were measured (Table IV). In the case of the $CuPAAA_1^+$ complex, the position of the absorption maximum is not pH-dependent in the pH range considered for the calculation of the stability constant. Assuming for the concentration of the absorbing species $CuPAAA_1^+$ that obtained from its "apparent" stability constant at each pH, we found a constant value of ϵ that was very close to that of the corresponding complex of the nonmacromolecular model.

In the case of the $PAAA_2$ complexes, a shift in the absorption maximum from 790 nm for the $CuHPAAA_2^{2+}$ species to 740 nm for the $CuPAAA_2^+$ species is observed. The limiting spectrum of the protonated complex species was determined at low pH, and the ϵ value relative to $CuPAAA_2^+$ was computed by taking into account the absorbance of $CuHPAAA_2^{2+}$. In this case, too, a constant value of ϵ was obtained by assuming a variation of the $CuPAAA_2^+$ stability constant with pH. This value is again in agreement with that obtained for the corresponding nonmacromolecular model.

Acknowledgment. We thank the Italian Ministry of Education for financial support. For stimulating discussion and fruitful suggestions we thank Prof. A. Sabatini of the University of Florence and Prof. F. J. C. Rossotti of the University of Oxford.

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Magnetic Effects on Photoinduced Emulsion Polymerization. Effects of Lanthanide Ion Addition

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Received April 4, 1985

ABSTRACT: Photoinduced emulsion polymerization of styrene with sodium dodecyl sulfate (SDS) as the surfactant and dibenzyl ketone (DBK) as an initiator was significantly prevented at 0 G in the presence of La^{3+}, Gd^{3+}, or Mg^{2+}. At 2000 G good yields of high molecular weight polystyrene were obtained in the presence of La^{3+} or Mg^{2+} but polymerization was significantly prevented in the presence of Gd^{3+}. These results are explained on the basis of a combination of salt effects on micellar structure and magnetic effects on the reactions of geminate triplet radicals in micelles. The presence of salts caused an increase in the size of micelles, which in turn resulted in a reduced efficiency of free-radical escape from the micelles, and the effect of magnetic field on photoinduced emulsion polymerization was counteracted by the presence of Gd^{3+}. The polymerization of methyl methacrylate was found to be unaffected by the addition of these ions in the absence or presence of external magnetic field.

Photoinduced emulsion polymerization provides the potential for combining the advantages of emulsion polymerization, such as the ease of production of high molecular weight polymers at relatively fast rates,[1] with those of the photoinitiation processes,[2] such as the formation of free radicals at low temperatures compared to those required for thermal initiation. The reaction of free radicals in micellar solutions have also been found to be influenced

0024-9297/86/2219-0042$01.50/0

by the presence of an external magnetic field and magnetic isotopes;[3] the observed effects are, in part, due to the hindered escape of radical pairs from the interior (hydrophobic part) of the micelles. The introduction of a water-insoluble monomer into a micellar solution, as practiced in emulsion polymerization, could be expected to alter the prevailing structures of micelles, and the structures of micelles could be further altered by the formation of polymer particles. However, the free radicals formed in the course of a free radical initiated emulsion polymerization of a water-insoluble monomer could be expected to be hindered from escape into the aqueous phase by the hydrophobic environment of the monomer-swollen micelles and monomer–polymer particles.[4] Therefore, magnetic effects could be expected and were observed[5] on the course of radical-initiated emulsion polymerization with water-insoluble initiators and monomers.

We have reported earlier that the photoinduced emulsion polymerization with dibenzyl ketone (DBK) as an initiator was influenced by the presence of external magnetic fields and magnetic isotopes.[5] The yield as well as molecular weight of the polymers produced in the presence of applied laboratory magnetic fields (>1000 G) were found to be higher in comparison to those obtained at 0 G. These results have been explained on the basis of magnetic field and magnetic isotope effects observed in the photolysis of aromatic ketones in micelles.[3] Recently, we have discovered that the cage recombination reactions occurring upon the photolysis of aromatic ketones in micelles are also influenced by the presence of salts of lanthanide ions.[6] The effects of the addition of lanthanide ions on photoinduced emulsion polymerization in the absence or presence of external magnetic fields have been investigated and are reported here.

Experimental Section

Styrene and methyl methacrylate were purified by washing with a 10% aqueous sodium hydroxide solution and then water followed by distillation under reduced pressure. Monomers were stored under an atmosphere of nitrogen in a refrigerator. Electrophoresis-grade (Bio-Rad) sodium dodecyl sulfate (SDS) was recrystallized from ethanol; dibenzyl ketone (DBK) (Aldrich) was recrystallized three times from a solvent mixture of hexanes and ethyl ether (anhydrous, Mallinckrodt). 4,4′-Azobis(4-cyanovaleric acid) (ACVA) (Aldrich) was obtained as a 75% dispersion in water and used as received. 2,2′-Azobis(2-methylpropanenitrile) (AIBN) (Polysciences) was recrystallized three times from methanol. 1-(4-*tert*-Butyl)phenyl-2-propanone (TBPP) was a gift of M. B. Zimmt of these laboratories and was prepared from 4-*tert*-butylphenylacetic acid.[7] The salts ($LaCl_3$, $GdCl_3$, $MgCl_2$, and $K_2S_2O_8$) were of >99% purity (Aldrich or Alfa) and were used as received. Hexane and tetrahydrofuran (THF) were of spectrophotometric grade. Deionized water was used for emulsion polymerization.

The polymerizations were performed in a 2-neck Pyrex flask equipped with an overhead stirrer and an inlet tube sealed with a rubber septum. An Oriel 1000-W lamp with potassium chromate–sodium carbonate filter solution[8] was used for irradiation. The polymerizations were carried out between the poles of an Alpha Model 4500 4-in. adjustable-gap electromagnet; the magnitude of the magnetic field generated between the poles was controlled by passage of an electric current and was measured by a Bell Model 640 gaussmeter.

The required amounts of SDS (0.05 M), initiator (4 mM), and salt (4 mM) were dissolved in water by sonication. A 10.0-mL volume of this solution was taken in the polymerization flask and deoxygenated by bubbling argon or nitrogen for 10 min. The flask was then placed between the poles of the electromagnet, and the solution was stirred under a positive pressure of argon. A 2.0-mL volume of monomer was introduced into the flask by a syringe; the irradiation was started after the reaction mixture was stirred for 10 min. After the desired reaction time, the reaction mixture was poured into excess (100 mL) ethanol or methanol. The precipitated product was recovered by filtration, washed repeatedly with hot water, and dried overnight in vacuum at 60 °C. The weight of the dried product was used to calculate the percent yield. The purity of polymers was checked by 200 MHz ^{1}H NMR spectra (Varian Model XL-200).

The molecular weights of polymers were determined by gel permeation chromatography (GPC) on Du Pont Model SE4000 and bimodal columns using THF as solvent. The columns were operated at 35 °C and calibrated with narrow molecular weight distribution (MWD) polystyrene standards. A Waters Model R401 differential refractometer was used for detection. The molecular weights of the samples were calculated from a plot of logarithm of molecular weight and retention volume of the standards.

The exit rates of benzyl radicals from micelles were determined by time-resolved laser flash spectroscopy.[9] These experiments were performed by M. B. Zimmt of these laboratories. A solution containing 0.05 M SDS, 4 mM sodium carbonate, 10 mM methylbenzyl ketone (MBK), and 20 mM Fremy's salt (potassium nitrosodisulfonate) (Aldrich) was used in these measurements. The decay rates of benzyl radicals generated by the photolysis of MBK in this micellar solution and in the presence of hexane (0.1 M) were determined by an earlier reported procedure.[9]

Results and Discussion

The percent of geminate radical coupling (cage effect) in the photolysis of aromatic ketones in SDS micelles was found to be insensitive to the nature of the added lanthanide ion in the absence of a laboratory field except for a modest salt effect.[6] However, the percent cage effect was significantly affected by paramagnetic lanthanide ions, such as Gd^{3+} (7 f electrons), but not by diamagnetic lanthanide ions, such as La^{3+} (0 f electrons), in the presence of a laboratory magnetic field (2000 G). Furthermore, the sensitivity of the cage effect to the added lanthanide ion was found to be related to the number of f electrons in the lanthanide ion and was maximized in the presence of Gd^{3+}. Since the cage effect is related to radical lifetimes and radical initiation efficiencies, we have investigated the effects of the addition of La^{3+} and Gd^{3+} on photoinduced emulsion polymerization in the absence and presence of an external magnetic field.

The photoinduced emulsion polymerization of styrene, with SDS as the surfactant and DBK as an initiator, at 0 G in the presence of La^{3+} or Gd^{3+} gave low yields of low molecular weight polystyrene (Table I) in comparison to the polymerization of styrene in the absence of any additive at 0 G. A similar reduction in the yield and molecular weight of the products was also found when the polymerization at 0 G was carried out in the presence of Mg^{2+}, which is also a diamagnetic ion. When the polymerizations in the presence of La^{3+}, Gd^{3+}, or Mg^{2+} were performed in a magnetic field of 2000 G, good yields of polystyrene were obtained in the presence of La^{3+} or Mg^{2+} and the molecular weights of the products obtained were comparable to those obtained in the absence of ions (Table I). However, only low yields of low molecular weight polystyrene were obtained when polymerization was carried out at 2000 G in the presence of Gd^{3+} (Table I).

The magnetic effects on the course of photoinduced emulsion polymerization of styrene can be explained on the basis of a reaction scheme for the photolysis of DBK in micellar solutions (Figure 1).[3] Photolysis of DBK initially yields a triplet phenacyl benzyl radical pair (^{3}RP) and leads, after decarbonylation, to a benzyl radical pair (^{3}RP′). The cage effect (which represents the combination of secondary benzyl benzyl radical pair ^{1}RP′) and the quantum yield of the reaction (which represents the efficiency of combination of primary radical pair ^{1}RP) are lowered in the presence of laboratory magnetic fields of the order of 1000 G or greater. For the secondary radical pair (^{3}RP′), the competition between exit from the micelle

Table I
Effects of Additives and Magnetic Field on DBK-Initiated Photoinduced Emulsion Polymerization of Styrene[a]

no.	magnetic field, G	additive[b]	reaction time, h	% yield[c]	mol wt[d] $M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1	0		2	92	810	209	3.9
2	0	$LaCl_3$	2.5	8	37	3	12.8
3	0	$GdCl_3$	5	17	56	12	4.5
4	0	$MgCl_2$	2	19	177	4	44.3
5	0	hexane	2	8	52	5	11.1
6	2000		2	91	818	157	5.2
7	2000	$LaCl_3$	2	91	719	202	3.6
8	2000	$GdCl_3$	2	11	437	11	39.9
9	2000	$MgCl_2$	2	81	695	247	2.8
10	2000	hexane	2	94	508	165	3.1

[a] [DBK] = 4 mM; styrene = 2.0 mL; monomer-to-initiator ratio = 437. [b] [DBK]/[additive] = 1 for multivalent ions, and 0.5 mL of hexane (0.4 M) was added to the reaction mixture. [c] Refers to the isolated amount of the polymer. [d] Determined by GPC with reference to narrow MWD polystyrene standards. M_w and M_n are weight-average and number-average molecular weight, respectively.

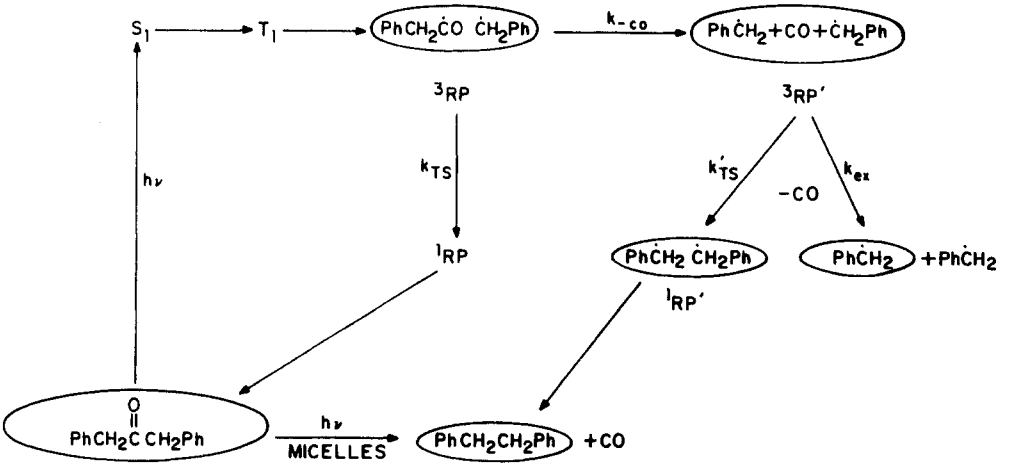

Figure 1. Schematic representation of DBK photodecomposition in micellar solutions (circles represent micelles).

and intersystem crossing (k_{ex} and k_{TS}') determines the cage value. Since k_{ex} is independent of magnetic field and k_{TS}' is slowed by an external magnetic field due to Zeeman splitting of the triplet sublevels, a lower cage effect results. For the case of primary radical pair (^{3}RP), the competition is between k_{-CO} and k_{TS}. As k_{TS} is slowed by the external field, recombination to generate the starting material becomes less efficient, and thus the quantum yield for the reaction increases.

The DBK-initiated emulsion polymerization of styrene can be schematically represented, as shown in Figure 2. The benzyl or phenacyl radical initially formed can add to styrene (M) to produce monomeric radicals ($M_2\cdot$ or $M_1\cdot$), as shown in I, II, and III. Although the decarbonylation step is not considered important in determining the effects of magnetic field on photoinduced emulsion polymerization, it is included in the proposed reaction scheme for the sake of completeness. The situation at the initiation stage of polymerization can be represented, in a simplified manner, as in ^{3}RP″, where R· represents a benzyl or a phenacyl radical and M· is a monomeric radical. The monomeric radical can propagate to give polymeric radicals ($M_m\cdot$) in the presence of R· as long as the triplet nature of the radical pair is preserved, because termination reactions of triplet radical pairs are forbidden by spin selection rules. The value of m, and therefore the degree of polymerization of the polymer, will be determined by the rate of intersystem crossing (k_{TS}'') under these conditions; that is, as soon as intersystem crossing occurs, singlet radical pairs terminate.

The presence of a triplet radical pair in the micelles is essential for the observation of magnetic effects. The escape of benzyl, phenacyl, or monomeric radicals from micelles can be expected during the course of photoinduced polymerization. The remaining radical can then propagate to produce polymers, as shown in V (Figure 2), but no magnetic effects will be observed in this case.

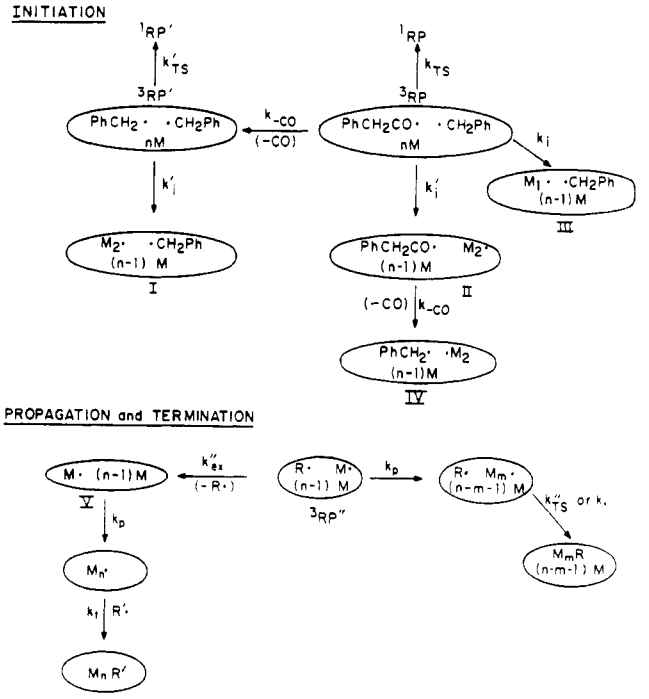

Figure 2. Schematic representation of DBK-initiated photoinduced emulsion polymerization of styrene (circles represent micelles). The terms on arrows represent rate constants for the shown reactions.

Table II
Effect of Lanthanum Ion on Emulsion Polymerization of Styrene at 0 G[a]

no.	additive[b]	initiator[c,d]	reaction time, h	% yield[e]	mol wt[f]		
					$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1		DBK	2	92	810	209	3.9
2	$LaCl_3$	DBK	2.5	8	37	3	12.8
3		TBPP	5	100	979	270	3.6
4	$LaCl_3$	TBPP	1	88	985	401	2.5
5		ACVA	2	79	886	300	3.0
6	$LaCl_3$	ACVA	2	76	796	320	2.5
7		AIBN	2	34	1025	579	1.8
8	$LaCl_3$	AIBN	2	33	1183	666	1.8
9		$K_2S_2O_8$	5	83	758	314	2.1
10	$LaCl_3$	$K_2S_2O_8$	5	98	895	273	3.6

[a] [Initiator] = 4 mM; styrene = 2.0 mL; monomer-to-initiator ratio = 437. [b] $[LaCl_3]/[initiator] = 1$. [c] ACVA = 4,4′-azobis(4-cyanovaleric acid); AIBN = 2,2′-azobis(2-methylpropanenitrile); TBPP = 1-(4-*tert*-butyl)phenyl-2-propanone. [d] All polymerizations were photoinduced except for potassium persulfate, which was a thermally initiated polymerization. [e] Refers to the isolated amount of the polymer. [f] Determined by GPC with reference to narrow MWD polystyrene. M_w and M_n are weight-average and number-average molecular weight, respectively.

The observed magnetic effects on photoinduced emulsion polymerization can be explained as follows on the basis of the reaction scheme shown in Figure 2. In the absence of an applied magnetic field the intersystem crossing of triplet radical pairs ^3RP and $^3RP'$ competes with the initiation step, and therefore only a small number of monomeric radicals as the triplet radical pair $^3RP''$ are produced. The growth of monomeric radicals in $^3RP''$ is also prevented by faster intersystem crossing (termination) of the triplet radical pair ($^3RP''$), and only low molecular weight products are produced. This is found to be true when polymerization at 0 G is performed in the presence of multivalent cations (Table I).

The prevention of polymerization at 0 G in the presence of ions can be attributed to the salt effect on the micellar structure,[10] that is, an increase in the size of micelles. A modest increase in the cage effect was also observed in the photolysis of aromatic ketones in the presence of added lanthanide ions[6] in the earth's magnetic field. Further proof of the relation of the effect of added ions to the increased micelle size was provided by the results of photoinduced emulsion polymerization of styrene performed in the presence of hexane. At 0 G only low yields of low molecular weight products were obtained in the presence of hexane (Table I). The addition of hexane to SDS micelles has also been shown to cause an increase in the size of micelles.[11]

The increased size of micelles in the presence of additives can be expected to lower the exit rate (k_{ex}) of radicals from the micelles. The exit rate of benzyl radicals from SDS micelles was estimated from the pseudo-first-order rate constant (k_{obsd}) for the decay of benzyl radicals in the presence of Fremy's salt.[9] The value of k_{obsd} was 1.08×10^6 s^{-1} in the absence of hexane and 0.72×10^6 s^{-1} after the addition of hexane (0.1 M) at 25 °C. Due to this lower exit rate of radicals from the larger micelles, the efficiency of intersystem crossing is increased in the presence of additives, and therefore the number of triplet radical pairs ($^3RP''$) produced is reduced. The observed effect, that is, prevention of the polymerization of styrene in the presence of additives at 0 G, can be explained on the basis of reduced initiating efficiency and efficient termination reactions.

The applied magnetic field slows the intersystem crossing of various triplet radical pairs, so that a large number of monomeric radicals ($^3RP''$) are produced. The slower intersystem crossing also allows for longer chain-growth periods (large values of m), and thus high molecular weight polymers are produced (Table I). The prevention of polymerization at 2000 G in the presence of added Gd^{3+} can be attributed to the paramagnetic nature of this ion, which causes the relaxation of the triplet states to the singlet state[6] and which reverses the effect of the external magnetic field, effectively returning the system to the situation at 0 G. Therefore, the presence of Gd^{3+} reduces the number of triplet radical pairs ($^3RP''$) produced and the degree of polymerization (m) due to faster intersystem crossing of various triplet radical pairs.

The formation of good yields of high molecular weight products at 2000 G in the presence of La^{3+}, Mg^{2+}, or hexane can be attributed to the increase in the concentration of radicals and their longer lifetimes due to slower recombination rates in the presence of an external magnetic field as discussed above.

A different set of experiments was performed in which the external magnetic field (2000 G) was switched off during the course of polymerization; that is, the current to the electromagnet was switched off when the reaction mixture had been irradiated for 45 min, and the irradiation was then continued for a total time of 135 min. This procedure (*2-0*), performed in the presence of La^{3+} under reaction conditions given in Table I, resulted in 23% yield of polystyrene ($M_w = 239 \times 10^3$; $M_n = 27 \times 10^3$; $M_w/M_n = 8.9$). The yield of the polymer was lower than that obtained in experiment 7, Table I. No significant amount of polystyrene was obtained when a polymerization mixture containing DBK, SDS, and styrene was irradiated for 45 min at 0 or 2000 G. The polymerization of styrene to high molecular weight products took place in the presence of an external magnetic field; after the magnetic field was switched off, a fast intersystem crossing of the radical pairs occurred, causing termination of the already formed polymeric radicals. Therefore, the yield as well as molecular weights of the products were reduced in comparison to thoseof polymer obtained in experiment 7, Table I. In contrast, when polymerization was performed under similar reaction conditions but irradiation was stopped after 45 min and the reaction mixture was then stirred in a magnetic field of 2000 G for a total time of 120 min, a 65% yield of polystyrene ($M_w = 860 \times 10^3$; $M_n = 393 \times 10^3$; $M_w/M_n = 2.2$) was obtained. The yield of polystyrene obtained in this procedure (2-2) was higher than that obtained in 2-0. The presence of an external magnetic field during the entire course of 2-2 reduced the rate of intersystem crossing, and the long-lived triplet radical pairs gave good yields of high molecular weight products. These results also support the proposed reaction scheme for the photoinduced emulsion polymerization of styrene.

The photoinduced emulsion polymerization of styrene with 1-(4-*tert*-butyl)phenyl-2-propanone (TBPP) as an

Table III
Effect of Lanthanide Addition on Photoinduced Emulsion Polymerization of Methyl Methacrylate (DBK Initiator)[a]

no.	additive[b]	magnetic field, G	reaction time, h	% yield[c]	mol wt[d]		
					$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1	$LaCl_3$	0	2	100	608	217	2.8
2	$LaCl_3$	2000	2	100	494	161	3.1
3	$GdCl_3$	0	2	100	513	173	3.0
4	$GdCl_3$	2000	2	100	615	225	2.7
5		0	2	95	677	190	3.6
6		2000	2	95	641	207	3.1

[a] [DBK] = 4 mM; MMA = 2.0 mL; monomer-to-initiator ratio = 467. [b] [Additive]/[DBK] = 1. [c] Refers to the isolated amount of the polymer. [d] Determined by GPC with reference to narrow MWD polystyrene standards. M_w and M_n are weight-average and number-average molecular weight, respectively.

initiator was not affected by the presence of La^{3+} at 0 G (Table II). The photodecomposition of TBPP is expected to produce an acetyl and a para-substituted benzyl radical. The acetyl radical can be expected to have a higher exit rate (k_{ex}) from the micelle than the benzyl radical,[12] and thus the escape of acetyl radicals can compete with the initiation and propagation of polymerization. The absence of a triplet radical pair in the micelle, that is, a situation analogous to that shown in V (Figure 2), implies that the polymerization will not be influenced by external magnetic fields.

Photoinduced emulsion polymerization of styrene was also performed with a water-soluble and an oil-soluble azo initiator, namely ACVA and AIBN. The polymerization of styrene with these initiators was not affected by the presence of La^{3+} at 0 G (Table II). Thermally initiated emulsion polymerization of styrene with potassium persulfate as an initiator was also not affected by the presence of La^{3+} at 0 G (Table II). These results indicate that the effects of lanthanide ion addition on DBK initiated emulsion polymerization of styrene are dependent upon the formation of a triplet radical pair in micelles.

The polydispersity index (PDI = M_w/M_n) of polystyrene obtained with DBK as an initiator was found to be higher in comparison to that of polystyrene obtained with AIBN, ACVA, or potassium persulfate as initiator. This can be attributed to the chain transfer reactions with singlet benzyl or phenacyl radicals produced during the photolysis of DBK. The PDI of polystyrene obtained at 2000 G (Table I, experiment 6) was greater than that of polystyrene obtained at 0 G (Table I, experiment 1) which could be attributed to the greater amount of triplet radical pairs present at 2000 G due to slow intersystem crossing.

There was no effect of the addition of La^{3+} or Gd^{3+} on the DBK initiated emulsion polymerization of methyl methacrylate in the presence or absence of an external magnetic field (Table III). Also, the photoinduced emulsion polymerization of methyl methacrylate was not significantly influenced by the presence of external magnetic fields (Table III). The different behavior of methyl methacrylate can be due to any of the number of features that distinguish methyl methacrylate from styrene. The most important feature from the point of view of this investigation is the polar nature of methyl methacrylate in comparison to that of styrene.[13] The polymerization of methyl methacrylate may be initiated in the aqueous phase by the radicals escaped from the micelles[14] and therefore will not be subject to the influence of external magnetic fields and related effects which seem to require the presence of a triplet radical pair in the initiation stage of polymerization.

In conclusion, the presence of additives, such as diamagnetic ions and hexane, has been shown to enhance the effects of external magnetic field on DBK-initiated photoinduced emulsion polymerization of styrene. The external magnetic field can be said to act as an "off-on switch" for polymerization in the presence of these additives. However, the absence of such effects in the polymerization of methyl methacrylate indicates that factors such as the site of initiation of polymerization and dynamic nature of micellar structures tend to operate in a fashion as to diminish the influence of magnetic fields on polymerization.

Acknowledgment. We thank the Air Force Office of Scientific Research and the 3M Corp. for their generous support of this research. We are grateful to M. B. Zimmt for performing laser flash photolysis experiments and helpful discussions.

Registry No. $LaCl_3$, 10099-58-8; $GdCl_3$, 10138-52-0; $MgCl_2$, 7786-30-3; styrene, 100-42-5; polystyrene (homopolymer), 9003-53-6; methyl methacrylate, 80-62-6; poly(methyl methacrylate) (homopolymer), 9011-14-7.

References and Notes

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