. In terms of the molecular motion, studying the network formation by a pulsed NMR method in a kinetic process, such as bulk polymerization, is therefore of interest and worth investigating as well as that by the gravimetric method,⁶⁻⁹ because the pulsed NMR method provides such a different perspective on the kinetic process of the reaction in real time.

In the present work, the proton spin-spin relaxation time of poly(methyl acrylate) (PMA) was measured in order to study network formation as a function of the reaction time at various temperatures by the pulsed NMR method. The results were considered in conjunction with that of ^{13}C DD/MAS NMR measurements and the polymer yield.

Experimental

Pulsed NMR measurements were carried out with a JEOL Mu-25 spectrometer operating at a frequency of 25 MHz. The proton spin-spin relaxation time (T_2) was obtained from the free induction decay (FID), which follows a 90° pulse.¹⁰ The pulse interval time was 10 s, which is sufficiently long to get the spins to be in the thermal-equilibrium state. The dead time of the apparatus was 10 μs . FID signals were accumulated 8 – 32 times to improve

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Fig. 1 Typical FID signal change in the polymerization of MA at 55°C. A, 250 min; B, 400 min; C, 500 min; D, 1800 min.

the signal-to-noise ratio. Methyl acrylate (MA) was distilled under reduced pressure. The monomer was sealed with benzoyl peroxide (BPO) (BPO:MA = 1:1000, mole ratio) in a glass tube (10 mm ϕ) under reduced pressure. Bulk polymerization was carried out in an NMR probe at several temperatures.

^{13}C dipolar decoupling (DD)/magic angle spinning (MAS) NMR spectra were measured by a Bruker DMX 500 spectrometer operating at a carbon frequency of 125 MHz. Another experiment concerning the polymerization was also performed under the same experimental conditions as mentioned above to calculate the polymer yield and to carry out ^{13}C DD/MAS NMR measurements. The reaction temperatures were regulated within $\pm 0.5^\circ\text{C}$ by an air-flow thermostat. After a certain reaction period, the polymerization was stopped by cooling the sample tube with liquid nitrogen. Poly(methyl acrylate) was precipitated by pouring the reacted methyl acrylate into a large amount of methanol. After the polymer was dried at 80°C under reduced pressure, its weight was measured. The polymer yield was calculated by the following equation:

$$\text{Polymer yield (\%)} = \frac{\text{Weight of produced PMA}}{\text{Weight of MA}} \times 100. \quad (1)$$

Results and Discussion

Change of free induction decay signal during the course of polymerization

Figure 1 shows a typical change in the FID signals during the course of MA polymerization at 55°C . The FID signal of MA during the early stage of polymerization was apparently of a single exponential curve with a long spin-spin relaxation time. On the other hand, the decay curve became non-exponential with a short relaxation time after a certain reaction time. It is obvious that the polymerization process reflects the change of the FID signals.

In general, as the polymerization proceeds, methyl acrylate changes from liquid to glassy, or the solid state, via gel or an elastic state. Under such circumstances, the sample at a certain conversion, the T_2 decays no longer obey a single exponential time dependence.

Thus, the FID curve in a course of polymerization can be fitted to a sum of Weibull functions:^{4,5}

$$S(t) = \sum S_{0i} \exp[-(t/T_{2i})^{E_i}]. \quad (2)$$

Here, E_i is the Weibull coefficient, S_{0i} the initial signal intensity of the i -th component at $t = 0$, and T_{2i} the proton spin-spin

Fig. 2 T_{2L} , T_{2M} , and T_{2S} vs. reaction time for MA at 55°C . $\circ$, T_{2L} ; $\bullet$, T_{2M} ; $\square$, T_{2S} .

relaxation time of the i -th component. The initial fraction of the i -th component (F_i) is given by

$$F_i = S_{0i} / \sum S_{0i}. \quad (3)$$

The Weibull coefficient can be taken as having either a Gaussian ($E = 2$), exponential ($E = 1$) or intermediate character ($1 \leq E \leq 2$). In this experiment, FID signals were found to be exponential at the early stage of polymerization, and became a sum of the exponential and Gaussian components as the polymerization proceeded.

Reaction time dependence of the spin-spin relaxation times

Figure 2 shows the change in T_2 of MA as a function of the reaction time at 55°C . Only a T_2 (T_{2L}) was obtained from the analysis of the FID signals at a reaction time less than 100 min. The sample at this stage was still mobile and in the liquid state, containing large amounts of monomers and very low-molecular-weight polymers, which allowed a correlation time of less than 10^{-6} s. These constituents of the sample have spectroscopically almost the same motions on a whole. Therefore, the sample yielded only a single exponential component with the Weibull coefficient (E) of 1. The T_2 value became smaller than that of the monomer due to an increase in the concentration of the low-molecular-weight polymer.

At relatively longer reaction times (over 100 min), the sample gradually became viscous and then began to solidify. The FID signal with a fast decay part was found to be non-exponential and the part continued to augment with the reaction time. The FID signal at this stage offered three different relaxation times, as analyzed in a manner described by Serizawa *et al.*⁴ As the polymerization proceeded, monomers decreased, whereas polymers increased. Therefore, it is reasonable to consider that T_{2L} can be assigned to monomers that are mobile and T_{2S} to polymerized molecules that are less mobile. That the longer relaxation time, T_{2L} (~ 1.2 ms), remains unchanged, is attributed to mobile species.^{3,11,12} Those are residual monomers and very low-molecular-weight polymers which are trapped among high molecular weight of the polymers during the polymerization. T_{2M} also changes from 450 μs down to 100 μs after this component begins to be observed. Fujimoto *et al.* pointed out that the low molecular weight of a polymer or a solvent-immersed polymer that are relatively mobile species have a longer T_2 compared to rigid species ($T_{2S} \sim 20$ μs).¹³ For an example of a non-network polymer, linear polymers in viscous state such as an epoxy resin, have two relatively long kinds of

relaxation times of T_2 (1 ms and 300 μ s).¹⁴ These two kinds of T_2 are comparable to T_{2M} and T_{2L} of this reaction. It is, therefore, expected that the structure of a linear polymer-monomer mixture can be visualized as quasi-entangled mobile molecules.

T_{2S} changed from *ca.* 100 μ s to *ca.* 20 μ s. The shortest relaxation times, T_{2S} (15–20 μ s), of Gaussian decay is attributed to rigid species that arose from solid aggregation of the high-molecular-weight polymer, amorphous solid.^{1–3} As is often the case with bulk polymerization, the reaction is followed by the “Trommsdorff effect (gel effect)”. The polymer chains propagate and begin to interpenetrate each other to form a tight entanglement of polymer chains (transient 3D network structure), which caused the motion of the polymer chain to be constrained.^{1–3} In the previous work,¹⁵ we also investigated the bulk polymerization process of MMA (methyl methacrylate) by pulsed NMR. The time course of the reaction proceeded in a similar manner to that of MA. The molecular weight of PMMA (poly(methyl methacrylate)) also increased, followed by a “gel effect” to reach a critical value in which entanglements of the polymer chain occurred. Soh *et al.* pointed out that in a bulk polymerization of MMA, the entanglement of polymer chains occurred as the polymer concentration and/or molecular weight increased.^{16–19} They also explained that the gel effect is closely related to a change of the free volume and the occurrence of the entanglement of a polymer chain whose molecular weight is more than *ca.* 10⁴.

Information of the molecular weight of PMA in our experiment was not obtained because of the reason mentioned in Ref. 20. The molecular weight of PMA is, however, anticipated to be high enough to cause an occurrence of entanglements of a polymer chain when T_{2S} begins to be observed.

At a higher conversion of the polymerization time, PMA becomes solid, even for a lower-molecular weight polymer (T_{2L}), and a loosely entangled polymer (T_{2M}) becomes plasticized by a large amount of high-molecular-weight polymers to decrease three kinds of T_2 values. These values of T_{2S} , T_{2M} , and T_{2L} are categorically different from each other, and do not merge throughout the whole reaction process. This means that each fraction of different T_2 belongs to a different mobility region during polymerization.

Reaction time dependence of each fraction of the T_{2S} , T_{2M} and T_{2L} components

Figure 3 shows the change in fraction of each T_{2S} , T_{2M} , and T_{2L} components, referred to as F_S , F_M , and F_L , respectively, as a function of the polymerization time at 55°C. F_S is zero until the reaction time reaches to 100 min, where it begins to increase sigmoidally to about 50% at a longer reaction time. On the other hand, F_L decreases abruptly at almost the same time as F_S shows an increase. F_M also appears and then keeps its value at between *ca.* 58 and 40%. In general, as the propagation proceeds, an increase in the amount of the polymer and a decrease in monomer concentration occur. The time course of these fractions, therefore, explains the polymerization process in terms of proton T_2 . The decrease in F_L , as mentioned above corresponding to a mixture of monomer and a low-molecular-weight polymer, as estimated from its value, was at first observed. At the propagation stage (onset of “gel effect”), those constituents gained molecular weight to transit into a higher molecular-weight region (F_M). F_M and F_S were then observed and the amount of F_S increased further with the reaction time through the transition of F_M , while keeping its value at between 45–50%. As for all the other polymerizations at different temperatures, the time course of these three kinds of components was similar to that at 55°C.

Fig. 3 F_{2L} , F_{2M} , and F_{2S} vs. reaction time for MA at 55°C. $\circ$, F_{2L} ; $\bullet$, F_{2M} ; $\square$, F_{2S} .

Fig. 4 F_S vs. reaction time for MA at various temperatures. $\circ$, 60°C; $\bullet$, 55°C; $\square$, 50°C; $\blacksquare$, 45°C; $\triangle$, 40°C.

Reaction time dependence of F_S and the polymer yield

Figure 4 shows that the dependence of F_S on the polymerization time at various temperatures. F_S at each temperature increases sharply at a certain reaction time and reaches a saturated value.^{15,21} This increase occurs at shorter times as the reaction temperature rises. Figure 5 shows the reaction time dependence of the polymer yield at various temperatures. As is well known, in the bulk polymerization of the methacrylate polymer, the yield vs. reaction time curve shows a sigmoidal increase due to “gel effect”, and has a saturated value.⁷ A similarity in the time course of the reactions can be observed in both Figs. 4 and 5, although there is a difference between the equilibrium values of F_S and the polymer yield. As we have pointed out, F_S corresponds to the amount of a tight entanglement of polymer chains, and F_M corresponds to the amounts of polymers whose molecular weight is lower (more mobile) than that belonging to F_S .¹⁵ The latter does not form a spectroscopically tight entanglement by itself, or a loosely entanglement. The onset of the gel effect corresponds to the occurrence of entanglement. Taking into account the meaning of F_M , we show the time course of $F_S + F_M$ at various temperatures in Fig. 6. The time course of the polymer yield resembles much more that in Fig. 6 than in Fig. 4. Figure 7 shows a comparison of the amount of $F_S + F_M$ and the polymer yield at various temperatures and reaction time. A straight line with a slope of 45 degree was obtained, although the yield slightly exceeded F_S in a region of a polymer yield less

Fig. 5 Polymer yields vs. reaction time for MA at various temperatures. ○, 60°C; ●, 55°C; □, 50°C; ■, 45°C; △, 40°C.

Fig. 6 $F_M + F_S$ vs. reaction time for MA at various temperatures. ○, 60°C; ●, 55°C; □, 50°C; ■, 45°C; △, 40°C.

than 20%. At the early stage of polymerization, there was a distribution of the molecular weight of polymers including monomers and oligomers.²² Those constituents were observed as the same degree of motion and undistinguishable by this method. Therefore, in this region, we tend to underestimate the values of $F_S + F_M$, compared to the polymer yield.

¹³C DD/MAS NMR spectroscopy

¹³C DD/MAS NMR spectra were also measured on samples recovered after a certain reaction period. Figure 8 shows the ¹³C DD/MAS NMR spectra of MA or PMA at various reaction times at 55°C. The carbon peaks belonging to the residual monomers or polymers can be observed separately, which qualitatively offers a spectroscopic view on the cross-section of the polymerization progress. As the polymerization proceeds, the sample becomes viscous and then solidified, and the ¹H-¹³C dipole-dipole interaction becomes conspicuous, accompanied by a broadening of the peaks. The peaks ascribed from the monomer can still be observed, even at a reaction time of 300 min, and do not disappear. This result supports the idea that a part of F_L is assignable to residual monomers that are trapped, and become less mobile (decrease in T_{2L}) due to the entangled high-molecular-weight polymers. The peaks of carbons within the main chain become broader with the reaction time as well as those of the carbons of the side chain in polymers, while the width of peak of the monomers remains narrow. These time dependences of the peak broadening correspond to the bulk

Fig. 7 Relationship between $F_S + F_M$ and polymer yields. ○, 60°C; ●, 55°C; □, 50°C; ■, 45°C; △, 40°C.

Fig. 8 ¹³C DD/MAS NMR spectra for MA and PMA at different reaction times at 55°C. 1) 30 min, 2) 90 min, 3) 180 min, 4) 300 min. A, COOCH_3 (polymer); B, COOCH_3 (monomer); C, $\text{CH}_2=\text{CH}$; D, $\text{CH}=\text{CH}$; E, COOCH_3 (polymer + monomer); F, $-\text{CH}_2\text{CH}-$; G, $-\text{CH}_2\text{CH}-$.

polymerization process in terms of the mobility of carbon, and also correspond to the results of those of proton T_2 and their components at 55°C.

Figure 9 shows an inverse of the half-height full width (FWHH) of the ¹³C peaks in the main and side chains against the reaction time. The methylene and methine carbons in the main chain become less mobile at a reaction time of 100 min, followed by peak-broadening of the carboxyl carbon, which is near in the position of the main chain. The motion of the methyl carbon at the end of side chain also becomes constrained. Carbons within the main chain become less-mobile at first to form an entanglement, and then affect the motion of the side chain. These results show that the polymerization of MA clearly reflects on the motion of the

Fig. 9 Full width at half-height (FWHH) of the MA and PMA peaks vs. reaction time at 55°C. ●, COOCH_3 ; ■, COOCH_3 ; △, $-\text{CH}_2\text{CH}-$; ▽, $-\text{CH}_2\text{CH}-$; dashed line represents $T_{2\text{total}}$. The values of FWHH of each MA peak are normalized by that at 30 min.

carbon as well as the proton.

For a comparison of the molecular motion of ^1H and ^{13}C during the course of polymerization, we calculated the total relaxation time, ($T_{2\text{total}}$), as follows:

$$1/T_{2\text{total}} = 1/T_{2\text{L}} \times F_{\text{L}} + 1/T_{2\text{M}} \times F_{\text{M}} + 1/T_{2\text{S}} \times F_{\text{S}}. \quad (4)$$

The time course of $T_{2\text{total}}$ represents comprehensively the occurrence of a tight entanglement of the polymer chain in terms of the proton motion because $T_{2\text{total}}$ takes into consideration of both the relaxation time and its fractions at the same time. The time course of the motion for the main chain and the side carbon chains inversely corresponds to that of $1/T_{2\text{total}}$ for protons at this temperature.

In bulk polymerization, therefore, the sample becomes solidified after the gel effect occurs, due to the occurrence of entanglement of the polymer chains. The solidification of a sample is mainly due to the main chain entanglement, followed by a hindrance of the side chain.

Conclusions

In this work, we showed that the polymer entanglement occurred at the onset of the gel effect, where the constituents underwent a transition from a liquid to a solid. This transition reflects the mobility of the ^1H and ^{13}C spins in the polymer. As for the proton mobility, three kinds of spin-spin relaxation times ($T_{2\text{S}}$, $T_{2\text{M}}$, $T_{2\text{L}}$) were observed, and the fractions (F_{S} , F_{M} , F_{L}) with these three relaxation times were obtained as the polymerization proceeded. From an NMR spectroscopic point of view, the time course of the three fractions shows a bulk polymerization progress with a decrease in the monomer and an increase in the polymer concentration. The $T_{2\text{L}}$ component arises from molecules that are too small to form an entanglement. The $T_{2\text{S}}$ component, on the other hand, arose from a motionally restricted region that contained a tight entanglement of the polymer chains. The $T_{2\text{M}}$ component of which molecular weight was adequately high belonged to the more mobile segment in the entanglement.

From the results concerning the carbon mobility, entanglement occurs due to the propagation of the main chain of a polymer, resulting in a motionless state of the main chain and the side chain. The residual monomers remain in the

entanglement, which contributes to a part of the F_{L} component. During the course of polymerization after an occurrence of the gel effect, the value of $F_{\text{S}} + F_{\text{M}}$ (amounts of entanglement) is equal to the polymer yield. This finding makes it possible to monitor the polymer yield in real time during polymerization and in a non-destructive manner.

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