Magnetic Field and Magnetic Isotope Effects on Photoinduced Emulsion Polymerization

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Abstract: The photochemically induced emulsion polymerization of styrene, methyl methacrylate, or acrylic acid is photosensitized by oil-soluble ketone initiators (e.g., dibenzyl ketone) to conversion and average molecular weights that are comparable to those achievable by employing conventional aqueous-soluble thermal initiators such as persulfates. The efficiency of polymerization and the average molecular weight of the polymers formed are significantly increased by the application of laboratory magnetic fields when photoinduced initiation is sensitized by oil-soluble ketones but not when aqueous-soluble thermal initiators are employed. With 1,1'-diphenyl-1,1'-azoethane as initiator, triplet-sensitized initiation, but not thermal or direct photoinduced initiation, shows magnetic field effects on the average molecular weight and the yield of the products. No magnetic field effects are observed for photoinitiated polymerization of styrene or methyl methacrylate in toluene solution. With dibenzyl ketone that is enriched with ^{13}C at both benzylic carbons as photoinitiator, the molecular weight distribution is bimodal. Varying the ratio of ^{13}C-enriched and natural-abundance DBK changes the relative yield of the lower and higher molecular weight fractions. It is concluded that external magnetic fields *decrease* the efficiency of triplet to singlet radical-pair intersystem crossing within micelles and accordingly increase the fraction of radical pairs that escape without terminating polymerization chains.

An important characteristic of emulsion polymerization (EP) is the production of high molecular weight polymers at a relatively rapid rate.[1] The simultaneous achievements of high-molecular-weight polymer and high polymerization rate result from the occurrence of initiation by single radicals at a large number of isolated microscopic reaction vessels (the micelle aggregates initially present), so that chain termination rates are decreased. Extensive work has been carried out on the mechanism of such polymerizations, and it has been found that, in general, water-soluble initiators are best suited for thermally initiating EP.[1] Oil-soluble initiators are commonly ineffective in EP either as thermal initiators or photoinitiators, presumably because such initiators produce pairs of radicals in the initial-polymerization loci and because these pairs undergo termination before substantial polymer growth can be effected.[1d] This result is generally expected if singlet radical pairs are generated in the initial bond-cleaving process. However, photochemically generated *triplet* radical pairs in micelles have been shown to survive long enough to compete, so that escape from micellar aggregates can compete with radical recombination in the micelle.[2-5] Furthermore, application of relatively weak magnetic fields (<500 G) has been shown to substantially enhance the efficiency of escape of radicals from micelle aggregates. Since enhanced escape of a radical from a radical pair should increase polymerization rates and molecular weights in EP, we have explored (1) the influence of the application of weak magnetic fields on the rate of EP and molecular weight distribution (MWD) of polymers produced in polymerizations initiated by dibenzyl ketone (DBK) and other ketones that are known to produce triplet benzyl radical pairs in direct photolysis and by triplet sensitization of 1,1'-diphenyl-1,1'-azoethane (DPAE) and (2) the ^{13}C isotope effects on polymer molecular weight distribution produced by DBK photoinitiation.

Results

Comparison of Molecular Weights and Yields as a Function of Initiation Method. Since photoinitiation has not been commonly employed for initiation of EP, we have compared averaged polymer

Chart I. Photoinitiators

$C_6H_5CH_2COCH_2C_6H_5$

DBK

$C_6H_5COCH_2C_6H_5$

PBK

$p\text{-}(CH_3)_3CC_6H_4CH_2COCH_2C_6H_4C(CH_3)_3\text{-}p$

t-BDBK

$C_6H_5{}^{13}CH_2CO^{13}CH_2C_6H_5$

DBK-2,2'-90%^{13}C

$C_6H_5CH(CH_3)N{=\!=\!=}NCH(CH_3)C_6H_5$

DPAE

$C_6H_5COCHOHC_6H_5$

BZ

$HO_2CCH_2COCH_2CO_2H$

KGA

$C_6H_5CH_2{}^{13}COCH_2C_6H_5$

DBK-1-90%^{13}C

$C_6H_5COC(CX_3)_2C_6H_5$

DPMP

$(CN)_2CCH_3N{=\!=\!=}NC(CN)_2CH_3$

AIBN

Table I. Molecular Weight and Yield of Emulsion Polymer

initiator[a]	monomer	$M_r \times 10^6$	yield, %	polymerization time, h
DBK	styrene	4.6	82	6
BZ	styrene	5.5	75	4
KGA	styrene	8.8	80	8
SP[b]	styrene	1.3	85	10
DBK	MMA	4.6	40	1
PBK	MMA[c]	3.5	82	1.5
DPMP	MMA[c]	2.6	60	1.5
t-BDBK	AA	6.5	25	1

[a] Except where specified, the typical initial solution contained 1–2% SDS, 0.05–0.06% initiator, 2–3 mL of monomer, and 5–6 mL of water at room temperature. Excitation wavelength was 313 nm (isolated from K_2CrO_4/Na_2CO_3 filter solution). [b] The polymerization was carried out at 65 °C. [c] The yield is low where styrene rather than MMA was used as monomer.

molecular weight (determined by viscosity measurements) and the yields of polymer achievable by various photoinitiators (see Chart I for structures) to those produced under conventional conditions employing sodium persulfate as an initiator. Our results (Table I) show that for EP of styrene photoinitiated by oil-soluble compounds such as dibenzyl ketone (DBK) and benzoin (BZ), they are effective photoinitiators, as is the water-soluble photoinitiator β-ketoglutaric acid (KGA).

Photoinitiators such as DBK, phenyl benzyl ketone (PBK), and 1,2-diphenyl-2-methylpropanone (DPMP) were also shown (Table I) to be effective photoinitiators of EP of methyl methacrylate (MMA). The EP of the water-soluble monomer, acrylic acid (AA), was also readily induced by photoinitiation by t-BDBK.

(1) (a) Blackley, D. C. "Emulsion Polymerization"; Wiley: New York, 1975. (b) Gordon, J. L. *High Polym.* **1977**, *29*, 143. (c) Alexander, A. E.; Napper, D. H. *Prog. Polym. Chem.* **1970**, *3*, 145. (d) Al-Shahib, W. A. G.; Dunn, A. S. *Polymer* **1980**, *21*, 42°.

(2) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G. C.; Kraeutler, B. *J. Am. Chem. Soc.*, **1980**, *102*, 4843.

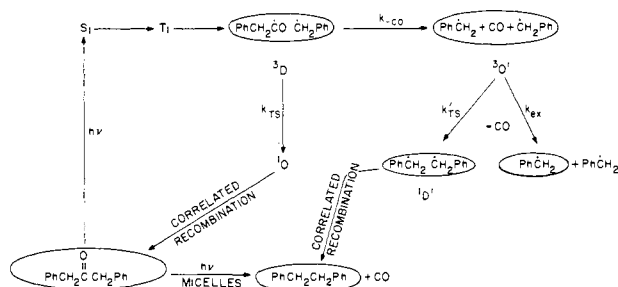(3) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7432.

(4) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.

(5) For preliminary report, see: Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tung, C.-H. *J. Am. Chem. Soc.* **1980**, *102*, 7391.

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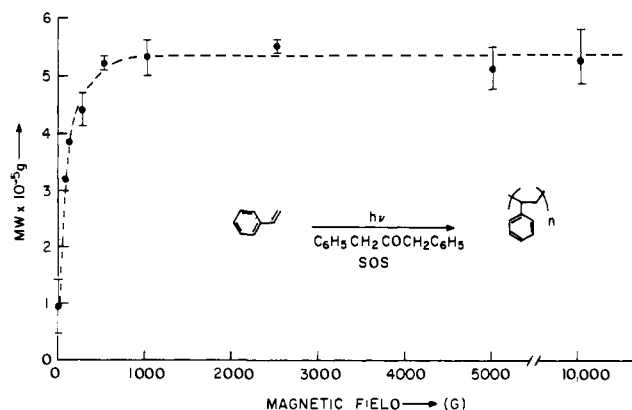
Figure 1. Magnetic field dependence of the average molecular weight (determined by viscosity measurements) of polystyrene produced by emulsion polymerization photoinitiated by dibenzyl ketone.

Scheme I

Table II. External Magnetic Field Effects on Molecular Weight and Yield of Emulsion Polystyrene

initiator[a]	magnetic field, G	$M_r \times 10^6$	yield, %	polymeri-zation time, h
SP	0	1.3	85	10
SP	6400	1.1	80	10
AIBN	0	4.7	45	1
AIBN	500	4.4	46	1
AIBN	5000	4.3	43	1

[a] The polymerization was carried out at 65 °C.

Figure 2. Typical size-exclusion chromatograms of polystyrene produced by EP in the earth's field ($\sim$0 G, dashed line) and in a moderately strong magnetic field of 5000 G (solid curve).

Figure 3. Typical size-exclusion chromatograms of polystyrene produced by solution polymerization of styrene at $\sim$0 G (solid curve) and 5000 G (dashed curve).

External Magnetic Effects on EP of Styrene. Photoinitiation by Dibenzyl Ketone (DBK). The photolysis of deaerated solutions of DBK has been shown[2-5] to generally proceed predominately via an initial homolytic α cleavage of the T_1 state, followed by decarbonylation and coupling of benzyl radicals to yield 1,2-diphenylethane (DPE). For aqueous micellar systems, Scheme I summarizes the significant aspects of the mechanism involving radical-pair chemistry. The primary triplet radical pair (^{3}D in Scheme I) does not escape the micelle cage but undergoes combination or decarbonylation reactions within the micelle cage. The secondary triplet radical pair (^{3}D$'$ in Scheme I) produced by decarbonylation either undergoes cage-combination reactions or one (or both) radical(s) escapes from the micelle cage to the bulk aqueous phase. The cage effect (defined as the yield of cage product, DPE, relative to DBK disappearance in the presence of radical scavenger in water) in aqueous micellar hexadecyltrimethylammonium chloride (HDTCl), is $\sim$32% at earth's magnetic field and $\sim$17% at 500 G. It has been proposed that a magnetic field increases the efficiency of escape of radicals from radical pairs produced in micellar aggregates by inhibiting the competing geminate cage recombination.[3]
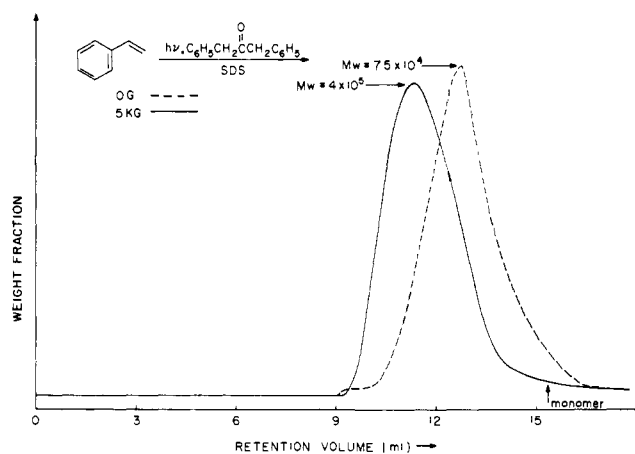
Figure 1 shows that relatively weak external magnetic fields can significantly influence the average molecular weight (M_r) of polymer photoinitiated by DBK in the emulsion polymerization of styrene.[5] For photochemical initiation of polymerization by DBK, (a) molecular weights ($\sim$10^6) achieved are comparable to those achieved by employing conventional water-soluble thermal initiators such as persulfates, (b) the average molecular weight (M_r) of the *isolated* polystyrene increases by a factor of 5 with increasing field strength, and (c) the major effect of magnetic field is in the range of 0–500 G. The isolated yield of polymer formed in comparable periods of irradiation varies qualitatively in the same manner; i.e., polymer yields are higher (for a given dose of irradiation) as the field is increased between 0 and 500 G. It was also found (Table II) that neither the M_r of polymer produced by water-soluble thermal initiator sodium persulfate (SP) nor the oil-soluble thermal initiator azobis(isobutyronitrile) varied with application of an external magnetic field (Table II).

Figure 2 shows a typical size-exclusion chromatogram of the polystyrene produced in emulsion polymerizations of styrene with
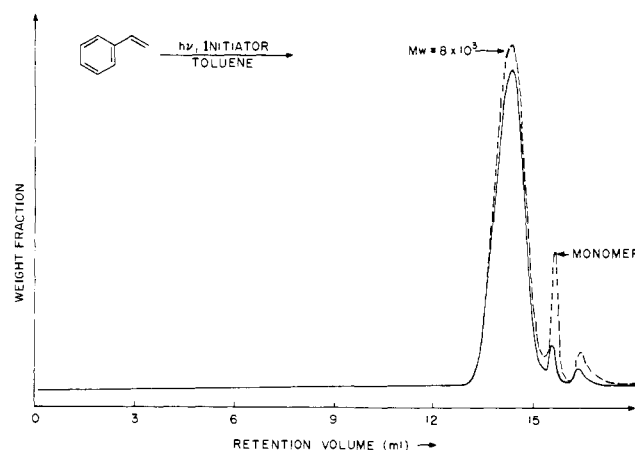
sodium dodecylsulfate (SDS) as a micelle-forming surfactant and DBK as a photoinitiator. The solid curve shows the characteristic higher molecular weight fraction produced in the presence of a magnetic field and the dashed curve shows the lower molecular weight fraction produced in the earth's magnetic field ($\sim$0.5 G). Figure 3 shows results that are typical of solution polymerization of styrene: relative to EP, lower molecular weight polymer is produced and the molecular weight is not influenced by magnetic field up to field strengths of 10000 G.

In order to determine which stage of polymerization is most sensitive to external magnetic field effects, polymerization was initiated at one magnetic field and then the field strength was changed after the initiation phase was completed ($\sim$20% conversion, see discussion). For example, if the polymerization was initially allowed to proceed to $\sim$20% conversion in the earth's field and then a magnetic field was applied, the M_r values observed were identical with those obtained when the entire polymerization was conducted in the earth's magnetic field. Conversely, if the

Table III. External Magnetic Field Dependence of Molecular Weight of Emulsion Polymer[a]

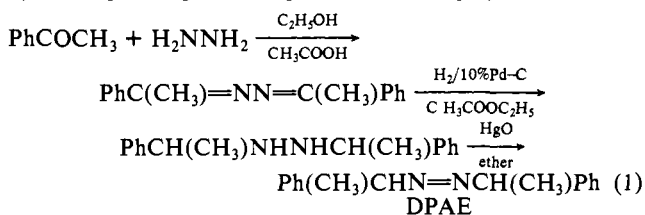| initiator	monomer	magnetic field, G	$M_r \times 10^6$	yield, %	polymerization time, h
DBK	MMA	0	4.6	40	1
DBK	MMA	100–5000	10.0	75	1
PBK	MMA	0	3.3	82	1.5
PBK	MMA	5000	5.5	84	1.5
DPMP	MMA	0	2.5	60	1.5
DPMP	MMA	5000	3.0	60	1.5
t-BDBK	AC	0	6.5	25	1
t-BDBK	AC	5000	13.1	53	1

[a] Typical initial reaction conditions: 1-2% SDS, 0.05-0.06% initiator, 2-3 mL of monomer, and 5-6 mL of water at ambient temperature. Excitation wavelength was 313 nm.

polymerization was initially allowed to proceed to ~20% conversion in a magnetic field of 5000 G and then the polymerization was completed in the earth's field, the M_r values observed were identical with those obtained when the entire polymerization was conducted in a magnetic field of 5000 G. Thus, *the initial stage of polymerization completely determines the M_r characteristics of the product.*

External Magnetic Field Effects on EP of MMA and AC. Table III shows that external magnetic fields can also influence the average molecular weight of a polymer produced by photoinitiation in the emulsion polymerization of monomers other than styrene such as methyl methacrylate (MMA) and acrylic acid (AC).

Initiation by 1,1'-Diphenyl-1,1'-azoethane (DPAE). Azobis-(isobutyronitrile) (AIBN) has recently been employed[1d] as an oil-soluble thermal initiator in EP. The efficiency of the initiation was found to be only 4% in EP, a result that contrasts with the typical efficiency of 50% that was observed for this initiator in bulk or solution polymerization. Since it is known that an external magnetic field enhances the efficiency of escape of radicals from triplet radical pairs produced in micellar aggregates, it is expected that azo compounds should be good initiators to rigorously examine the postulate that triplet radical pairs are needed for significant magnetic field effects, because one can generate either single radical pairs by thermolysis (or by direct photolysis) or one can generate triplet radical pairs by triplet sensitization.

The initiator, 1,1'-diphenyl-1,1'-azoethane (DPAE), was selected for examination as an azo photoinitiator and was prepared by the sequence given in eq 1.[6] Emulsion polymerizations of

$$PhCOCH_3 + H_2NNH_2 \xrightarrow[CH_3COOH]{C_2H_5OH}$$

$$PhC(CH_3){=}NN{=}C(CH_3)Ph \xrightarrow[C\,H_3COOC_2H_5]{H_2/10\%Pd{-}C}$$

$$PhCH(CH_3)NHNHCH(CH_3)Ph \xrightarrow[ether]{HgO}$$

$$Ph(CH_3)CHN{=}NCH(CH_3)Ph \quad (1)$$
$$DPAE$$

styrene were initiated by (1) thermal decomposition of DPAE at 65 °C, (2) direct photolysis of DPAE at 320–600 nm, or (3) triplet sensitization of DPAE using *p*-methoxyacetophenone as triplet sensitizer.[7] The isolated yields of polymer are low relative to those achieved with ketone photoinitiation; however, quantitative comparison of yields is difficult because of the different conditions employed in these experiments. Figure 4a shows the molecular weight distribution (MWD) produced in the thermally initiated and the direct photoinitiated emulsion polymerization of styrene (SDS as surfactant). The significant results are (1) that compared to comparable conditions with DBK as photoinitiator, the polystyrene produced has a relatively low MWD, and (2) that there is no magnetic field effect on the MWD. In contrast, a dramatic external magnetic effect is apparent on the molecular weight
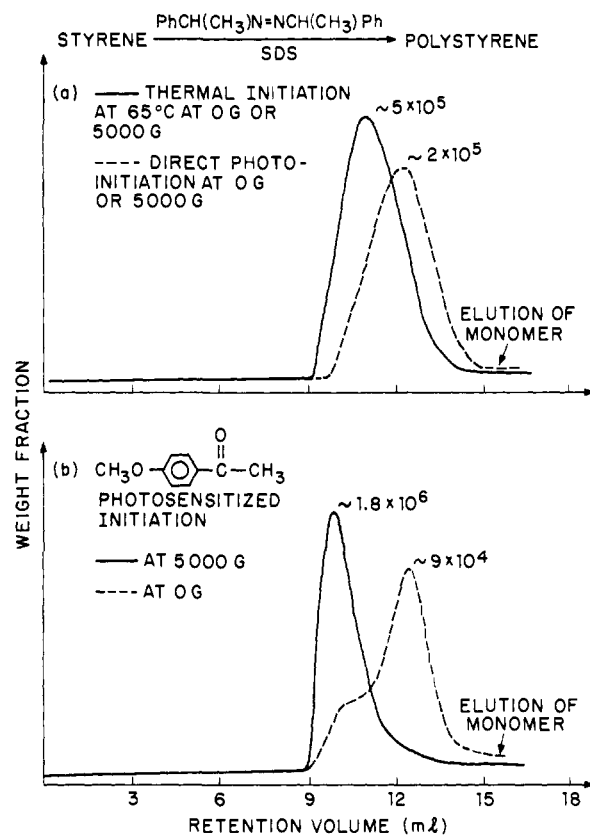

Figure 4. Typical size-exclusion chromatograms of polystyrene produced by EP of styrene with DPAE as initiator. Conditions as indicated in the figure.

distribution (MWD) of the polystyrene produced by triplet sensitization. From Figure 4b, it is seen that the MWD of the isolated polymer shifts to higher values when an external magnetic field of 5000 G is applied. Thus, a magnetic field dependence of the MWD is unique to triplet-sensitized initiation, since neither the yield nor the MWD of the polymer produced by thermal or direct photolysis of DPAE was found to be varied with application of an external magnetic field. These observations lend strong support to the postulate that micellized triplet radical pairs are required for the observation of significant magnetic field effects.
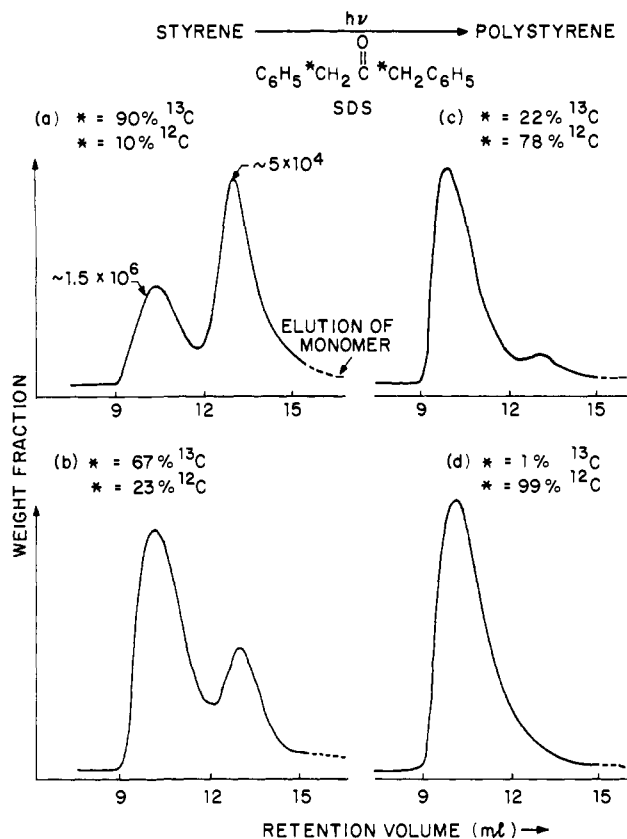
Quantitative rate data for the systems discussed so far are impractical because of the opacity of the milky appearing solutions that result because of the occurrence of the monomer droplets as a separate phase. Increasing the concentration of detergent to 0.5 M results in clear solutions with good optical properties. However, these solutions do not display any of the magnetic field effects or the magnetic isotope effects that were observed for the solutions containing monomer droplets. It is expected that at high detergent concentrations, the size of SDS micelles will increase, and it is likely that the monomer-swollen micelles under these conditions will be much larger than those that exist at the lower concentrations employed for the experiments involving monomer droplets as a second phase. In terms of our general theory of magnetic field and magnetic isotope effects, we expect that if the space available to the triplet radical pair becomes too great, the situation is equivalent to that of the radical pair in homogeneous solution; i.e., the magnetic effects will disappear.

[13]C Isotope Effects on Polymer Molecular Weight Distribution (MWD) Produced by Dibenzyl Ketone (DBK) Photoinitiation. The photolysis of dibenzyl ketone (DBK) in micellar (HDTCl) solution has been shown to have a remarkable magnetic isotope effect on the extent of cage reaction to form diphenylethane.[2,8]

(6) Seltzer, S. *J. Am. Chem. Soc.* **1961**, *83*, 2625.

(7) Engel, D. S.; Bishop, D. J.; Page, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 7009.

(8) The ideas employed here are essentially those of the radical-pair theory of CIDNP: Kaptein, R. *Adv. Free-Radical Chem.* **1975**, *5*, 381. Closs, G. *Proc. Int. Congr. Pure Appl. Chem. 23rd* **1971**, *4*, 19. Lawler, R. G. *Acc. Chem. Res.* **1972**, *5* 18. Turro, N. J. *Pure Appl. Chem.* **1981**, *53*, 259.

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Figure 5. Typical size-exclusion chromatograms of polystyrene produced by EP of styrene with combinations of DBK and DBK-$2,2'$-^{13}C as photoinitiators. See text for discussion. The sharp cutoff at short elution times may be an artifact, and lead to a low estimation of the high molecular weight fraction.

DBK that is enriched in ^{13}C at both benzylic carbon positions shows a dramatically higher cage effect (cage $\sim$46%) than is shown for natural-abundance DBK (cage $\sim$32%) or for DBK that is ^{13}C enriched in the carbonyl carbon position (cage $\sim$33%). This result is consistent with the postulate that geminate triplet $C_6H_5{}^{13}CH_2 \cdot \, \cdot{}^{13}CH_2C_6H_5$ radical pairs undergo intersystem crossing to singlet radical pairs followed by rapid recombination more rapidly than geminate radical pairs that do not contain ^{13}C because ^{13}C nuclei enhance hyperfine-induced intersystem crossing.[9]

Experiments were run in order to establish whether ^{13}C magnetic isotope effects could be observed with the efficiency and with the polymer molecular weight distribution (MWD) produced by DBK photoinitiation. The efficiency of $C_6H_5{}^{13}CH_2CO^{13}CH_2C_6H_5$ (DBK-$2,2'$-^{13}C, 90%) as a photoinitiator is significantly less than that of DBK, while the efficiency of $C_6H_5CH_2{}^{13}COCH_2C_6H_5$ (DBK-1-^{13}C, 90%) as a photoinitiator is the same as that of DBK. Furthermore, the molecular weight distribution (MWD) of the polymer produced by mixture of DBK and DBK-$2,2'$-^{13}C photoinitiation shows significantly ^{13}C isotope effects (Figure 5).

In the experiments comparing isotopically substituted DBK's, the emulsion solution was stirred vigorously with a magnetic stirring bar that was driven by a magnetic stirrer. The magnetic field generated in the proximity of the sample by the bar and magnetic stirrer was of the order of 200 G. From the figure, it is noted that there are dramatically different patterns of MWD when DKB or DBK-$2,2'$-^{13}C was used as photoinitiator. In general, there are two maxima in the polymer MWD: a maximum corresponding to a low-molecular-weight polymer and a maximum corresponding to a high-molecular weight polymer. For DBK-$2,2'$-^{13}C as an initiator, the formation of low-molecular-weight
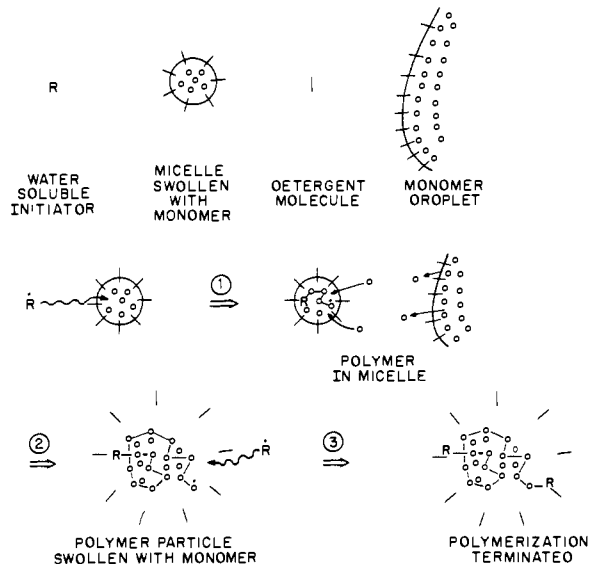
Figure 6. Schematic representation of the conventional mechanism for EP initiated by a water-soluble initiator. See text for discussion.
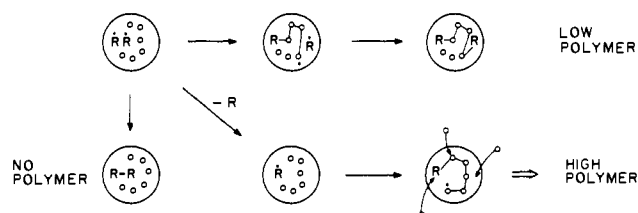
Figure 7. Schematic representation of the reaction pathways for radical pairs in EP during the initial stages of polymerization.

polymer is favored, while with DBK with natural abundance, the formation of high-molecular-weight polymer is favored. The bimodal nature of the MWD was found to be independent of the concentration of photoinitiator over a $\sim$5-fold change.

An investigation of the MWD produced by DBK-$2,2'$-^{13}C as a function of conversion revealed that the bimodal distribution was more pronounced and that the contribution of the lower molecular weight portion was greater at low ($\sim$10%) conversions. At higher conversions, the higher MWD fraction only increased in relative importance. Application of an external magnetic field has an effect that is qualitatively similar to that of increased conversion, i.e., the bimodal distribution becomes less pronounced as the strength of the applied field is increased, and the value of the higher MWD increases also, for the same extent of conversion. Finally, at comparable conversion and in the absence of a magnetic field, variation of the intensity of the excitation light by a factor of 4–5 results in only minor variations in the bimodal distribution.
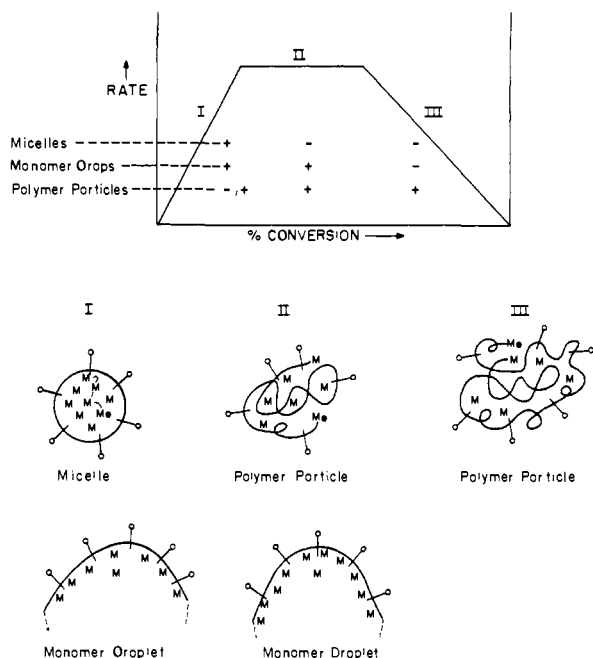
Discussion

An idealized schematic description of a conventional thermal emulsion polymerization[11] is shown in Figure 6. Aqueous soluble initiators are employed so that initiation will typically involve entry of a single radical into a monomer-swollen micelle. The rate of termination is relatively slow compared to propagation because it requires the entry of a second radical (shown in Figure 6) or association of two growing polymer chains. When an oil-soluble initiator is employed, radicals are produced in pairs (Figure 7), resulting in a competition between chain termination and escape of a radical from the propagating locus. If escape occurs, then the resulting situation is qualitatively equivalent to that produced

(9) Buchachenko, A. L. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 761.
(10) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Kraeutler, B. *J. Am. Chem. Soc.* **1981**, *103*, 3886.

(11) (a) Alexander, A. E.; Napper, D. H. *Prog. polym. Chem.* **1970**, *3*, 145. (b) Gordon, J. L. *High Polym.* **1977**, *29*, 143. (c) Blackley, D. C. "Emulsion Polymerization"; Wiley: New York, 1975. (d) Walling, C. "Free Radicals in solution"; Wiley: New York, 1957; p 203 ff. (e) Smith, W. V.; Ewart, R. W. *J. Chem. Phys.* **1948**, *16*, 592.

Figure 8. Schematic representation of the conventional stages of EP. See text for discussion.
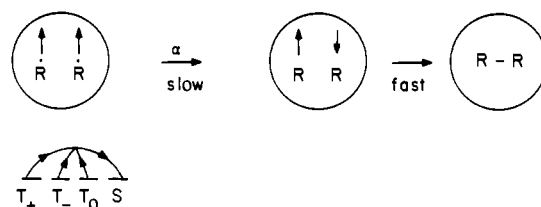

Figure 9. Schematic representation of the influence of a laboratory magnetic field on the efficiency of the cage reaction of a micellized geminate triplet radical pair. In the earth's magnetic field (~ 0 G), intersystem crossing form all three triplet sublevels ($T_\pm$, T_0) to S occurs, and a fraction, α, of the total *geminate* triplet population undergoes cage recombination (in the general case disproportionation is also possible). When the value of the applied field is greater than the quantity a (the effective value of electron–nuclear hyperfine coupling that leads to intersystem crossing in the radical pair), intersystem crossing from $T_\pm$ to S is inhibited, so that (in the limit) only $\alpha/3$ of the geminate triplet population undergoes cage recombination and $2\alpha/3$ undergo escape to form free radicals.

by an aqueous soluble initiator, i.e., a single radical in a propagating locus.

Three idealized stages are considered as occurring during a conventional emulsion polymerization (Figure 8): (I) an initial stage in which the loci of initiation of polymerization are micelles swollen with monomer molecules during which (a) dispersed monomer droplets serve as a reservoir of monomer molecules, (b) "nuclei" of growing polymer particles are produced in micelles, and toward the end (10–20% conversion of monomer), (c) the number and size of growing polymer particles increase and the number of micelles decrease because detergent molecules become preferentially adsorbed on growing polymer particles which swell with monomer that is available from the dispersed droplet reservoir; (II) a second stage during which (a) the major growth of polymer occurs as the volume of monomer-swollen polymer particles increases and the volume of monomer reservoir decreases and (b) the loci of polymerization are considered to be exclusively the polymer particles; and (III) a final stage during which the monomer droplets disappear completely and the unreacted monomer exists only in swollen particles.
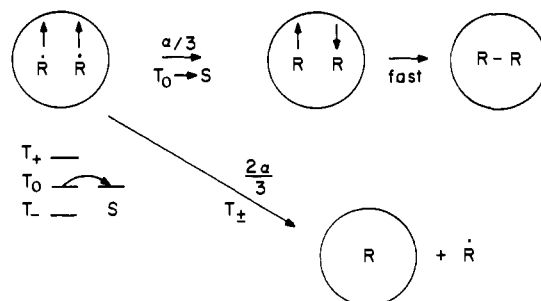
What is the mechanistic basis of the magnetic field effect and at what stage(s) of the polymerization does it operate? From recent work[2] on cage reactions of triplet radical pairs in micelles, we postulate that it is the Zeeman splitting of the $T_\pm$ triplet levels from the singlet level (Figure 9) that causes the magnetic field effect by decreasing $T_\pm \rightarrow$ S intersystem crossing and thereby allows for an increase in the efficiency of radical escape. A decrease in the efficiency of cage destruction of radicals simultaneously allows a more efficient initiation of polymerization and formation of a greater number of polymer particles (by reducing the extent of radical-pair combination in micelles), a more efficient overall initiation (by escaping radicals that enter other micelles), and a less efficient termination (by inhibiting the extent of combination of propagating radicals and initiator radicals). This postulate is consistent with the relatively low magnetic fields needed to influence polymerization, because fields of the order of 100 G are sufficient to suppress intersystem crossing in typical carbon-centered radical pairs.[8,9]

Although under comparable reaction conditions the photoinitiation efficiencies of DBK and DBK-*1*-^{13}C, 90% are comparable and produce comparable values of MWD, DBK-*2,2′*-^{13}C, 90% is less effective as a photoinitiator and produces a bimodal MWD. We attribute these results to ^{13}C magnetic isotope effects. In the case of DBK and DBK-*1*-^{13}C, 90%, after photoinitiated cleavage

and loss of CO, a pair of $C_6H_5{}^{12}CH_2\cdot$ radicals are produced as the active particles for initiation of polymerization. In the case of DBK-*2,2′*-^{13}C, 90%, a pair of $C_6H_5{}^{13}CH_2\cdot$ radicals act as the active particles. It has been shown that the ^{13}C magnetic isotope effect causes $C_6H_5{}^{13}CH_2\cdot$ radical pairs to undergo more efficient cage recombination than $C_6H_5{}^{12}CH_2\cdot$ radical pairs[2] in micellar photolysis. Applying this information to EP, we postulate that the basis of the poorer photoinitiation efficiency of DBK-*2,2′*-^{13}C, 90%, is a higher efficiency of radical-pair termination which allows for less efficient escape of single radicals, thereby creating a situation that is unfavorable for extended propagation.

Other interpretations of the isotope effects such as chain-transfer impurities in DBK-*2,2′*-^{13}C, 90% are rendered unlikely because the same methods were employed to synthesize both isotopically substituted DBK's; yet only DBK-*2,2′*-^{13}C and not DBK-*1*-^{13}C produces the bimodal MWD. Furthermore, DBK, DBK-*2,2′*-^{13}C, and DBK-*1*-^{13}C also show a similar MWD in solution polymerization. The observation that the polymerization characteristics are independent of DBK concentration demonstrate that the initiator itself is not an effective chain-transfer agent.

The observation of a bimodal distribution implies that two domains of space (or time) operate simultaneously during the polymerization. It is important to note that the low-molecular-weight fraction of the bimodal distribution is only important at low conversions at low fields and that the molecular weight of this fraction reqiures that some mechanism exists which allows for the execution of ~ 500 propagation events in a single space (time) domain. Conventional wisdom obtained from results in homogeneous solution suggests that the rate of propagation of styrene is much too slow to expect that the correlation of a triplet radical pair would persist during the time required for formation of a polymer of such a size. Thus, if our qualitative explanation is correct, either the rate of propagation for the polymerization of styrene is much faster in micelles or the correlation of triplet character is preserved longer than expected (or some combination of both).

Conclusion

Emulsion polymerization photoinitiated by DBK is subject to both external magnetic field and magnetic isotope effects.[12] The observed average molecular weight increase that occurs upon application of laboratory magnetic field results from a decreased efficiency of cage reactions and more efficient escape of a radical from the radical pairs produced at the early stage of polymerization. The remarkably different molecular weight distribution initiated by DBK and DBK-2,2'-^{13}C may result from different efficiency of recombination of different isotopic (^{13}C) benzyl radical pairs. The conventional aqueous-soluble thermal initiator (sodium persulfate) or an oil-soluble initiator that thermolyzes or photolyzes to produce micellized singlet radical pairs (AIBN and DPAE) do not display significant external magnetic field effects on the emulsion polymerization. With 1,1'-diphenyl-1,1'-azoethane (DPAE) as initiator, only micellized triplet radical pairs showed significant external magnetic field effects on the average molecular weight of the polymer produced, i.e., by generation of same initiating radical pairs by direct photolysis or thermolysis, and the only difference from triplet-sensitization-generated radical pairs is the spin multiplicity of the radical pairs.

Experimental Section

Materials. Styrene and methyl methacrylate (Aldrich Chemical Co.) were washed with 10% sodium hydroxide and dried over anhydrous sodium sulfate after repeated washings with distilled water. Further purification was carried out by distillation under reduced pressure, and the purified sample was stored at 0 °C under nitrogen. Acrylic acid (Aldrich Chemical Co.) was distilled three times under reduced pressure. Dibenzyl ketone (DBK, Aldrich Chemical Co.) was sublimied at 10^{-1} torr. DBK-1-^{13}C, DBK-2,2'-^{13}C, and 1,1'-diphenyl-1,1'-azoethane (DPAE) were prepared by the method described in the literature.[6,10] Water was double distilled (first distillation from $KMnO_4$). Sodium dodecylsulfate (SDS, Bio-Rad Lab., electrophoresis purity reagent) was used without further purification.

Preparation of Samples for Polymerization. DBK (usually 0.001 M) was dissolved in aqueous SDS solution (usually 0.05 M) by shaking the solution overnight at room temperature and protecting it from light. For DPAE as initiator, 0.0026 M DPAE with or without 0.01 M sensitizer *p*-methoxyacetophenone in 0.1 M aqueous SDS solution was prepared as that of DBK as initiator. Five milliliters of the resulting clear colorless solution and 1 mL of monomer were placed in a 2-cm diameter Pyrex tube. The oxygen was removed by bubbling argon through the solution for at least 30 min at room temperature. After argon bubbling, the deoxygenated solution was sealed by an air-tight mechanical stirring shaft.

Polymerization at Zero or Variable Applied Laboratory Fields. An emulsified, deoxygenated solution was placed between the poles of an Alpha Model 4500 4-in. adjustable-gap electromagnet. A nominal zero magnetic field was produced by applying a small current to compensate for any residual fields within the gap. The magnitude of the magnetic field at the sample under these conditions was measured to be 0 ± 0.5 G. A variable magnetic field was produced by applying a current. The magnitude of the applied field was measured by a Bell Model 640 gaussmeter. While vigorously stirred mechanically, this solution was irradiated at room temperature with a 1000-W high-pressure mercury lamp. The excitation light (313 nm for DBK or DPAE triplet sensitization as initiator, isolated with K_2CrO_4 filter solution or 350 nm for DPAE direct photolysis as initiator, isolated with $CuSO_4 \cdot 5H_2O$ filter solution) was focused onto a 1.5-cm diameter area of the Pyrex tube. Typical polymerization times are 8 h for polystyrene, 2 h for poly(methyl methacrylate), and 1 h for poly(acrylic acid).

Isolation of Polymer. Polystyrene and poly(methyl methacrylate) were precipitated in excess, stirred methanol and separated. The isolated polymer was dried in vacuo for 24 h. For isolation of poly(acrylic acid), the reacted solution was dialyzed (after being added inhibitor *p*-methoxyphenol) by using Fisher membrane (size 0.719/NF) for 5 days. After dialysis, the diluted polymer solution was concentrated in vacuo and finally frozen and dried. The percent yield of the polymer was based on the initial amount of monomer.

Characterization of the Polymer. Average molecular weights (M_r) of nonbimodal distribution polymers were determined from the intrinsic viscosities measured at 25.0 ± 0.05 °C. The conversion of intrinsic viscosity to molecular weight follows the equation $[y] = kM^a$, where k and a are obtained from the literature ($k = 10.5 \times 10^{-3}$ mL/g, $a = 0.73$ for polystyrene in toluene; $k = 7.1 \times 10^{-3}$ mL/g, $a = 0.73$ for poly(methyl methacrylate) in toluene; $k = 0.1458$ mL/g, $a = 0.6$ for poly(acrylic acid) in 80:20 dioxane–H_2O).[13] The polymer molecular weight distribution (MWD) was determined on a Du Pont Model 8800 size-exclusion chromatograph with SE4000 and Bimodal columns that could separate polymer molecular weight between 10^7 and 2×10^2. Tetrahydrofuran (Fisher, HPLC grade) was used as eluent solvent and a Du Pont UV spectrophotometer as detector. The column performance was checked with polystyrene standard (Pressure Co.) to ensure a linear relationship between polymer molecular weight and retention volume (M_r 10^3–10^6).

Registry No. PMMA, 9011-14-7; DBK, 102-04-5; BZ, 119-53-9; KGA, 542-05-2; PBK, 451-40-1; DPMP, 13740-70-0; *t*-BDBK, 64321-35-3; DPAE, 5661-68-7; DBK-2,2'-^{13}C, 77787-71-4; DBK-1-^{13}C, 68120-92-3; polystyrene, 9003-53-6; poly(acrylic acid), 9003-01-4.

(12) Reports of magnetic field effects on solid-state radiation-induced polymerizations have been reported by Mori et al. (Mori, K.; Tabata, Y.; Oshima, K. *Kogyo Kagaku Zasshi* **1970**, *73*, 1215; *Ibid.* **1970**, *73*, 815). Also, a report of the failure to observe a magnetic effect on the solution polymerization of styrene has appeared: Breitenbach, J. W.; Richter, F. *Monatsh. Chem.* **1949**, *80*, 315.

(13) Brandrup, J.; Immergut, E. H. *Polym. Hand., 2nd Ed.* **1975** (polystyrene and poly(methyl methacrylate)). Miller, M. L.; O'Donnel, K.; Skogman, J. *J. Colloid Sci.* **1962**, *17*, 649 (poly(acrylic acid)).