

SHORT COMMUNICATIONS

Evidence for Disproportionation in Termination Reaction of Styrene Polymerization by α,α' -Azobisisobutyronitrile

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Analysis of initiator fragments at the end of polymer chain is a straightforward method for assessing the relative importance of combination and disproportionation in the termination reaction in radical polymerization. It has been demonstrated utilizing ^{14}C -labeled α,α' -azobisisobutyronitrile (AIBN) that poly-(methyl methacrylate) radicals undergo substantial disproportionation while polystyrene radicals terminate exclusively by combination at a temperature up to 60°C .^{1,2} However, Berger and Meyerhoff³ reported for styrene polymerization at 52°C using ^{14}C -labeling method and kinetic analysis that both combination and disproportionation compete with each other. Recently, NMR studies were carried out to examine the end group of polymer chain using ^{13}C -,⁴⁻¹⁰ ^2H -,^{9,11} ^{19}F -,¹² or ^{15}N -labeled⁹ initiator. Moad *et al.*⁷ reported that the number of initiator fragments per molecule was 1.7—1.8 for the polystyrene obtained in bulk polymerization with ^{13}C -labeled AIBN at low conversions and that transfer to initiator by 1-cyano-1-methylethyl group transfer or by hydrogen atom abstraction did not occur in the polymerization at low conversions. This may indicate that the disproportionation reaction is not of negligible importance in the polymerization of styrene.

In our previous paper,¹³ totally deuterated methyl methacrylate was polymerized with undeuterated AIBN and benzoyl peroxide, and the resultant polymer was analyzed for initiator fragments by ^1H NMR spectroscopy. From the results, the relative importance of combination and disproportionation in the termination reaction was estimated. In the present work it was found by utilizing this totally deuterated monomer technique that disproportionation is not of negligible importance in the termination reaction in radical polymerization of styrene.

Styrene and styrene- d_8 were obtained commercially. These were purified by fractional distillation under reduced nitrogen pressure and redistilled under high vacuum over calcium hydride just before use. Commercial AIBN was recrystallized from ethanol. AIBN- d_{12} was prepared from acetone- d_6 by the method of Overberger *et al.*¹⁴ Polymerization was carried out in a glass ampoule under dry nitrogen. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was collected by filtration, washed thoroughly with methanol and dried under high vacuum at 60°C .

^1H NMR spectra of the polymers were measured on a JEOL JNM-FX 100 (100 MHz)

Table I. Number of initiator fragments per polymer molecule for the polystyrene prepared by AIBN at 60°C

AIBN	Monomer	Solvent	Yield	M_n	AIBN fragment	
mol l^{-1}	mol l^{-1}		%		mol/mol	
0.17	Styrene- d_8	8.6	Bulk	14.6	23700	1.59
0.17	Styrene	8.4	Bulk	11.7	18400	1.52
— ^a	Styrene	7.7	Solution	—	—	1.67
0.2 ^b	Styrene	8.4	Bulk	8.0	22000	1.70
0.009 ^c	Styrene	0.9	Benzene	5.5	6600	1.65
0.02	Styrene	2.0	Benzene	14.1	8090	1.56

^a Data taken from ref 3. ^{14}C -labeled AIBN was used. The initiator concentrations were 0.00054–0.0150 mol l^{-1} , and M_n 's were 4.42×10^5 – 1.14×10^5 .

^b Data taken from ref 7. ^{13}C -labeled AIBN was used.

^c AIBN- d_{12} was used.

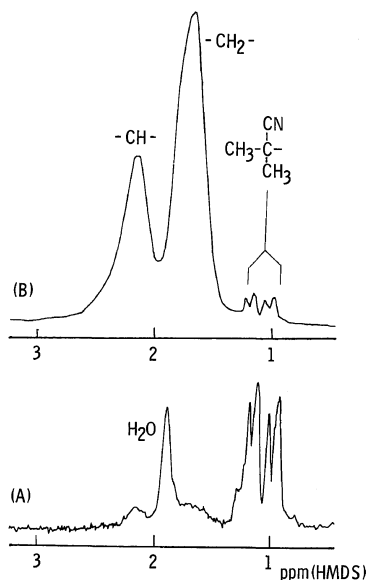


Figure 1. ^1H NMR spectra of (A) poly(styrene- d_8) and (B) polystyrene prepared by AIBN in bulk at 60°C. Nitrobenzene- d_5 , 110°C, 100 MHz.

or JEOL GX-270 (270 MHz) spectrometer in nitrobenzene- d_5 at 110°C or in chloroform- d at 55°C. Tetramethylsilane was used as the internal standard. ^2H NMR spectra were measured on a JEOL GX-400 spectrometer at 61 MHz in nitrobenzene containing 3.86 wt% nitrobenzene- d_5 . The ^2H chemical shift was referred to the highest-field peak of nitro-

benzene- d_5 . The molecular weights of the polymers were measured on a JASCO FLC-A10 chromatograph with Shodex GPC columns A-80M (50 cm \times 2) with the maximum porosity of 5×10^7 using tetrahydrofuran as an eluent.

Styrene- d_8 was polymerized in bulk with undeuterated AIBN at 60°C. The results are shown in Table I and the ^1H NMR spectrum of the polymer is illustrated in Figure 1A. The resonances centered at 0.94 and 1.11 ppm showed the ^1H spin-lattice relaxation time, T_1 , of 0.94 and 0.96 s, respectively, but were not observed when the polymer was prepared with AIBN- d_{12} . The T_1 values were much shorter than those which would be expected for the contaminants of small molecules (~ 10 s) but longer than the T_1 's for the protons of the groups within polymer chain (~ 0.1 s). Thus, the resonances were assigned to the initiator fragment, 1-cyano-1-methylethyl group located at the chain end of the polymer molecule. The splitting into two peaks at 0.94 and 1.11 ppm of equal intensities is due to the existence of an adjacent asymmetric center in the polymer chain. Further splittings of these peaks may be due to the tacticity of the first few monomer sequences at the chain end. The intensity of these initiator residue signals was measured relatively to that of the remaining

Disproportionation in Styrene Polymn. by AIBN

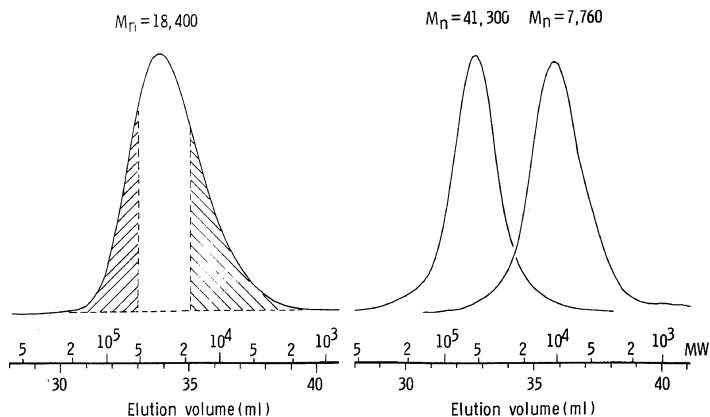


Figure 2. Fractionation by GPC of polystyrene prepared by AIBN in bulk at 60°C.

protons in nitrobenzene- d_5 used as a solvent. The amount of the remaining protons in nitrobenzene- d_5 was determined by the precision coaxial tubing method.¹⁵ From the results, the number of initiator fragments per polymer molecule was calculated to be 1.59, indicating that there exist two types of polymer molecules which contain one and two initiator fragments, respectively.

Undeuterated polystyrene ($M_n = 18400$) prepared in bulk with AIBN at 60°C showed small NMR peaks at 1.01 and 1.18 ppm (Figure 1B), which were assigned by Johns *et al.* to the methyl protons of initiator fragments.¹⁶ Since these peaks were situated considerably apart from the strong signals of the backbone methylene and methine protons, the intensity could be determined accurately enough and the number of initiator fragment per chain was calculated to be 1.52 (Table I). From the polystyrene, a lower ($M_n = 7760$) and a higher ($M_n = 41300$) molecular weight portions were fractionated using GPC. It was found that the former had 1.44 initiator fragments per chain and the latter 1.77 (Figure 2). This shows that the polymer molecules containing two initiator fragments on both ends are larger in molecular weight than those containing one initiator fragment.

Styrene was also polymerized in benzene at 60°C with AIBN- d_{12} (Table I). In the ^2H NMR

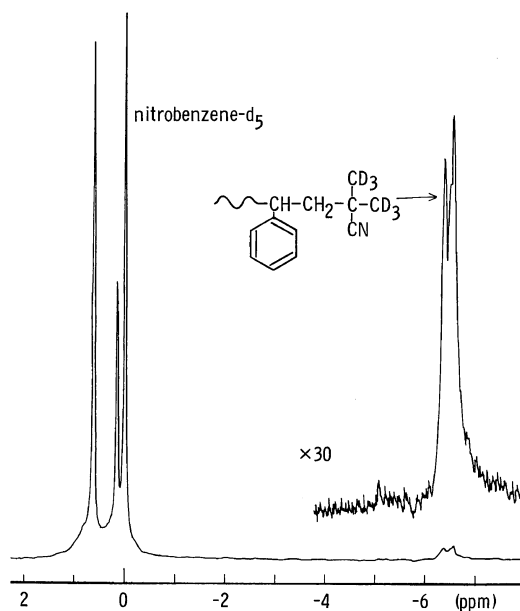


Figure 3. ^2H NMR spectrum of polystyrene prepared by AIBN- d_{12} in benzene at 60°C. Nitrobenzene + nitrobenzene- d_5 (3.86 wt%), 110°C, 61 MHz.

spectrum of the polymer measured in a nitrobenzene- d_5 /nitrobenzene mixture, there appeared the signal at -6.4 ppm, assignable to the initiator fragment, $(\text{CD}_3)_2\text{C}(\text{CN})$ -group at the chain end (Figure 3). The measurement of the relative intensity of this signal to that of nitrobenzene- d_5 indicated that the polymer contained 1.65 initiator fragments per chain. The polymerization of styrene in benzene with

undeuterated AIBN gave similar results as shown in Table I.

^1H NMR analyses of AIBN fragments in deuterated and undeuterated polystyrenes and ^2H NMR analysis of AIBN- d_{12} fragments in undeuterated polystyrene, are consistent with each other. This clearly indicates that the polystyrene prepared at 60°C with AIBN had the initiator fragments of 1.5–1.7. The values were less than 2.0, which would be expected when the polymer radicals terminate only by combination reaction and any transfer reactions can be neglected. Moad *et al.*⁶ reported that the number of initiator fragments in the polystyrene prepared with ^{13}C -labeled AIBN in bulk at 60°C and at low conversions were 1.7–1.8 per chain. Monomer transfer constant for styrene is 10^{-4} – 10^{-5} , that is, one transfer reaction to monomer occurs every 10^4 – 10^5 propagation reactions. In the polymerization in this work the degrees of polymerization are less than 3×10^2 , and therefore, the effect of transfer to monomer can safely be neglected. Actually, the polystyrene prepared in bulk did not show the ^1H NMR signals owing to the vinyl group of styrene residue which would be introduced through the chain transfer reaction to styrene monomer by aromatic substitution or abstraction. Similarly, the transfer to benzene can also be neglected since the transfer constant is in the order of 10^{-6} . It has been established that transfer to initiator is of no importance in the polymerization with AIBN. Recently, it was found using ^{13}C -labeled AIBN that transfer to the initiator by 1-cyano-1-methylethyl group transfer or by hydrogen atom transfer did not occur in the polymerization of styrene at low conversion.⁶ A signal due to terminal methylene deuterium introduced from initiator by deuterium transfer is expected to appear in the region of -6 – -4 ppm. Such a signal was not observed in appreciable intensity in the ^2H NMR spectrum of polystyrene prepared in benzene with AIBN- d_{12} at 60°C . Direct thermal polymerizations were negligible under the

conditions mentioned in Table I (less than 0.02% in yield even in the bulk polymerization). Then, the results obtained in this work clearly indicate that in the radical polymerization of styrene termination reaction by combination is predominant but disproportionation is not of negligible importance. The accuracy in the determination of the number of initiator fragments per chain might not be great since the cumulative errors are associated with the determination of molecular weight and intensity of NMR signals. However, all the results obtained in the polymerizations under different conditions gave the number of initiator fragments per chain of less than 2.0. This and the fractionation data shown in Figure 2 should be the strong additional support for the coexistence of disproportionation and combination in the termination reaction in the polymerization of styrene.

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Disproportionation in Styrene Polymn. by AIBN

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