NOTES

Pulsed NMR Investigation on the Polymerization II. Bulk Polymerization of Methacrylic Acid

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In a previous publication,[1] we reported that the polymerization of methyl methacrylate (MMA) can be studied by the pulsed NMR technique. The free induction decay (FID) of poly(methyl methacrylate) (PMMA) was found to consist of three different components, having a long spin–spin relaxation time (T_{2l}), an intermediate one (T_{2m}), and a short one (T_{2s}). The fraction of the T_{2l} component is associated with the concentration of monomers and/or low molecular weight materials, whereas that of the T_{2s} component corresponds to the fraction of entanglements of polymer chains responsible for the network structure in the reaction mixture.

This paper is concerned with the bulk polymerization of methacrylic acid (MAA). The results are compared with those for the polymerization of MMA which involves formation of entanglement of polymer chains. PMAA has carboxyl groups which can be responsible for the formation of the three dimensional network structure in addition to the effect of entanglement of main chains.

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 FID which followed a 90° pulse. The width of the 90° pulse was adjusted from 5 μs to 10 μs. The pulse interval time was 7 sec. 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. In the analysis of FID in this experiment, the initial portion of FID was obtained by extrapolation, because it could not be observed owing to the dead time.

Methacrylic acid was distilled twice under reduced pressure. The monomer was sealed with benzoyl peroxide (BPO : MAA = 1 : 171, mole ratio) in a glass tube (7 mmϕ) under reduced pressure. The bulk polymerization was carried out in the NMR probe. Another experiment of bulk polymerization was carried out under the same experimental conditions as mentioned above to obtain the yield. The reaction temperature was regulated by an air flow thermostat. PMAA was obtained by pouring the reaction mixture into a large amount of ether. The polymer was dried at 70°C under vacuum and weighed. The polymer yield was calculated by the following equation,

Polymer Yield (%)

$$= \frac{\text{Weight of Produced PMAA}}{\text{Weight of MAA}} \times 100$$

Figure 1 shows the change in spin–spin relaxation time (T_2) as a function of the reaction time at 42°C. In the beginning of the polymerization, MAA has only one T_{2l}. At the reaction time of 200 min, FID signals consist of three different T_2 times, the long one, T_{2l}, the intermediate one, T_{2m}, and the short one, T_{2s}. The FID signals obtained could be ana-
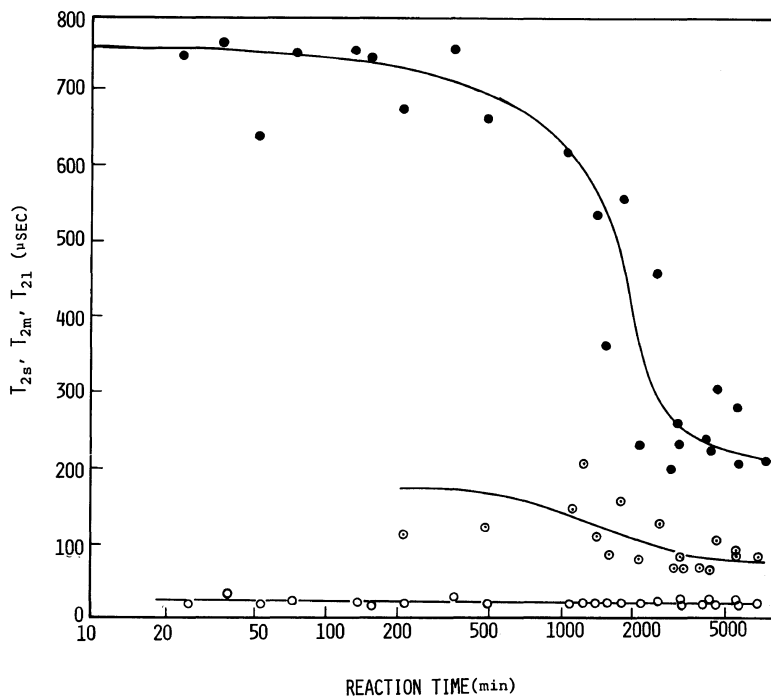

Figure 1. T_{2s}, T_{2m}, and T_{2l} vs. reaction time for MAA at 42°C. $\bigcirc$, T_{2s}; $\odot$, T_{2m}; $\bullet$, T_{2l}. MAA = 1.41×10^{-2} mol; BPO = 8.25×10^{-5} mol.
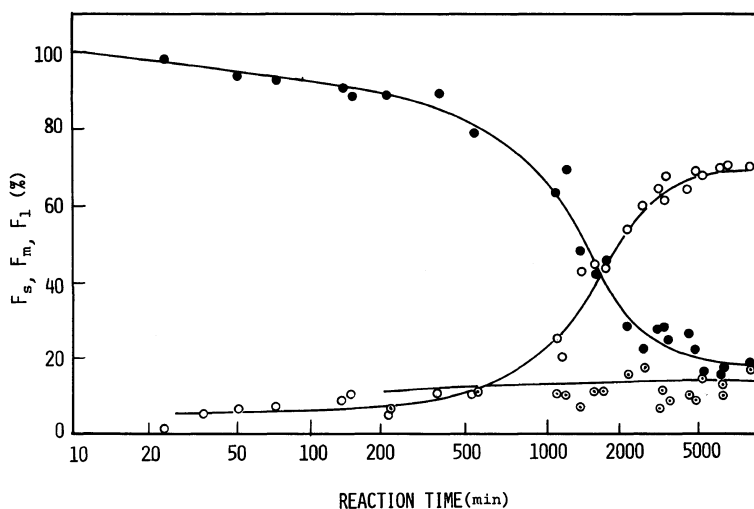

Figure 2. F_s, F_m, and F_l vs. reaction time for MAA at 42°C. $\bigcirc$, F_s; $\odot$, F_m; $\bullet$, F_l.

lyzed in the way proposed by Fujimoto *et al.*[2-4] Two (T_{2l}, T_{2m}) of the terms obey an exponential function while the remaining (T_{2s}) obeys a Gaussian function.

Figure 2 shows fractions of T_{2s}, T_{2m}, and T_{2l} components, referred to as F_s, F_m, and F_l, respectively, as a function of the reaction time at 42°C. F_s increases sigmoidally with reaction time, showing an abrupt increase at the reaction time 1000 min. On the other hand, F_l abruptly decreases at the reaction time 1000 min, where T_{2l} shows an abrupt decrease. As the temperature rises, the increases in F_s and decrease in F_l occur at shorter reaction times. As we have pointed out in the previous paper,[1] the fraction of T_{2s} component is attributable to the rigid species which arise from the aggregation of high molecular weight polymers and the fraction of T_{2l} component corresponds to the monomer and/or low molecular weight polymer. Such behavior of components of T_{2s} and T_{2l} as a function of reaction time clearly reflects the process of polymerization of MAA through the change in mobility of protons. The fraction of T_{2m} component begins to appear at a time where T_{2s} reaches to a few percent. This component remains almost

unchanged throughout the reaction, and is often observed in FID for polymer melts.[4,5] However, the meaning of F_m has not been clarified yet.

Figure 3 shows the plots of the polymer yield (dotted line) and the fraction of T_{2s} component (solid line) against the reaction time. The fraction of the T_{2s} component at each temperature gradually increases from the beginning of the reaction, and then shows a sharp increase owing to the "gel effect",[6] while the yield curve remains almost below the F_s curve until the occurrence of the "gel effect". The F_s at each temperature is equal to the yield at and after the occurrence of the "gel effect" and has almost the same saturated value as that for F_s. This tendency (F_s exceeds slightly the polymer yield in the early stage of the reaction) is in contrast with the results obtained for PMMA previously.[1]

Folland *et al.*[7,8] pointed out that T_2 is sensitive to the formation of the entanglement of polymer chains (network structure) and that F_s is ascribed to the entanglement of polymer chains responsible for the network structure. The network structure of PMAA could be considered to arise from two factors, the as-
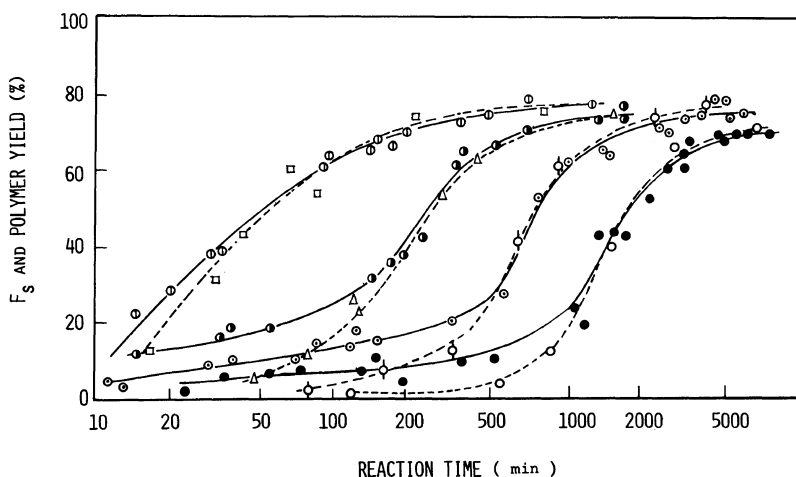

Figure 3. F_s and polymer yield *vs.* reaction time at various temperatures. —●—, F_s at 42°C; ---○---, yield at 42°C; —⊙—, F_s at 50°C; ---◌---, yield at 50°C; —◑—, F_s at 60°C; ---△---, yield at 60°C; —⊕—, F_s at 70°C; ---□---, yield at 70°C.

sociation of carboxyl groups in the side chain and the aggregation of the main chains adequately long enough to form the entanglement. The carboxyl groups in a straight chain fatty acid[9] are known to form associates by hydrogen bonding. Carboxyl groups in PMAA also could associate with each other to form the three dimensional network structure. This could explain the fact that the glass transition temperature (T_g) of PMAA (501K) is much higher than that for PMMA (atactic PMMA: 378K, isotactic PMMA: 311K, syndiotactic PMMA: 378K).[10] Therefore, PMAA forms more easily the network structure than PMMA especially in the early stage of polymerization (before the occurrence of the "gel effect") where the contribution of the main chain to the formation of network structure is not predominant. After the "gel effect", the contribution of the main chain to the formation of the entanglement becomes predominant and high molecular weight polymers produced form entanglement. These effects make the value of F_s equal to that of the polymer yield.

Although some discrepancies between F_s and the polymer yield are observed before the occurrence of the "gel effect", it is concluded that the time course of the polymerization of MAA as in the case of MMA can be studied by the pulsed NMR method nondestructively and continuously through the mobility of protons.

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