quantitatively accounts for these SANS results. It should be emphasized that χ represents the *only* fitting parameter in this analysis. Within experimental error, equivalent values of χ have been determined from these two separate mixtures, as indicated in Table I. Also illustrated in Figure 1 (dashed curves) are the calculated scattering curves in the limits of ideal mixing ($\chi = 0$) and single-phase stability ($\chi = \chi_s$).

On the basis of an average measured value of $\langle\chi\rangle = 1.7 \times 10^{-4}$ (Table I), the homogeneous state for sample PSHD3 is calculated (eq 7) to be thermodynamically unstable ($\chi/\chi_s = 1.12$) at $T = 160$ °C. The SANS results depicted in Figure 1c lead us to conclude that this mixture has indeed begun to phase separate; i.e., the low-q scattering intensity deviates in form and magnitude from that predicted for homogeneous mixtures ($0 \leq \chi \leq \chi_s$). This SANS behavior is analogous to that previously described for a phase-separated isotopic mixture of 1,4-polybutadienes.[1]

A preliminary investigation of the temperature dependence of χ for perdeuterated and normal polystyrenes has confirmed that these mixtures are also characterized by an UCST. A specimen of mixture PSHD2 was annealed at 215 °C for 12 h, quenched to room temperature, and examined by SANS, revealing $\chi = 1.3 \times 10^{-4}$; this constitutes a 32% reduction[9] from the value determined at 160 °C (Table I). We are presently examining the detailed temperature and composition dependence of χ for this system. These results will be presented in a future report.

Finally, it is interesting to note that Strazielle and Benoit[10] have observed that perdeuterated and normal polystyrenes are characterized by slightly different solution thermodynamic properties. By analyzing the temperature dependence of the second virial coefficient of polystyrene–cyclohexane solutions near the Θ temperature, they estimated the difference in solubility parameters (cohesive energy densities) between normal and perdeuterated polystyrenes to be $\delta_H - \delta_D = 0.038$ (0.048) $(\text{cal/cm}^3)^{1/2}$, where the value in parentheses incorporates corrections for excluded volume effects. Following Hildebrand,[11] the segment–segment interaction parameter can be approximated as

$$\chi = \frac{V_m}{RT}(\delta_H - \delta_D)^2 \qquad (8)$$

where V_m is the segment molar volume. Thus, *10 years ago*, the isotope effect in molten polystyrene could be estimated to be $\chi = 1.7 \times 10^{-4}$ (2.7×10^{-4}) at 160 °C!

In conclusion, we have definitively demonstrated with small-angle neutron scattering measurements that mixtures of perdeuterated and normal polystyrenes are characterized by a small, positive interaction parameter, $\chi = (1.7 \pm 0.4) \times 10^{-4}$ at $T = 160$ °C, and an upper critical solution temperature. These findings parallel our previous discovery of an isotope effect in binary mixtures of perdeuterated and normal 1,4-polybutadienes;[1] extrapolation of $\chi(T)$ determined for 1,4-polybutadienes[1] yields $\chi = (5.2 \pm 1.8) \times 10^{-4}$ at 160 °C.[12] It is our conviction that *all* amorphous mixtures of deuterated and protonated polymers will exhibit such phase behavior, as anticipated by Buckingham and Hentschel.[2]

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Registry No. Perdeuterated polystyrene (homopolymer), 27732-42-9; polystyrene (homopolymer), 9003-53-6; neutron, 12586-31-1.

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(9) This reduction of 32% in χ is subject to less than a 5% error, since both measurements (160 and 215 °C) reflect the same relative error resulting from the uncertainties in N and in the SANS intensity calibration.
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(12) We expect the isotope effect for polystyrene to be smaller than for polybutadiene since the ratio of hydrogen to carbon is smaller in the former.

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Observation of a Persistent Methacrylate Radical in the Decomposition of Methyl 2,2′-Azobis(isobutyrate) and the Polymerization of Methyl Methacrylate

Conformational and electronic states of the propagating polymer radicals of vinyl monomers such as acrylates, acrylonitriles, and acrylamides have been studied by means of ESR spectroscopy[1] under different conditions, i.e., in a frozen matrix or in a heterogeneous solution, from an actual polymerization system because of the difficulty in obtaining a high concentration of polymer radical. To avoid such deviation of the experimental conditions ESR studies using low molecular weight radicals such as captodative substituted radicals[2] have been carried out under similar conditions to those of an actual polymerization system. Recently, we employed 2,2′-azobis(isobutyronitrile) (AIBN) and methyl 2,2′-azobis(isobutyrate) (MAIB) as covenient models for the propagating polymer radicals in the polymerization of methacrylonitrile and methyl methacrylate (MMA).[3] Subsequently we found that the primary radical from MAIB, a model for the poly(MMA) radical, showed interesting behavior in the ESR spectrum and product distribution.

We describe herein the observation by ESR of a persistent methacrylate radical generated from the decomposition of MAIB or the chain-transfer reaction in the radical polymerization of MMA.

Sample solutions in an ESR cell were degassed by the freeze–thaw technique and finally filled with helium gas. ESR spectra were recorded on a JEOL JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity while heating or irradiating (1-kW Xe lamp) the sample in the cavity.

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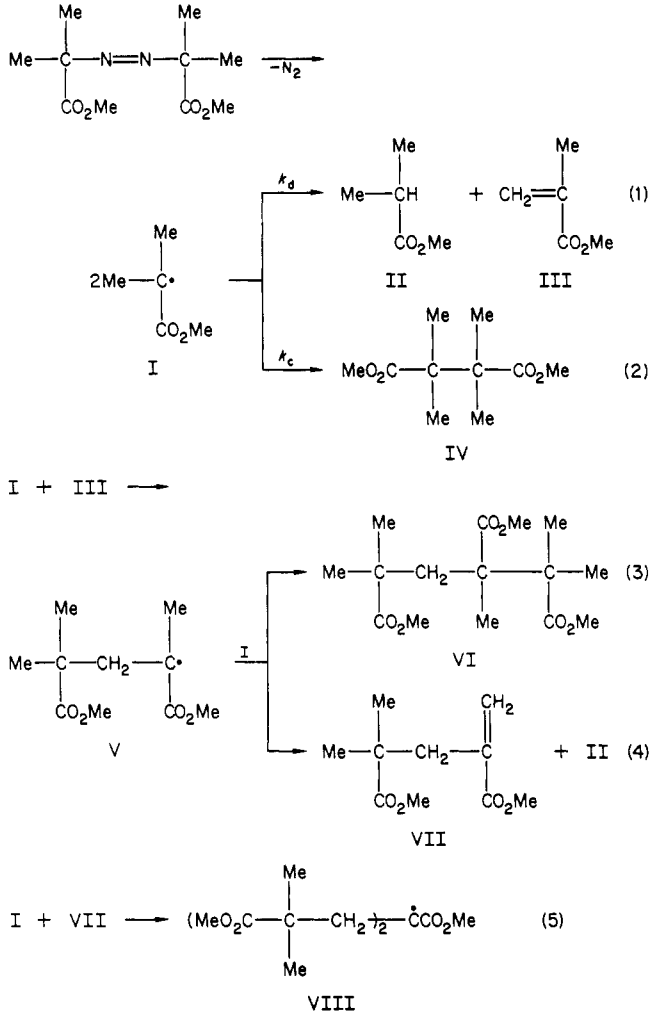
ESR spectra obtained from both pyrolysis at 94 °C and photolysis at 25 °C of MAIB in toluene exhibit a septet (21.3 G) of quartets (1.2 G) due to the primary radical produced by the unimolecular decomposition at first (Figure 1A), but after 10–20 min broad lines consisting of a quintet of quartets appear overlapping with the original lines as shown in Figure 1B,C, where the outer lines are omitted. The observed line shape and the measured hyperfine splitting constants (a) of the newly formed radical indicate the production of the persistent radical VIII ($a_{\beta\text{-H}}$ = 11.7 G and $a_{\delta\text{-H}}$(OMe) = 1.3 G, g = 2.0033) generated from reactions 1–5, whose spectrum is similar to that of the radical R-CH_2-($H_9C_4O_2C$)C($CH_2CO_2C_4H_9$)-CH_2-($H_9C_4O_2C$)$\dot{C}CH_2CO_2C_4H_9$ ($a_{\beta\text{-H}}$ = 13.7 G and $a_{\delta\text{-H}}$-(OCH_2) = 1.1 G).[4]



When a *tert*-butyl or a methyl-d_3 substituent was introduced in place of the ester methyl group in MAIB, which are termed BAIB and MAIB-d_6, the quartet splittings by the hydrogen atoms at the methyl group disappeared in the ESR spectra as shown in Figure 2, where the outer lines of the septet are also omitted. The quintets newly generated in spectra B, C, and D are essentially the same as that of $(Me_3CCH_2)_2\dot{C}CMe_3$ with four equivalent β-hydrogens ($a_{\beta\text{-H}}$ = 12.4 G),[5] suggesting the absence of conformational change and steric compression between the $MeO_2CCMe_2CH_2$ groups within a temperature range from 25 to 94 °C. From comparison of spectra B and D, the rate of the reaction providing the VIII homologue for BAIB seems to be faster than that for MAIB-d_6 in spite of similar decomposition rate constants, 1.1×10^{-4} and 1.0×10^{-4} s^{-1} at 80 °C for MAIB and BAIB, respectively. Such difference in the rate probably depends on the preferential

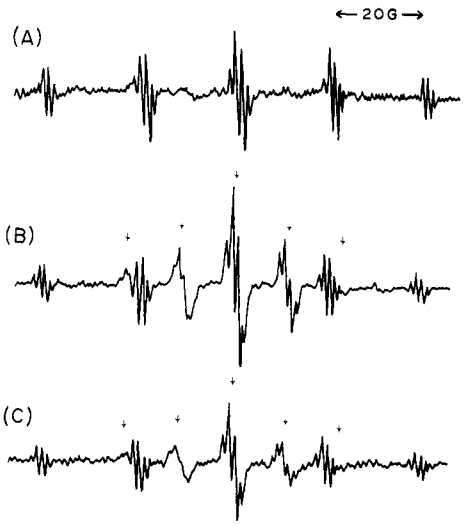


Figure 1. ESR spectra observed during pyrolyses at 94 °C (A and B) and photolysis at 25 °C (C) of MAIB in toluene. Arrows indicate absorptions due to VIII. Reaction time: (A) 2, (B) 22, and (C) 10 min; [MAIB] = 4 M.

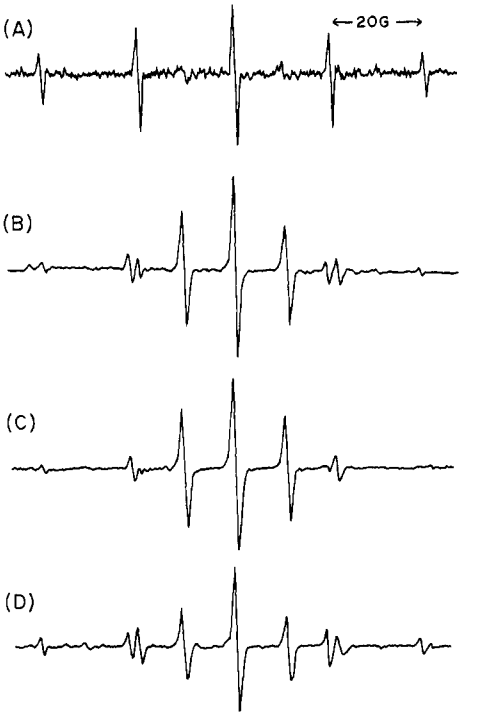


Figure 2. ESR spectra observed during pyrolyses at 94 °C (A and B) and photolysis at 25 °C (C) of BAIB and pyrolysis at 94 °C (D) of MAIB-d_6 in toluene. Reaction time: (A) 3, (B) 28, (C) 27, and (D) 31 min; [BAIB] = 0.5 (A) and 2 M (B and C), [MAIB-d_6] = 2 M.

production of the III homologue for BAIB because of the depression of reaction 2 by the steric effect of the *tert*-butyl group.[6]

The product distributions found for pyrolysis at 80 °C and photolysis (100-W high-pressure mercury lamp) at 25 °C in toluene were 42.1 (IV), 36.4 (II), and 13.8% (VI)[7] and 42.7 (IV), 38.5 (II), and 13.8% (VI), respectively, after 100% conversion. Isolation of VI in fairly good yield strongly suggests that the reaction giving VIII proceeds through the radical intermediate V and the methacrylate derivative VII since reactions 3 and 4 are similar to reactions 1 and 2. Failure to isolate VII from the reaction mixture can be attributed to the fast reaction of 5. In contrast, the ESR spectrum of the decomposition of AIBN in toluene gave only a septet of triplets due to the primary

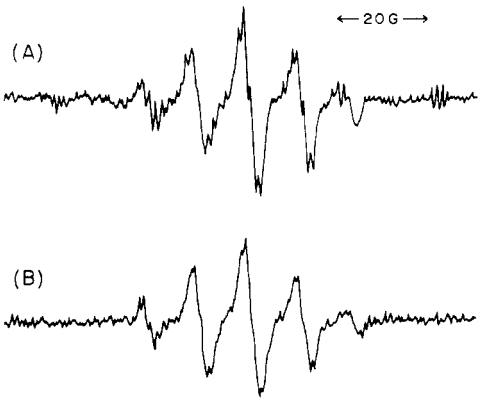
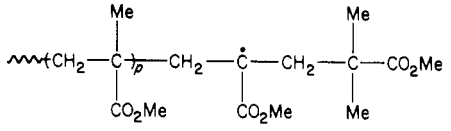


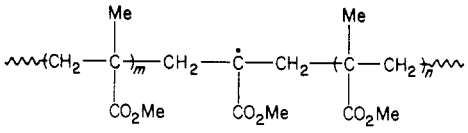
Figure 3. ESR spectra observed during pyrolysis at 94 °C (A) and photolysis at 25 °C (B) of MAIB in the presence of MMA in toluene. Reaction time: (A) 12 and min (B) 25; [MAIB] = 2 M, [MMA] = 4 M.

radical even after a long time, and absorptions corresponding to radical VIII were not detected. This is compatible with the low disproportionation/recombination ratio (≤ 0.11)[3] of the rates (k_d/k_c) of the primary radical-radical reaction for AIBN.

The quintet of quartets with high intensity is observed in the ESR spectra of the decompositions of MAIB in the presence of MMA as shown in Figure 3. Such acceleration was not observed in the ESR spectra when methyl acrylate and *p*-methoxystyrene were added to a MAIB solution as predicted from the reaction scheme. It is reasonable to consider that the persistent polymer radicals IX and X are also contained in these systems since the polymer was precipitated by pouring the reaction mixture into methanol, in contrast to the case in the absence of MMA, and k_d/k_c ratio of the termination in the polymerization of MMA is high, 1.9 at 25 °C[8] and 2.6 at 80 °C.[9] Polymerization of MMA by AIBN also gave a similar quintet of quartets in the ESR spectrum although its intensity was low.



IX



X

Although the present work was carried out under limiting conditions such as high concentration of initiator and low [monomer]/[initiator] ratio, the results obtained here will be helpful in understanding the elemental reactions of the polymerizations of methacrylates and their polymer structures as well as the decomposition mode of azo compounds, especially in high concentrations of initiator.

Registry No. MAIB, 2589-57-3; MMA, 80-62-6.

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Adam-Gibbs Formulation of Nonlinearity in Glassy-State Relaxations

Relaxation in and below the glass transition temperature range is both nonexponential and nonlinear. The nonexponential character is conveniently and accurately described by the response function

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \qquad 1 \geq \beta > 0 \qquad (1)$$

where τ_0 is a characteristic relaxation time and β is a measure of nonexponentiality. The nonlinear character is most conveniently treated by the method introduced by Tool[1] and generalized by Narayanaswamy,[2,3] in which τ_0, or some other characteristic time, is made a function of the departure from equilibrium. A commonly used functional form is the Narayanaswamy expression (N)

$$\tau_0 = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (2)$$

where A, x, and Δh^* are constants, R is the ideal gas constant, and T_f is the fictive temperature introduced by Tool.[4] Several investigators[5-12] have shown that Boltzmann superposition of eq 1 and 2 describes enthalpy relaxation during cooling, annealing, and heating with reasonable accuracy. However, eq 2 has several shortcomings:

(1) It predicts an Arrhenius temperature dependence for the equilibrium state, in conflict with the well-established WLF or Fulcher temperature dependences. Associated with this are unphysically large values of Δh^* (values as high as 450 kcal mol^{-1} have been reported).

(2) The nonlinearity parameter x has no clear physical interpretation.

(3) The physical significance (if any) of the strong inverse correlation between x and Δh^* [11] is unknown.

(4) The parameter x varies systematically with aging time and temperature.[13]

Recently, Scherer[14] has proposed the Adam-Gibbs equation[15] as a theoretical basis for treating nonlinearity.

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