Pulsed NMR Investigation on the Polymerization of Methyl Methacrylate

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(Received March 5, 1986)

ABSTRACT: Nuclear magnetic resonance transversal relaxation time (T_2) was measured as a function of polymerization time for methyl methacrylate at various temperatures. Three kinds of relaxation times, T_{2l} (long), T_{2m} (intermediate), and T_{2s} (short) are observed as the polymerization proceeds. T_{2l} decreases drastically at a certain reaction time, while T_{2s} changes only slightly throughout the process. The fraction of the T_{2l} component decreases abruptly when T_{2l} decreases, while that of the T_{2s} component increases. The former reflects the decrease in monomer concentration, whereas the latter corresponds to the entanglement of polymer chains to form network structure. The relationship between the fraction of T_{2s} component and the polymer yield was found to be linear, which gives useful information on this polymerization process in terms of mobility.

KEY WORDS Pulsed NMR / Free Induction Decay / Spin-Spin Relaxation Time / Poly(methyl methacrylate) / Bulk Polymerization / Entanglement of Polymer Chains / Network Structure /

So far there have been a number of attempts to observe the polymerization process in a direct manner.^{1–4} Optical microscopy,⁵ X-ray diffraction,⁶ thermal analysis,⁷ and calorimetric method⁸ have been employed for this purpose. Among others, the pulsed nuclear magnetic resonance (NMR) method appears to be particularly suited for studying the polymerization process, because the spin-spin relaxation time is an NMR parameter sensitive to change in molecular mobility which is greatly affected by polymerization.^{9–12}

There has been a study on the kinetics of polymerization, which monitors the change in chemical shift of high resolution NMR spectra.¹³ In this paper, the proton spin-spin relaxation time (T_2) of poly(methyl methacrylate) (PMMA) was measured as a function of polymerization time by the pulsed NMR technique. The results were discussed in terms

of the yield of polymerization and the molecular weight of the resulting polymer.

EXPERIMENTAL

Pulsed NMR measurements were carried out with a Bruker P-20 wide line spectrometer operating at a frequency of 19.8 MHz. The spin-spin relaxation time was obtained directly from the free induction decay (FID) which follows a 90° pulse. The width of the 90° pulse was adjusted from 5 μ s to 10 μ s. The pulse interval time was 7 s. The dead time of the apparatus was 5 μ s. The FID's were accumulated to improve the signal-to-noise ratio with a Transient Memory M-100E adapted to an Averager TMC-600 of Kawasaki Electronica Co., Ltd.

Methyl methacrylate (MMA) was distilled twice under reduced pressure. The monomer was sealed with benzoyl peroxide (BPO)

(BPO:MMA = 1:136, molar ratio) in a glass tube (7 mm ϕ) under reduced pressure. The bulk polymerization was carried out in the NMR probe. Another experiment of the bulk polymerization was also carried out under the same experimental conditions as mentioned above to obtain the yield and molecular weight. The reaction temperature was regulated by an air flow thermostat. After a certain period of reaction, the polymerization was stopped by cooling the sample with liquid nitrogen. Poly(methyl methacrylate) (PMMA) was precipitated by pouring the reaction mixture into a large amount of methanol. The polymer was dried at 80°C under reduced pressure and then its weight was measured. The polymer yield was calculated by the following equation;

Polymer yield (%)

$$= \frac{\text{Weight of produced PMMA}}{\text{Weight of MMA}} \times 100 \quad (1)$$

The average molecular weight was obtained from the intrinsic viscosity measured in acetone at 25°C by using Bischoff's equation.^{14,15}

RESULTS AND DISCUSSION

Change of Free Induction Decay Signal in the Course of Polymerization

The FID signal of MMA in the early stage of polymerization was apparently of a single exponential type with a long spin-spin relaxation time. On the other hand, the decay curve later became nonexponential. It is obvious that the change in the FID signal shows the progress of polymerization. It has been suggested that the FID curve is exponential for molecules with a shorter correlation time of motion in the liquid state, and that the curve is nonexponential,¹⁶ i.e., Gaussian, for those with a longer correlation time in the rigid state. As the polymerization proceeds the system changes from the liquid state to the solid or

glassy state via the viscous liquid or elastic gel state. We assume that in the course of polymerization the system consists of various components with different T_2 . Thus, the FID curve of the polymerization system $S(\tau)$ can be fitted to the Weibull function¹²

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

Here, τ is the time, E_i is the Weibull coefficient, S_{0i} , the signal intensity of the i -th component at $\tau=0$, and T_{2i} is the spin-spin relaxation time of the i -th component. The fraction of the j -th component, F_j , is given by

$$F_j = S_{0j} / \sum_i S_{0i} \quad (3)$$

The Weibull coefficient can be taken on either Gaussian ($E=2$), exponential ($E=1$) or intermediate character.⁹ In this experiment, the FID signals were found to be exponential at the early stage of polymerization, and then became the sum of exponential and Gaussian components. In analysis of FID in this experiment, the initial portion of FID was obtained by extrapolation, because it could not be observed for the sake of the dead time. Figure 1 shows the logarithm of the FID of MMA at a reaction time of 17 h plotted against τ . At times longer than 120 μ s, exponential data fall on a straight line, L_1 ,

Figure 1. Analysis of FID signal of MMA: reaction time, 17 h; reaction temp, 45°C; MMA = 1.12×10^{-2} mol; BPO = 8.26×10^{-5} mol.

Figure 2. T_{2s} , T_{2m} , and T_{21} vs. reaction time for MMA at 45°C: $\circ$, T_{2s} ; $\odot$, T_{2m} ; $\bullet$, T_{21} .

giving a longer T_{21} . Furthermore, at times 40–120 μs , the deviation from the line L_1 (open circles) falls on another straight line L_2 , giving an intermediate T_{2m} . At times less than 40 μs , deviation from L_1 and L_2 does not fall on a straight line. This initial portion of the curve C_3 is shown in the inset of Figure 1 plotted against the square of time. The plot is linear, indicating the curve C_3 is Gaussian with shorter T_{2s} . Thus, we obtain three components with different T_2 . The mass fraction of each component was determined from the intercept of the vertical axis ($\tau=0$) of each component.

Reaction Time Dependence of Spin-Spin Relaxation Times

Figure 2 shows the change in spin-spin relaxation time of MMA as a function of the reaction time at 45°C. Only T_{21} was obtained to the rigid species which arise from the solid reaction time less than $t=200$ min. At relatively longer reaction times, the FID was found to be nonexponential, and three different relaxation times were obtained. The longer relaxation time, T_{21} , is attributed to mobile species, which are residual monomers and/or low molecular weight polymers. On the other hand, the shortest relaxation time T_{2s} (15–20 μs) of the Gaussian decay is attributed to the rigid species which arise from the solid aggregation of the high molecular weight

Figure 3. F_s , F_m , and F_1 vs. reaction time for MMA at 45°C: $\circ$, F_s ; $\odot$, F_m ; $\bullet$, F_1 .

polymer.^{16,17} T_{21} remains unchanged at reaction times shorter than 200 min where it decreases abruptly and component with T_{2s} and T_{2m} begin to be observed. There is no significant change in T_{2m} at reaction times longer than 400 min. The appearance of the component with T_{2m} is somewhat later than that of T_{2s} . The appearance of the components with T_{2s} and T_{2m} and decrease of that with T_{21} occur at shorter reaction times as the polymerization temperature rises.

Reaction Time Dependence of Fraction of T_{2s} , T_{2m} , and T_{21} Components

Figure 3 shows the change in fraction of T_{2s} , T_{2m} , and T_{21} components referred to as F_s , F_m , and F_1 , respectively, as a function of reaction time at 45°C. F_s is zero until the reaction time reaches 200 min, where it abruptly increases to reach about 80% at longer reaction times. On the other hand, F_1 decreases abruptly at almost same time as T_{21} shows an abrupt decrease. The abrupt increase in F_s and the abrupt decrease in F_1 clearly show that the polymerization occurs.

McCall *et al.*¹⁸ pointed out in their study on the mixture of polyethylene and paraffin wax that polyethylene is plasticized by the paraffin wax and that the paraffin wax, in turn, is greatly hindered in motion. It is probable that at longer reaction times MMA and low molecular weight PMMA are hindered in motion by high molecular weight PMMA, resulting in

decrease in T_{21} . F_m is larger than F_1 at longer reaction times. The meaning of F_m is not clarified yet at present. The T_{2m} component has been also observed for polymer melt.^{19,20}

Reaction Time Dependence of F_s

Figure 4 shows the dependence of F_s on the reaction time at various temperatures. F_s at each temperature increases abruptly at a certain reaction time and reaches a saturated value. The abrupt increase occurs at shorter times as the reaction temperature is raised. Figure 5 shows the reaction time dependence of the polymer yield at various temperatures. As well known, in the bulk polymerization of MMA the polymer yield vs. reaction time curve shows a sigmoidal increase owing to the "gel effect"^{21,22} and has a saturated value. This is because the termination reaction is hindered.²³ The polymer yield curves obtained in this experiment are similar to those of F_s . Figure 6 shows the plot of F_s vs. the polymer yield at various reaction times and temperatures. A straight line with a slope of 45° was obtained, although the yield slightly exceeds F_s at polymer yield less than 20%. Table I shows the comparison between F_s and the polymer yield at final stage of polymerization. Taking into the account of experimental errors, F_s is equal to the polymer yield at each temperature. The results show that the pulsed NMR gives us a useful tool for monitoring the polymer yield continuously.

Reaction Time Dependence of Molecular Weight

Figure 7 shows the dependence of the molecular weight of PMMA on the reaction time. The molecular weight increases in a similar manner as the polymer yield curve. As the temperature is raised, the molecular weight becomes lower. Soh²⁴ pointed out that in the bulk polymerization of MMA, the entanglement of polymer chains occurs as the polymer concentration and/or the mo-

Figure 4. F_s vs. reaction time for MMA at various temperatures: ○, 45°C; ○, 50°C; ⊕, 55°C; ●, 60°C; ●, 65°C.

Figure 5. Polymer yield vs. reaction time for MMA at various temperatures: ○, 45°C; ○, 50°C; ⊕, 55°C; ●, 60°C; ●, 65°C.

Figure 6. Relationship between F_s and polymer yield: ○, 45°C; ○, 50°C; ⊕, 55°C; ●, 60°C; ●, 65°C.

Table I. Comparison of F_s with polymer yield at various temperatures

Temp/°C	$F_s^a/\%$	Polymer yield ^a /%
45	81.0 ± 2.3	80.0 ± 3.8
50	88.4 ± 1.7	89.5 ± 6.7
55	88.9 ± 1.6	82.9 ± 1.2
60	90.0 ± 1.3	85.8 ± 6.6
65	88.3 ± 3.7	85.5 ± 4.1

^a Average of five measurements. **Figure 7.** Dependence of molecular weight of PMMA on reaction time: ○, 45°C; ◐, 50°C; ◑, 55°C; ●, 60°C; ●, 65°C.

lecular weight increase and that the “gel effect” is closely related to the change of free volume and the occurrence of the entanglement of polymer chains. The critical molecular weight that gives rise to the entanglement effect has been reported to be about 10,000.²⁴ From Figures 4 and 7, the molecular weight where the T_{2s} component begins to appear is higher than the critical molecular weight. It could be possible to conclude that the component of T_{2s} corresponds to regions containing entanglements of polymer chains in the reaction mixture. Folland *et al.*²⁵ also pointed out that the spin-spin relaxation time is sensitive to the presence of entanglements when they are present sufficiently for a network structure.

Figure 8. T_2^+ vs. molecular weight of PMMA at various temperatures: ○, 45°C; ◐, 50°C; ◑, 55°C; ●, 60°C; ●, 65°C.

Molecular Weight Dependence of Mean Spin-Spin Relaxation Time

Relationship between the molecular weight of PMMA and the mean spin-spin relaxation time (T_2^+) is given in the Figure 8. T_2^+ is defined as the time at which the total magnetization decays to $1/e$ of its initial value.²⁶ T_2^+ decreases with increasing molecular weight. The slope of the T_2^+ vs. molecular weight plot was found to change at the point where the “gel effect” occurs. This change implies that a drastic decrease in mobility of whole system occurs at this point. Cosgrove *et al.*²⁷ showed that the dependence of T_2 on the molecular weight for polystyrene solution has a sharp break at a characteristic molecular weight, indicating that the system transforms from relatively viscous solution to entangled network. The abrupt decrease in T_2^+ observed in our experiment would be related to the occurrence of a large amount of entanglements of polymer chains which results in the transition of the reaction mixture from solution to immobile glassy solid and in the decrease of free volume of the system. This transition occurs at molecular weight of *ca.* $0.8\text{--}1.1 \times 10^6$, independent of temperature. For the PMMA formed in the early stage of polym-

erization, which has an average molecular weight less than 10^6 , the entanglement exists but only a part of the molecules contributes to affording the T_{2s} components because of the low concentration of the entanglement.

CONCLUSION

In the bulk polymerization of MMA, three kinds of spin-spin relaxation times (T_{2s} , T_{2m} , T_{2l}) were observed, and the fractions (F_s , F_m , F_l) of components with three relaxation times were obtained as functions of reaction time and temperature. The T_{2l} component arises from molecules that are too small to form the entanglement. The T_{2s} component arises from the motionally hindered region which contains entanglement. In the course of polymerization after the "gel effect" occurs, the value of F_s becomes almost equal to that of the polymer yield. This finding makes it possible to estimate the polymer yield in a nondestructive manner. In this work we showed the time course of polymerization directly and continuously observed by the pulsed NMR. This method is also useful for studying the behavior of the mechanical properties in the polymerization or the cross-linking of rubber, because the spin-spin relaxation time is sensitive to the formation of entanglement of polymer chains (network structure).

Acknowledgements. The author wishes to thank Professor M. Kasagi and Professor M. Nagai of the National Defense Academy and Professor K. Hikichi of Hokkaido University for their critiques and comments.

REFERENCES

1. C. Chachaty and A. Forchioni, *J. Polym. Sci., A-1*, **10**, 1905 (1972).
2. A. Forchioni and C. Chachaty, *J. Polym. Sci., A-1*, **10**, 1923 (1972).
3. Y. Shioji, S. Ohnishi, and I. Nitta, *J. Polym. Sci., A-1*, **1**, 3373 (1963).
4. C. Chachaty, M. Latimier, and A. Forchioni, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 189 (1975).
5. G. Adler, D. Ballantine, and B. Baysal, *J. Polym. Sci.*, **48**, 195 (1960).
6. G. Adler and W. Reams, *J. Chem. Phys.*, **32**, 1698 (1960).
7. C. Chachaty, M. Magat, and L. Terminassian, *J. Polym. Sci.*, **48**, 139 (1960).
8. R. Bensasson and A. Dworkin, *C. R. Acad. Sci., (Paris)*, **256**, 4903 (1963).
9. S. Kaufman, *J. Polym. Sci., A-2*, **9**, 829 (1971).
10. H. Tanaka, *J. Appl. Polym. Sci.*, **28**, 1707 (1983).
11. R. Folland and A. Charlesby, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 339 (1978).
12. H. Serizawa, M. Ito, T. Kanamoto, K. Tanaka, and A. Nomura, *Polym. J.*, **14**, 149 (1982).
13. S. Kobayashi, H. Danda, and T. Saegusa, *Bull. Chem. Soc. Jpn.*, **47**, 2699 (1974).
14. J. Bischoff and V. Desreux, *Bull. Soc. Chim. Belges*, **61**, 10 (1952).
15. J. Brandrup and E. M. Immergut, Ed., "Polymer Handbook," 2nd ed, Interscience, New York, N. Y., 1975.
16. I. Kamel and A. Charlesby, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 803 (1981).
17. R. Folland and A. Charlesby, *Polymer*, **20**, 211 (1979).
18. D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Polym. Sci.*, **59**, 301 (1962).
19. H. Tanaka, *J. Appl. Polym. Sci.*, **27**, 2197 (1982).
20. D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, **71**, 998 (1967).
21. G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).
22. E. Trommsdorff, H. Köhle, and P. Lagally, *Makromol. Chem.*, **1**, 169 (1948).
23. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949).
24. S. K. Soh and D. C. Sundberg, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1345 (1982).
25. R. Folland, J. H. Steven, and A. Charlesby, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1041 (1978).
26. R. A. Assink, *J. Appl. Polym. Sci.*, **26**, 3689 (1981).
27. T. Cosgrove and R. F. Warren, *Polymer*, **18**, 255 (1977).