

Magnetic field effect on polymers and polymerization

Sukumar Maiti* & Dibyendu S Bag

Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

Received 17 November 1994

The influence of magnetic field on polymerization reaction, polymer structure and properties has been discussed in the light of the radical pair theory and the cage effect to explain the kinetics of polymerization and crosslinking reactions. The rate of polymerization and crosslinking increases due to the singlet ($\leftrightarrow$) triplet intersystem crossing mechanism. While the molecular weight increases, the molecular weight distribution decreases under magnetic field. The polymer microstructure viz., tacticity, copolymer composition and monomer sequence in the copolymer chain are also affected by the magnetic field. Polymerization of liquid crystal monomers under magnetic field results in highly oriented liquid crystal polymers. As a result, the polymer properties like crystallinity, chain flexibility, solubility, thermal behaviour are also changed. Conducting polyacetylene and magnetic polymers prepared under magnetic field also exhibit higher conductivity and magnetic properties respectively. Studies on biopolymers, solid state and plasma polymerization under magnetic field have also been reported.



Dr Sukumar Maiti



Dibyendu Sekhar Bag

Dr Sukumar Maiti is Professor of Polymer Materials since 1976 at the Materials Science Centre, IIT, Kharagpur. He has extensive research and development experience in industry, both in USA and in India. He has authored/coauthored 3 books, published over 200 research papers and more than 50 technical reports and popular science articles. He is also editor of the Journal of Polymer Materials.

Dibyendu Sekhar Bag, after obtaining M.Sc. in Chemistry from IIT, Kharagpur, joined Prof Maiti's research group on a CSIR fellowship for his Ph.D. work on Magnetic Field Effect on Polymerization.

Introduction

The term 'magnetokinetics' i.e., the magnetic field (MF) effects on the kinetics of chemical reactions dates back to the discovery of nuclear and electronic spin polarization phenomena during chemical reactions (CIDNP, CIDEP). Though the so-called radical pair mechanism is the heart of these phenomena, there are also other mechanisms based on singlet-triplet, triplet pairs, or triplet-doublet pairs. The field of magnetokinetic chemical and related physical phenomena was reviewed earlier. Recently Steiner and Ulrich¹ have made a comprehensive review.

In early eighties a few polymerizations and crosslinking reactions were studied under magnetic field. The orientation of the liquid crystal (LC) polymer by external fields including magnetic field² and to stabilize the alignment by freezing, crystallizing, drying, or by gel formation under magnetic field have been studied recently. The aim of this review is to report the results on the polymerization and crosslinking reactions under the influence of applied magnetic field, to throw some light on the mechanism of such polymerization, and to examine the effect of magnetic field on the properties of such polymers such as solution viscosity, molecular weight (MW), molecular weight distribution (MWD), tacticity, change in mesomorphic state etc.

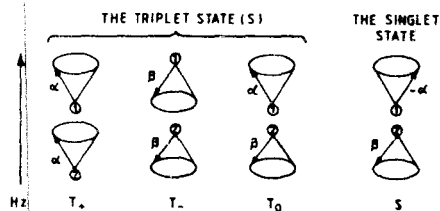


Fig. 1—Vector model of the three magnetic sublevels of a triplet radical pair and a singlet state of a radical pair. An "up" spin vector is represented by α and a "down" spin vector is represented by β .

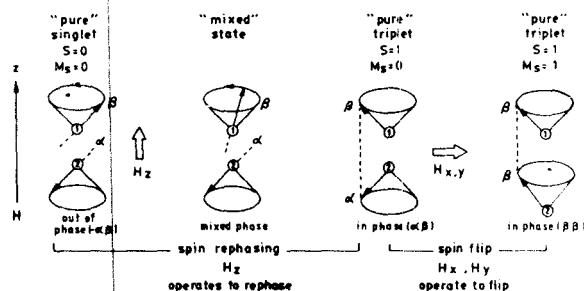


Fig. 2—Vector model of spin rephasing resulting from a different precessional rate of the spin of one electron relative to the other electron about the z-axis (H_z). A magnetic component along x and y-axis (H_x or H_y) produces a torque which can flip an electron spin.

Radical pair theory and the influence of magnetic field on radical reactions

In the radical pair theory^{3,4}, the two radicals generated by homolysis of a bond in a molecule may remain as either singlet (S) or triplet (T_+ , T_0 , T_-) states. The spin states (singlet or triplet) once prepared would remain in these states forever, if magnetic torques operating on them are identical. But the mixing of singlet and triplet states i.e., the intersystem crossing (ISC) from a singlet to a triplet or *vice versa*, results from the occurrence of different magnetic torques that either rephase or flip one of the spin vectors to the other. A magnetic field arising from within the molecule (local magnetic field) provides the magnetic torque required to rephase and/or to flip the electron's spin vector. The local magnetic field and hence the magnetic torque is generated by electron's orbital motion (spin-orbit induced magnetic fields: spin-orbit coupling) or due to other magnetic spins (magnetic spin associated with an electron's spin or with a nuclear spin; spin-spin coupling).

Figure 2 describes the schematic representation for singlet-triplet mixing and intersystem crossing (ISC). A conversion between S and T_0 occurs if

the precessional rates of the two spin vectors of two electrons are slightly different. The local magnetic field arising from the electron spin influences each electron's spin to the same extent and therefore, does not affect the relative precessional rates of two spin vectors of two electrons. So this cannot be a cause of mixing of S and T_0 by rephasing the spin's precessional rate. But the local magnetic fields due to spin-orbit coupling (equivalent to different 'g-factors') and hyperfine coupling (coupling of nuclear spin with the odd electron) at different radical centres are different. So the Δg -mechanism and also the hyperfine interaction (hfi) mechanism allow evaluation of the difference in precessional rate of the two spin vectors and cause the mixing of S and T_0 states.

If, the local magnetic field acting in the z-direction (H_z differs for two electrons, rephasing of the spin vector occurs but the orientation (α or β) of the spin vectors relative to z-axis remains the same i.e., 'up' electron remains up and 'down' electron remains down. As a result S and T_0 states are mixed and a pseudo-equilibrium is set up until a perturbation (e.g. chemical reaction or diffusion out of the cage) removes S or T_0 from the equilibrium. Local magnetic fields in the x and y planes (H_x and H_y) may also cause rephasing but also may provide a torque to twist one of the spins to flip (say, the α -spin of one electron into a β -spin) and also cause reorientation relative to the z-axis. In other words, local magnetic fields, H_x and H_y , can flip the electron spin and cause conversion of S into either T_+ or T_- .

So far the discussion has been dealt with the ISC efficiency due to local magnetic field. There may be some effect of external (laboratory) magnetic field on such ISC of a radical pair and hence on radical pair reactions. Actually there are two possible mechanisms by which the course of a radical reaction can be influenced by the external magnetic field. In the presence of external magnetic field, different Larmor precessional rates of the radicals rephase S into T_0 and *vice versa*. The difference in precessional rates of two electrons ($\Delta\omega$) is given by

$$\Delta\omega = (\Delta g \beta H_0 / \hbar) \pm (a_1 - a_2)I \quad \dots (1)$$

g-factor effect

Hyperfine effect

where, $\Delta g = |g_1 - g_2|$, g_1 and g_2 are the g-values of two electrons, β is the Bohr magneton, $\hbar$ the Planck's constant, H_0 the external magnetic field, a_1 and a_2 the hyperfine coupling constants of two radicals and I the nuclear spin. So, the rephasing rate enhances as Δg and/or the flux density (H_0)

increases (Δg -mechanism). The singlet $\leftrightarrow$ triplet conversion due to hyperfine interaction (hfi-mechanism) can also work without an external magnetic field. But in low magnetic field comparable to local magnetic field, hyperfine interaction induces ISC from the singlet to the three triplet states (T_+ , T_0 , T_-) whereas in a sufficiently high external magnetic field only $S \rightarrow T_0$ transition occurs. However, there is also relaxation mechanism which is less effective than Δg - and hfi-mechanism⁴. The relaxation transition rate also depends on external magnetic field. But being of small importance in case of free radicals it is neglected here.

Another important influence of external magnetic field is the Zeeman splitting of triplet states (T_+ , T_0 , T_-). In the absence of a magnetic field all the three triplet sublevels themselves energetically degenerate as well as with the singlet state. All the three triplet sublevels interconvert with the singlet state, when the Zeeman interaction is small relative to other interactions (such as hfi whose strength is given by the hyperfine coupling constant). But when a magnetic field is applied, Zeeman splitting of the three magnetic sublevels of triplet states, i.e., T_+ , T_0 , T_- occurs. As a result, the energy of T_+ is raised, T_- is lowered and T_0 remains unchanged. The magnitude of this splitting equals to $g\beta H_0$. Since the singlet state has no net magnetic moment (spin paired), its energy is unchanged by the application of magnetic field. Therefore, in the presence of external magnetic field, only T_0 and S possess identical energies and hence only T_0 state is accessible to switch into S state and *vice versa* (Fig. 3).

The triplet radical pair cannot recombine directly until it passes into the singlet state. So, the recombination probability is proportional to the population in the singlet state. Therefore, depending upon the starting radical pair (singlet or triplet) and the effect associated with external magnetic field on different 'g-factors' (Δg -mechanism), hfi-mechanism or Zeeman splitting of triplet sublevels, the corresponding cage or escape products are determined as a consequence of singlet $\leftrightarrow$ triplet ISC. For example, starting with a triplet radical pair the proportion of the cage products decreases in the presence of an external magnetic field^{4,6}, because only T_0 is amenable to ISC due to Zeeman splitting. Starting with a singlet radical pair, on the other hand, the cage product increases for the same reason. Again since the rephasing time shortens as Δg and/or the magnetic flux density

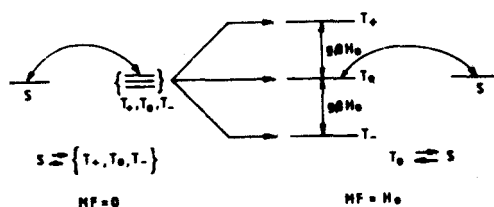


Fig. 3—Schematic representation of the Zeeman splitting of the triplet sublevels (T_+ , T_0 , T_-). The effect of Zeeman interaction $g\beta H_0$ is to energetically split $T_{\pm}$ and thereby inhibit singlet $\leftrightarrow$ triplet ISC from or to these sublevels⁴.

increases, starting with a radical pair in a singlet state, the triplet state is more frequently reached and hence part of the cage products decreases in relative to the escape products^{3,6}. This concept is useful for the radical polymerization and cross-linking reactions.

Homopolymerization under magnetic field

A few radical polymerizations have already been studied under magnetic field (MF) with various vinyl monomers and initiators under different conditions. These polymerization systems along with respective percentage conversion, molecular weight (MW) and M_w/M_n are listed in Table 1. The MF dependence of MW of a few polymers is shown in Fig. 4.

Photopolymerization

Turro *et al.*⁷ utilized the radical pair theory for the polymerization of vinyl monomers under MF. Zeeman splitting of triplet states in the presence of an external MF increases the polymer yield and the MW for the photoinduced emulsion polymerization of styrene. Emulsion acts as a cage for the radical reactions including polymerization.

An important characteristic of emulsion polymerization is to produce high MW polymer with a rapid rate and for which water-soluble thermal initiators are best suited. Oil-soluble initiators are commonly ineffective in emulsion polymerization because such initiators produce pairs of radicals in the micelle (polymerization loci), thereby favouring termination before substantial polymer growth can occur. But in the presence of MF high MW polymer can be achieved even by using an oil-soluble photoinitiator. The effect of MF is observed in the case of oil-soluble photoinitiator (e.g., dibenzylketone, DBK) and not in the case of water-soluble photoinitiator (e.g., β -ketoglutaric acid) and water-soluble thermal initiator (e.g., sodium persulfate), or oil-soluble initiator that thermolyzes or photolyzes to produce micellized singlet radical pairs (e.g., 2,2'-azo-

Table 1—Homopolymerization under magnetic field (MF)

Monomer ^a	Polymerization technique ^b	Initiator ^c	Polymerization condition			MF (KG)	Magnetic field effect ^e			Reference
			Light or heat	Special additives ^d	Time (h)		% conversion	Mw x 10 ⁻⁵	R_p/R_n	
S	EP	DBK	UV	SDS	—	5	—	4.0(0.75)	—	7
S	EP	DBK	UV	SDS+LaCl ₃	2(2.5)	2	91(8)	7.19(0.37)	3.6(12.8)	9
S	EP	DBK	UV	SDS+MgCl ₂	2	2	81(19)	6.95(1.77)	2.8(44.3)	9
S	EP	DBK	UV	SDS+hexane	2	2	94(8)	5.08(0.52)	3.1(11.1)	9
S	EP	DBK	UV	SDS	2	2	91(92)	8.18(8.10)	5.2(3.9)	9
S	EP	Benzoin	UV	SDS	1.5	1	79(72.4)	5.0(4.9)	2.66(3.37)	10
S	EP	DPAE+MAP	UV	SDS	—	5	—	18(0.9)	—	8
S	EP	DPAE	UV	SDS	—	5	—	2(2)	—	8
S	EP	DPAE	65°C	SDS	—	5	—	5(5)	—	8
S	EP	AIBN	65°C	SDS	1	5	43(45)	0.43(0.47)	—	8
S	EP	Na ₂ S ₂ O ₈	65°C	SDS	10	6.4	80(85)	0.11(0.13)	—	8
S	SL	DBK	UV	—	—	5	—	0.08(0.08)	—	8
MMA	EP	DBK	UV	SDS	1	5	75(40)	100(46)	—	8
MMA	EP	PPK	UV	SDS	1.5	5	84(82)	55(33)	—	8
MMA	EP	DPMP	UV	SDS	1.5	5	60(60)	30(25)	—	8
AA	EP	t-BDEK	UV	SDS	1	5	53(25)	131(65)	—	8
S	BP	AIBN	UV	—	1	12	—	0.56(0.56) ^f	—	16
S	BP	AIBN	UV	PVN ₁	1	12	—	2.7(0.56) ^f	1.54(2.27)	16
S	BP	AIBN	UV	PVN ₂	1	12	—	3.1(0.89)	—	16
S	BP	AIBN	UV	—	1	2	—	0.72(0.72)	—	14
S	BP	AIBN	UV	PVB ₁	1	2	—	2.4(0.74)	—	14
S	BP	AIBN	UV	PVB ₂	1	2	—	2.8(0.77)	—	14
S	BP	AIBN	UV	N-PEG-N	—	8	—	—	1.54(2.27)	15
S	BP	AIBN	UV	N-PEG-B	—	1	—	—	1.53(2.31)	15
S	BP	AIBN	UV	B-PEG-B	—	1	—	—	1.54(2.31)	15
AN	BP	AIBN	60°C	—	1	1.1	69(47)	12.7(7.1)	—	25
BMA	EP	K ₂ S ₂ O ₈	70°C	DBNS	0.5	1.1	360 ^g	—	—	22
BMA	BP	BPO	70°C	—	0.5	1.1	71 ^h	—	—	22
BMA	SL	BPO	70°C	—	0.5	1.1	17 ^h	—	—	22
BMA	SL	BPO	70°C	—	0.5	1.1	30 ⁱ	—	—	22
MMA	EP	BPO	70°C	—	0.5	1.1	80.3(38.12)	4.3(3.2)	—	21
MMA	A	—	60°C	HEMA	10	1.8	11(6.6)	—	—	29
MMA	A	—	60°C	PEG-300	10	1.8	8.2(6.2)	54.1(42.4) ^f	—	29
MMA	A	—	60°C	PMEO/8.7	10	1.8	19.3(8.8)	57.1(34.6) ^f	—	29
MMA	A	—	60°C	Poly(St ₁ -b-MAA _{NA₂})	10	1.8	9.7(0.9)	100.8(40.7)	—	29

a. S=Styrene, MMA=Methylmethacrylate, AA=Acrylic acid, AN=Acrylonitrile, BMA= Butylmethacrylate

b. EP=Emulsion polymerization, SL=Solution, BP=Bulk, A=Aqueous

c. DBK=Dibenzyl ketone, DPAE=(1,1'-diphenyl-1,1'-azoethane), MAP=p-methoxyacetophenone, PPK=Phenylbenzyl ketone, DPMP=1,2-diphenyl-2-methyl propanone, t-BDEK= p-t-butyl dibenzyl ketone.

d. SDS=Sodium dodecyl sulfate, PVN₁=Polyvinyl naphthalene (conc.=1.62x10⁻³ mol /l), PVN₂=PVN (conc.9.12x10⁻³ mol /l), PVB₁=Polyvinyl benzophenone (conc.=0.98x10⁻³ mol /l), PVB₂=PVB (conc.=8.17x10⁻³ mol /l), DBNS=Dodecyl benzene sodium sulfonate, PEG=Polyethylene glycol (MW=300), PMEO=Poly(oligo ethylene oxide methacrylate) (n=8.7)

e. The figures within parentheses indicate corresponding values in the absence of magnetic field (MF).

f. The number average molecular weight.

g. The conversion rate increased by MF (%).

h. The percentage of conversion increased by MF.

i. The percentage of conversion decreased by MF.

bisobutyronitrile, AIBN; 1,1'-diphenyl-1,1'-azoethane, DPAE), or even direct photoinduced initiation⁸. The effect of MF is also changed by the salt effects on micellar structure⁹.

The external MF effect on photoinduced emulsion polymerization of styrene has been explained on the basis of photolysis of DBK producing trip-

let radical pairs in micellar solution. In the absence of an applied MF, ISC from all the three triplet sublevels (T₊, T₀, T₋) to singlet (S) occurs and a fraction of the total geminate triplet population undergoes recombination within micelle. But in the presence of an applied MF only ISC from T₀ to S occurs since the degeneracy of T_± with S is lift-

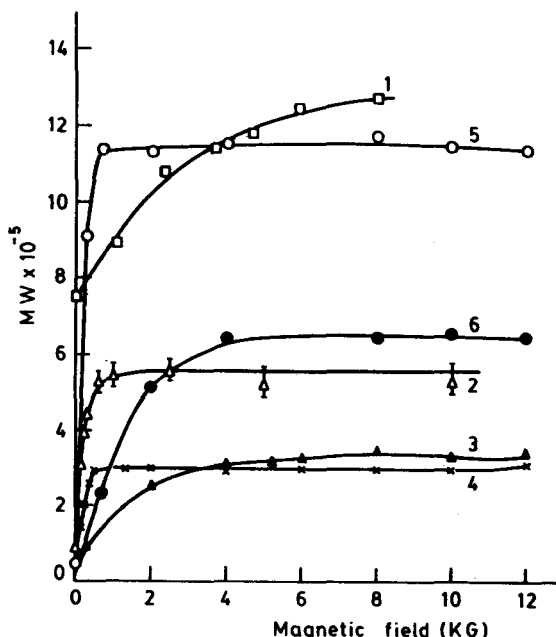


Fig. 4—The variation of molecular weight (MW) with magnetic field: (1) PAN prepared in bulk²⁵, (2) PS produced by photoinduced emulsion polymerization⁷, (3) PS prepared in bulk in presence of PVN (MW = 1.81×10^4 , conc. = 1.62×10^{-3} mol/l)¹⁴, (4) PS prepared in bulk in presence of PVB (MW = 1.15×10^4 , conc. = 2.76×10^{-3} mol/l)¹⁴, (5) PS prepared by aqueous polymerization in presence of B-PEG-N ($M_n = 600$, conc. = 1.45×10^{-4} mol/l)¹⁵, (6) PS prepared by aqueous polymerization in presence of N-PEG-N ($M_n = 600$, conc. = 1.45×10^{-4} mol/l)¹⁵.

ed. So, only 1/3 of the geminate triplet population undergoes cage recombination and 2/3 escape from the micelle. So, the isolated radical in the micelle can grow uninterrupted until another radical enters and terminates the radical. This is responsible for both increased rate of polymerization and high MW of polymer in the micelles under MF.

Turro *et al.* showed mainly the variation of MW of the polymer with MF (Fig. 4, curve 2). It was reported that MW increased by a factor of five by the application of MF of 0.5 KG, and that the variation of polymer yield with MF was the same as that of MW. However, these authors did not study the effect of MF on the polymerization kinetics. The effect of MF was observed at the early stage of polymerization but it was not clear why the MF effect was not observed in the latter stage. Mondal *et al.*¹⁰ studied the kinetics of the same emulsion polymerization system with benzoin as photoinitiator instead of DBK. These authors claimed that the polymer particle nucleation period is shortened in the presence of MF and hence the rate of polymerization is increased.

The increase in rate of emulsion photopolymerization of methyl methacrylate (MMA)¹¹ initiated by triethylaminebenzophenone and that of vinylacetate¹² initiated by benzoin under MF (0.8 KG) were reported. The influence of MF on MW is also observed when conversion is low. But when the polymerization attains the limiting conversion the effect of MF on MW is negligible.

Huang *et al.*^{13–15} utilized a second polymer solution [viz. polyvinyl naphthalene (PVN) and polyvinyl benzophenone (PVB), polyethylene glycol (PEG) with naphthyl end groups (N-PEG-N), PEG with benzoylbenzyl end groups (B-PEG-B) and PEG with a naphthyl group at one end and a benzoylbenzyl group at the other (B-PEG-N)] to provide the cage in order to get the MF effect on photopolymerization of vinyl monomers such as MMA and styrene in bulk or in aqueous solution without adding an emulsifying agent. Besides providing a cage, the dissolved polymer also acts as photosensitizer. The polymers formed under MF possessed higher MW, narrower molecular weight distribution (MWD), higher stereoregularity and thermal stability¹³. The MW increases with the MF strength (Fig. 4, curves 3 to 6). By UV-irradiation, the triplet energy transfer from the excited sensitizer moiety of the added macromolecules to small initiator molecules produces triplet radical pair because of spin conservation, and these radicals initiate polymerization. The MF effect lies again on the energy splitting of the triplet sublevels (T_+ , T_0 , T_-) and so only T_0 remains degenerate with S. Thus about two thirds of the radical pairs remain in the triplet state. Or in other words the triplet radical pairs have much longer life-time and it is difficult to recombine them since the spins are parallel. As a result the triplet chain initiating species and propagating radicals have more life-time to react with monomers rather than chain termination resulting in higher MW polymer. Again the MWD of the polymer is narrow because of similar life time of propagating triplet radical pair.

However, MW and concentration of the added polymers are important for the MF effect¹⁶. The influence of MF is not observed if naphthalene or benzophenone and PVN or PVB with a MW and concentration less than the critical value are used. The polymer entanglement (similar to cage) provides efficient contact distance between macromolecules and small AIBN molecules for the benefit of triplet energy transfer (critical distance: 10–15 Å). It may also be noted here that to get optimum MF effect, the reaction must be carried out at low conversion (~20%) so that

the variation of viscosity of bulk solution is not big enough to offset the influence of the variation of local viscosity.

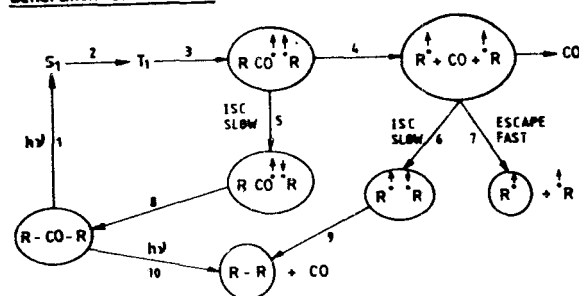
The MF effect on the rate of polymerization also varies with the viscosity of the medium for the dye (methylene blue) sensitized photopolymerization of acrylamide using triethanol amine as reducing agent¹⁷. The rate of polymerization was found to increase in ethylene glycol or in water-glycerol mixture, but not in aqueous medium only. The photoreduction of methylene blue involving a triplet state forms triplet radical pairs containing radical ions. In the presence of MF the two-fold increase of the semiquinone free radicals and escape of the radicals from the cage enhance the rate of polymerization. The cage effect may be due to the added ethylene glycol or glycerol as solvent. The viscosity of the media has also an important role in MF effect. The restricted movement of the radical in a viscous medium is, therefore, also a cause of MF effect.

Mechanism of photopolymerization in the cage

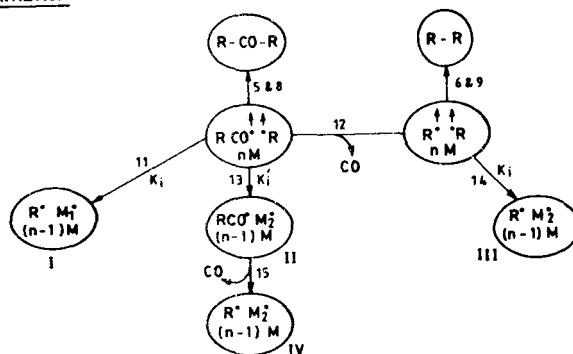
The triplet radical pair is commonly produced by photoexcitation of ketone initiators like dibenzyl ketone, benzoin, benzophenone etc. Considering $R-CO-R$ as an example, the generation of triplet radical pair and polymerization of vinyl monomer (M) in cages (micelles) under MF are shown in Fig. 5. Initially the photolytic cleavage of the ketone produces a triplet, $^3(RCO\cdot\cdot R)$, radical pair (step 3) followed by decarboxylation to $^3(R\cdot\cdot R)$ (step 4) or coupling of the $RCO\cdot$ and $R\cdot$ to produce singlet radical pair, $^1(RCO\cdot\cdot R)$ (step 5) and then $(R-CO-R)$ (step 8). The triplet radical pair, $^3(R\cdot\cdot R)$ produces singlet radical pair, $^1(R\cdot\cdot R)$ (step 6) and finally the cage product, $R-R$ (step 9) or one of the radicals, $R\cdot$ exits from the cage (step 7). Only the recombination back to singlet from the corresponding triplet radical pairs (steps 5 and 6) is lowered in the presence of MF. But steps 4 and 7 are directly independent of MF effect. So in the competition between steps 5 and 4, and steps 6 and 7, steps 4 and 7 predominate. As a result higher extent of radical escape from the cage occurs. The actual mechanistic basis of the MF effect is the lowering of the triplet to singlet ISC in steps 5 and 6 due to Zeeman splitting of the triplet states, which enhances the radical escape from the cage and consequently the quantum yield for the polymerization in the cages increases.

The $RCO\cdot$ or $R\cdot$ radical formed can initiate polymerization and produce monomeric radical (M_1 or M_2) as shown in steps 11, 13 and 14. The

Generation of Radicals



Initiation



Propagation and Termination

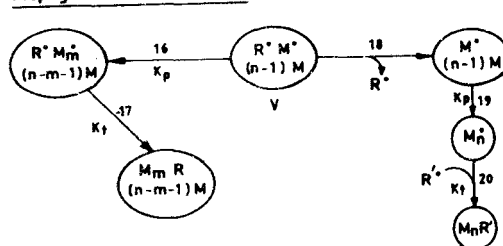


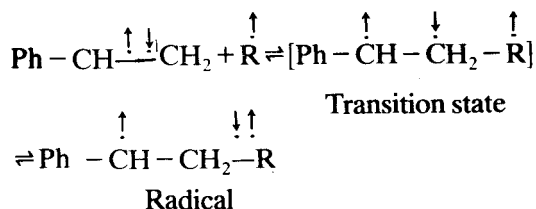
Fig. 5—Schematic representation of photodecomposition of ketone initiators in cages and a radical polymerization of vinyl monomers (M) under magnetic field (circles represent cages).

propagation starts in the cages as shown in I, II, III and IV. These are represented in a simplified manner as in V, where M is a monomeric radical. The monomeric radical in the presence of $R\cdot$ can also propagate to give polymeric radical (M_m) as long as the triplet nature is preserved (step 16). As soon as ISC from triplet to singlet occurs, the growing polymeric radical terminates and gives the polymer M_mR (step 17). The polymer yield and the degree of polymerization M are, therefore, determined by the triplet to singlet ISC efficiency and are increased in the presence of MF. The escape of one radical, $R\cdot$ from the cage (step 18) leads to the uninterrupted propagation of the isolated radical to form polymeric radical, M_n (step 19). Thus propagation continues until a second radical, $R\cdot$ enters and terminates the propagation (step 20). The indirect effect of MF which

increases the rate of radical escape from the cage also leads to higher polymer yield and MW of the polymer.

Thermal radical polymerization

Schmid, Muhr and Marek¹⁸ polymerized styrene under MF (16 KG) at 80°C. The reduced rate of polymerization under MF was explained to be due to the orientation of reacting molecules. It is likely that an external MF would orient not the radicals but only the spin moments of the odd electrons. The chain propagation step in the field free space occurs by a preliminary uncoupling of the π -electrons. The process can be represented as follows¹⁹.



In the presence of a strong external MF, the uncoupled state is more probably

$[\text{Ph}-\text{CH} \begin{array}{c} \uparrow \quad \uparrow \\ \text{---} \end{array} \text{CH}_2-\text{R}]$, where all three electron spin moments are oriented with respect to the external field. Such a configuration would not lead to bond formation in either direction and hence agrees with the observed deceleration by the external MF. Wojtczak²⁰ found a strong inhibition of acetaldehyde polymerization in aqueous solution by steady MF but the rate increased under an alternating MF.

The radical photopolymerization also follows the above mentioned chain propagation. If the mechanism of MF effect is the orientation of spin moments, the rate and polymer yield of radical polymerization of vinyl monomer should always decrease. In photopolymerization, the predominance of triplet $\leftrightarrow$ singlet ISC should be considered for the increased rate of polymerization. But the rate and yield of thermal radical polymerization of vinyl monomers should always decrease. However, recently²¹⁻²⁹ experimental evidences are available where both the rate of polymerization and polymer yield increase in thermal polymerization under MF. Some of the properties of the polymer synthesized under MF are also improved than those of the polymers prepared without MF.

Simionescu *et al.* polymerized MMA²¹ in bulk, and butyl methacrylate²² by various methods of polymerization (bulk, solution and emulsion) initiated by thermal decomposition of dibenzoyl

peroxide (BPO) in the presence and absence of MF (1.1 KG). The increased rate in bulk, emulsion and solution polymerization in polar solvents in the above cases was observed under MF. But in non-polar solvents the rate of polymerization decreases. The induction period and activation energy of polymerization decrease while the MW and thermal stability of the polymers increase. But the electrical conductivity shows lower values as compared to those of the poly(butyl methacrylate) obtained in the absence of MF. These observations were explained by the radical shifting from the singlet to the triplet state under the influence of MF which increases initiation efficiency through the reduction of 'cage' recombination reaction. But how the singlet to triplet conversion is influenced by MF and how the cage is made in bulk and solution polymerization are not clear. Though the solvent may act as cage, it is more reasonable to assume that the cage may be formed by the polymer itself. The singlet to triplet conversion is also possible in the presence of MF if $\Delta g \neq 0$ (as discussed in Eq. 1).

The thermal decomposition of BPO produces two identical radicals, viz., $\text{C}_6\text{H}_5\text{COO}^\cdot$ having the same g-factor i.e., the Δg value for initially formed radical pair is zero. So at the initial stage of polymerization there should not be any possibility of $S \leftrightarrow T_0$ conversion under the influence of MF. The possibility of one decarboxylation and formation of a radical pair ($\text{C}_6\text{H}_5\text{COO}^\cdot \cdot \text{C}_6\text{H}_5$) cannot be excluded. But more possible formation of the radical pair ($\text{C}_6\text{H}_5^\cdot \cdot \text{C}_6\text{H}_5$) after both decarboxylation results in zero Δg . The decrease in activation energy of polymerization under MF is also contradictory since the energy change even by the strongest external (laboratory) MF²³ of 100 KG is merely 0.03 kcal/mol even for paramagnetic molecules. However, in the course of the study on the bulk copolymerization of styrene and acrylonitrile initiated by BPO under UV-irradiation, it is also observed that the yield of copolymer increases under MF. The decomposition of BPO thermally as well as by UV-irradiation is complicated in the presence of magnetic field²⁴.

It has been reported that the polymer yield increases in the bulk polymerization of acrylonitrile (AN) at 60°C initiated by AIBN under MF²⁵. The MW of PAN also increases with the increasing MF strength (Fig. 4, curve 1). The PAN polymer prepared under MF was thermally more stable and of higher degree of syndiotacticity than that prepared without MF. It may be noted that the thermal decomposition of AIBN produces radicals

with $\Delta g=0$, and therefore the $S \rightarrow T_0$ ISC is not enhanced by the MF, consequently the rate of polymerization should not increase. The bulk polymerization of AN is heterogeneous in nature with polymer precipitating out of the monomer and is quite different from the bulk polymerization of styrene, MMA and butyl methacrylate. The higher rate and MW under MF may be due to the influence of MF on the termination by combination of macroradicals which in turn is governed by the restricted translational motion of macroradicals as it precipitates out.

Polymerization of AN in aqueous solution using the redox initiator system of H_2O_2 and thiourea at room temperature under MF has been carried out in the authors' laboratory²⁶. The polymerization kinetics show sinusoidal shape with MF. This may be due to the sinusoidal change of viscosity and density of water under MF²⁷. However, detailed work is necessary to understand the process clearly. It may be possible that the sinusoidal nature of aqueous polymerization of AN (initiator being water soluble) under MF is determined by the diffusion process of radicals and monomer molecules controlled by the sinusoidal change of viscosity and density of water.

Imoto *et al.*²⁸ reported aqueous polymerization of MMA initiated by the hydrophilic macromolecule, poly(2-hydroxyethyl methacrylate) (PHEMA) at 20-30°C under a MF of 141 KG. The initiation mechanism of polymerization takes place through the hydrogen atom transfer from the monomer complexed at the OH groups of PHEMA to the free monomer. The polymer produced in three layers, viz., the MMA layer, the aqueous layer and the hydrophobic area (HA) formed by swollen PHEMA were isolated separately by precipitating out in methanol. Polymerization proceeds almost entirely in the HA and even by heating to 85°C for 3 h it hardly proceeds in water phase in the absence of MF. But in the presence of MF, the polymerization of MMA increases markedly in HA and takes place not only in the HA but also in water phase and the conversion in water phase reaches between 1/3 and 1/2 of the conversion in HA. Again, the conversion of monomer and MW of the polymer increase with increase in MF strength in the range of 0-1 KG. But there is a tendency²⁹ for the conversion to saturate beyond 1 KG. The tendency of grafting MMA onto PHEMA is high, (>90%) regardless of the intensity of MF.

Though the initiation mechanism of PHEMA in the HA is different from the photoinduced po-

lymerization in cages, the effect of MF is quite analogous. At the first step of polymerization a radical pair in a singlet (S) state is generated in the HA formed by the mother (added) polymer, PHEMA, which in the presence of MF is converted into the triplet state by ISC. This ISC may be due to different g-factors of the two different radicals and is pronounced by the MF. Since the radical pair in the triplet state cannot recombine, these two radicals can initiate polymerization. As a result the monomer conversion and the MW of the polymer produced increase with increase in MF. Again, since the recombination rate of radical pairs diminishes, the ease of radical escape from the HA to aqueous phase increases, thereby, causing polymerization in the aqueous phase in the presence of MF. The overall activation energy with and without MF are 29.5 and 30.3 kJ/mol respectively.

There is also effect of MF on the radical polymerization of vinyl monomers initiated by several other kinds of hydrophilic macromolecules. Depending upon the hardness and the tightness of hydrophobic areas (reaction areas) formed by different kinds of mother polymers e.g., graft or block copolymers or the mother polymers of different tacticity, the extent of MF effect varies. The order of the mother polymers for enhancement of polymerization is: PEG-300 < PHEMA < PMEO/4.0 < PMEO/8.7 < Poly(St_1 -Co-MEO₂) and Poly(St_1 -r-MAA-Na₂) < Poly(St_1 -b-MAA-Na₂).

Copolymerization under magnetic field

Simionescu *et al.*³⁰ tried graft polymerization of acrylonitrile (AN) onto the film of carboxymethyl cellulose immersed in aqueous $CeSO_4$ and H_2SO_4 solution initiated by various forms of energy one of which is the MF (1.44 KG) at 49-60°C. But no grafting took place under MF. However, in the presence of MF (12 KG) the graft copolymerization of isoprene onto tetrafluoroethylene-propylene copolymer³¹ and that of MMA onto polyvinyl alcohol (PVA)³² using UV-radiation and benzophenone as catalyst occurs. The graft ratio as well as stereoregularity of grafts in both the cases increased with MF reaching the maximum stereoregularity at 85% graft ratio at the MF of 12 KG.

Since PVA is a water soluble polymer, the graft copolymerization of MMA onto PVA is very similar to the emulsion polymerization. The cage formed by PVA macromolecules contains MMA and benzophenone. Under UV-irradiation, the excited benzophenone triplet abstracts a hydrogen atom from the tertiary carbon of PVA and pro-

duces a triplet radical pair consisting of ketyl and PVA. In the presence of MF due to Zeeman effect, the longer life of triplet pairs ensures formation of higher graft ratio of the copolymer. The grafted copolymers prepared under MF showed improved moisture and heat resistance properties. This is perhaps due to the increased graft ratio and greater stereoregularity of the copolymers obtained under MF.

Thermal emulsion copolymerization of vinyl acetate/MMA/acrylamide was also reported under MF³³. Decrease in reaction time and increase in rate of copolymerization under MF (1.3 KG) were reported. However, the effect of MF on various aspects of copolymerization such as the copolymer composition, reactivity ratio of the comonomers, comonomer sequence, steric arrangements of the comonomers in the chain etc. has not been reported. In the authors' laboratory, studies have been made in the copolymerization of styrene and acrylonitrile under MF and effects of MF on monomer reactivity ratio, monomer sequence in copolymer formed, copolymer composition and tacticity of the copolymer chain have been examined³⁴.

Synthesis of liquid crystal polymers under magnetic field

Polymers having rod-like conformation, or with mesomorphic or potentially mesomorphic side groups may display liquid crystal (LC) behaviour. To obtain mesomorphic phase in polymers, the monomers required need not necessarily be always mesomorphic in nature. Again, the mesomorphic order of polymers obtained by polymerization of monomers from LC phases is not necessarily that of the monomers. A nematic monomer may also yield a polymer with smectic ordering. Though examples of synthesis of LC polymers under MF where monomer is not LC are available, the main attention is to polymerize under MF the LC monomers which have mesomorphic side groups that produce well oriented polymers (Table 2). Here, it may be mentioned that the LC polymer itself can be oriented under MF; this feature is, however, beyond the scope of the present review.

Liebert and Strzelecki³⁵ copolymerized two LC monomers: *p*-acryloyloxybenzylidene-*p*-cyanoaniline(I) and di(*N*-*p*-acryloyloxybenzylidene)-*p*-diaminobenzene(II) from their nematic phase under MF (8 KG). The polymer obtained was highly oriented and crystalline, having the same mesomorphic phase as that of monomers. Similarly, the polymerization of LC vinyl monom-

Table 2—Liquid crystal (LC) monomers and their structures polymerized under magnetic field (MF).

Monomer	Reference
I. $\text{CH}_2 = \text{CH} - \text{COO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{CN}$ <i>p</i> -acryloyloxybenzylidene- <i>p</i> -cyanoaniline	35
II. $\text{CH}_2 = \text{CH} - \text{COO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{N} = \text{CH} - \text{C}_6\text{H}_4 - \text{COO} - \text{CH} = \text{CH}_2$ Di(<i>N</i> - <i>p</i> -acryloyloxybenzylidene)- <i>p</i> -diaminobenzene	35,39
III. $\text{CH}_2 = \text{CH} - \text{COO} - \text{C}_6\text{H}_4 - \text{COO} - \text{C}_6\text{H}_4 - \text{OC}_6\text{H}_{13}$ (4- <i>n</i> -hexyloxyphenyl)-4-acryloyloxybenzoate	36
IV. $\text{MeO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{CH} = \text{CH}_2$ OH N-(<i>p</i> -methoxy- <i>o</i> -hydroxybenzylidene)- <i>p</i> -aminostyrene	37
V. CH_3 $\text{CH}_2 = \text{C} - \text{COO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{OC}_2\text{H}_5$ N-(<i>p</i> -methacryloyloxybenzylidene)- <i>p</i> -ethoxyaniline	38
VI. $\text{CH} = \text{CH} - \text{COO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{C}_4\text{H}_9$ N-(<i>p</i> -acryloyloxybenzylidene)- <i>p</i> - <i>n</i> -butylaniline	39
VII. $\text{CH}_2 = \text{CH} - \text{COO} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{N} = \text{CH} - \text{C}_6\text{H}_4 - \text{COO} - \text{CH} = \text{CH}_2$ Di(<i>N</i> - <i>p</i> -acryloyloxybenzylidene) hydrazine	39
VIII. $\text{CH}_2 = \text{CH} - \text{C}_6\text{H}_4 - \text{N} = \text{CH} - \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 - \text{CH} = \text{CH}_2$ <i>p</i> -phenylene bis (N-methylene- <i>p</i> -aminostyrene)	39

er, (4-*n*-hexyloxyphenyl)-4-acryloyloxybenzoate(III) under MF results in a fully oriented polymer useful in integrated optics and optoelectronics³⁶. The rate of polymerization, the viscosity and solubility of the polymeric product of the nematic LC monomer, N-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminostyrene(IV), were not affected by the application of MF (1.3 KG) during its polymerization³⁷.

Perplies *et al.*³⁸ studied the orientation as well as rate of polymerization of LC monomer under a strong MF (70 KG). The LC vinyl monomer, *p*-(4-ethoxyphenyliminomethylidene)-*p*-ethoxyaniline(V), gave a LC polymer of the smectic A type. The increase in rate under MF was observed during the polymerization of the monomer from its nematic phase and not from its isotropic phase. The acceleration rate was explained by the transformation of the nematic cluster structure to homogenous nematic structure by the MF and this homogeneous order has been ascribed by the

authors to the decrease in the chain termination step.

Clough *et al.*³⁹ polymerized various LC monomers above the respective crystal melting temperature without addition of initiator under MF (4.5 KG). The polymerization of the monomer, di(*N-p*-acryloyloxybenzylidene)-*p*-diaminobenzene(II) in its nematic phase gave a smectic polymer having side chains aligned with the field and the polymer backbone chains confined to perpendicular to the side groups. Copolymerization of nematic(II) with *N-(p*-acryloyloxybenzylidene)-*p-n*-butylaniline(VI) (1:1) also gave a smectic polymer. High degrees of side chain orientation (orientation parameter, $f=0.7$) have been achieved under MF. Thermal expansion of this polymer showed large anisotropy. But the polymerization of both the monomers, di(*N-p*-acryloyloxybenzylidene) hydrazine(VII) and *p*-phenylene bis (*N*-methylene-*p*-aminostyrene)(VIII) in their nematic state resulted in polymers with nematic order. This phenomenon appears to be dependent on the ability of interacting side groups to pack into an orderly layered arrangement without disturbing the regular disposition of the polymeric backbone.

The main objective of these polymerizations was the orientation of the polymers under MF although Perplies *et al.*³⁸ studied the rate of polymerization also. However, the polymerization of γ -benzyl-L-glutamate N-carboxy anhydride (BLG-NCA) under MF (3.6 KG) provides an example where the monomer is not LC but the polymer obtained is LC⁴⁰. The MW of the polymer, poly(γ -benzyl-L-glutamate) (PBLG) obtained under MF was also higher. The activation energies of polymerization with and without application of MF are the same. So the rate of acceleration may be explained by the suitable alignment of BLG-NCA monomers and/or growing polymer chains by the MF.

Crosslinking reaction under magnetic field

Thermal crosslinking reaction

Very few curing/crosslinking reactions of polymers under MF were available before 1980. Different filled and reinforced polymer systems show better physico-mechanical properties when cured under MF. The alignment of the magnetic filler particles during curing under MF improves the properties of the crosslinked product. Polyester composites containing Fe powder (particle size 4-20 μ) and aligned under MF (0.4 KG) during curing, showed improved tensile and flexural properties⁴¹.

The physico-mechanical properties of filled and reinforced epoxy resin increased 20-30% on crosslinking under constant MF⁴². The physico-mechanical properties of epoxy resins crosslinked under MF showed a sinusoidal variation with the pronounced maximum at 0.6-0.7 KG when ED-5 was crosslinked in a MF with diethylene triamine, triethylene tetramine, hexamethylene diamine and a reaction product of polyethylenepolyamine with dimerized fatty acid esters of linseed oil⁴³. The flex strength of polyamine crosslinked epoxy resin ED-5 increased to maximum within the first 15 min of treatment under the MF. Longer exposure to the MF produced no further improvement of flexural strength⁴⁴. Crosslinking of ED-20 epoxy resin with polyethylene polyamine at 60°C for 6 h in a MF resulted in a highly crosslinked, more oriented polymer as compared to the polymer obtained without MF⁴⁵.

Crosslinking of phenol-furfural resin in a MF increased the microhardness and hence mechanical properties of the crosslinked polymer⁴⁶. The bending strength of the crosslinked polymer increased by 30-40% when crosslinked under MF.

Like the orientation of certain filler particles in a polymer matrix, the orientation of matrix polymers, particularly liquid crystal (LC) polymers, is also possible under MF. It is also possible to first orient the polymer matrix under MF and then freeze the oriented structure by crosslinking. One advantage of magnetically oriented networks over mechanically oriented network is that it does not lose its orientation upon heating readily. Poly(γ -benzyl-L-glutamate) (PBLG) was thermally crosslinked with 1,6-hexanediamine under MF to get a permanent chain alignment of the polymer⁴⁷. The permanent chain alignment of nematic phase lasted over a year when crosslinked under MF.

Barclay *et al.*⁴⁸ treated some prepolymers under MF in order to obtain aligned and cured polymers. The epoxy terminated prepolymers based on oligoethers of 4,4'-dihydroxy- α -methylstilbene (DHMS) were crosslinked with stoichiometric amount of methylene dianiline (MDA) in the nematic state of the prepolymers under MF (135 KG). The magnetically aligned LC epoxy networks show different improved properties over the non-aligned or mechanically aligned networks. A significant degree of alignment was observed by the wide angle X-ray diffraction (WAXD) of the resulting crosslinked networks. For example, a particular thermoset prepared from the mesogenic prepolymers under MF achieved an orientation

parameter (f) of 0.57 in contrast to the maximum value of 0.16 achieved mechanically. Magnetically oriented networks retain their orientation to temperatures well above T_g and show reduction in the coefficient of thermal expansion (CTE).

Similarly, the well-oriented and thermally stable (at least 100°C above the T_g) crosslinked LC triazine network with low values of CTE in the direction of the applied MF was obtained by thermal cyclotrimerization of dicyanate compounds of ring-substituted bis(4-hydroxyphenyl) terephthalates under MF (135 KG)⁴⁹. The resulting 1,3,5-triazine rigid-rod networks formed a mesophase as the curing reaction proceeded and the mesophase flowed less readily and was eventually 'frozen' as the crosslinked network was formed and grown to full potential. By the influence of MF, alignment of the LC phase during curing process produced smectic ordered triazine networks. The curing of LC prepolymers in the presence and absence of MF may be shown as in Fig. 6.

The application of MF may also influence the kinetics and the efficiency of crosslinking where initiators/sensitizers are used to produce radicals for crosslink formation. The radical can be generated either by photodecomposition or by photoexcitation of added initiator/sensitizer. The influence of MF on photocrosslinking reactions will be discussed later. Martl *et al.*^{50,51} observed the influence of MF on the thermal crosslinking of (z)-1,4-polybutadiene with bis(2,4-dichlorobenzoyl) peroxide (CBP) at different temperatures and with different concentrations of CBP. With increase in the MF strength the crosslink density decreased. However, the influence of MF on the kinetics of crosslinking reactions was not reported.

Photocrosslinking reaction

Morita *et al.*⁵² observed the enhancement of the photocrosslinking of bromo- and chloro-methylated polystyrene (BCMS) using 2,4-diisopentyl thioxanthone (DITX) and UV-light ($\lambda > 330\text{ nm}$) under MF. With similar technique, the photocrosslinking of poly(styrene-co-vinyl benzylazide) (AZMS) of different MW and also with different triplet sensitizer system like DITX, 2-chlorothioxanthone (CTX) and Michler's ketone (MK) has been studied in the presence and absence of MF⁵³. Without the use of sensitizer, crosslinking of AZMS by direct excitation has also been reported^{54,55}. The efficiency (i.e., rate) of photocrosslinking increases by 45% (at 1 KG) for AZMS/DITX system and by 20% (at 5 KG) for AZMS/CTX system (MW of AZMS 12,900) over

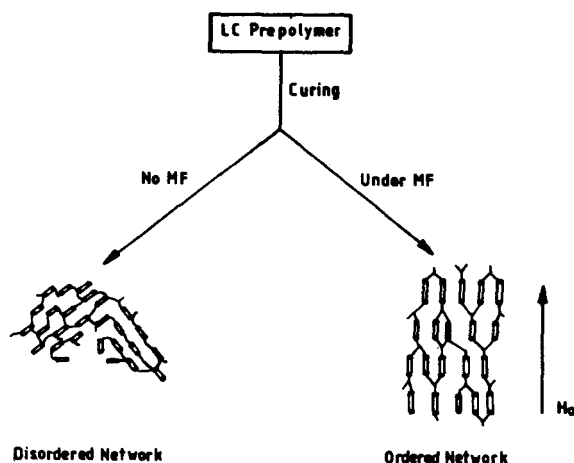


Fig. 6—Schematic representation of the magnetic field effect on the network formation of LC prepolymers.

that in the absence of MF. On the other hand, for direct excitation of AZMS (MW=10,300) under MF (0.89 KG) the gel fraction of AZMS decreases, and the efficiency of photocrosslinking decreases by 20%.

The degree of crosslinking measured by sol/gel analysis increased for the photocrosslinking of butadiene-styrene copolymer with ketonic initiator (eg, benzophenone or deoxybenzoin) by uv-radiation under the influence of MF (10 KG)⁵⁶. The rate and mechanisms of crosslinking for sensitized, direct excitation and photolysis of initiator systems are different (Fig. 7). The discussion on these systems follows.

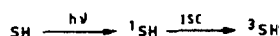
Mechanism of photocrosslinking

The photocrosslinking reaction follows a radical mechanism and the effect of MF is explained on the basis of radical pair model. The mechanisms of photocrosslinking with various initiating systems (e.g., sensitized excitation^{52,53}, direct excitation^{54,55} and photolysis of initiator⁵⁶) are schematically represented in Fig. 7.

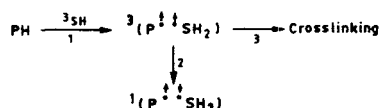
i(a) For the polymer (PH)/triplet sensitizer (SH), where the polymer has no photoactive group⁵², the only process of crosslinking is through the sensitizer. The triplet sensitizer (^3SH) by the abstraction of H-atom from the polymer (PH) forms a triplet radical pair, $^3\text{P}\cdot\text{SH}_2$ (step 1, Fig. 7). The influence of MF decreases the rate of conversion of triplet into singlet (step 2) as a result of the Zeeman splitting of the triplet state. Consequently, the concentration of the triplet radical pairs increased. Thus the availability of the radicals for crosslinking became enhanced which caused the increased efficiency of crosslinking (step 3, Fig. 7).

(b) In the triplet sensitized photocrosslinking

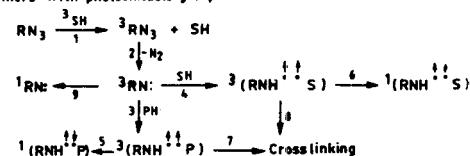
I. Sensitized Excitation:



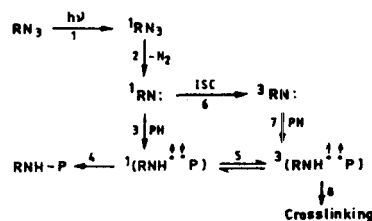
(a) Polymers having no photoexcitable group



(b) Polymers with photoexcitable group



II. Direct Excitation:



III. Photolysis of Initiators:

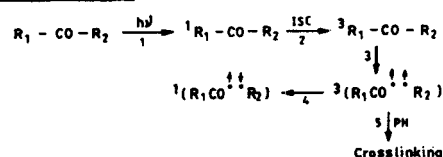


Fig. 7—Schematic representation of the mechanism of photocrosslinking under magnetic field. RN_3 represents polymer molecule (PH) (e.g. AZMS), SH represents sensitizer molecule (e.g., DTIX, CTX, MK etc.) and R_1-CO-R_2 represents ketone initiator (e.g., benzophenone, deoxybenzoin etc.)

of the polymer (RN_3 or PH) having photoactive groups⁵³ (e.g., azido group in AZMS), the triplet sensitizer (3SH) produces triplet polymer (3RN_3) (step 1). Triplet nitrene (${}^3RN:$) originating from 3RN_3 (step 2) and then abstracting H-atom from the polymer or the sensitizer, forms a triplet radical pair, ${}^3(RNH \cdot P)$ (step 3) or ${}^3(RNH \cdot S)$ (step 4). The decreasing rate of ISC (steps 5 and 6) under the influence of MF increases the efficiency of crosslinking (steps 7 and 8). The possibility of ISC of triplet nitrene to singlet nitrene (step 9) cannot be excluded, but again ISC rate decreases by two fold under MF. Besides, triplet nitrene is much more reactive than singlet nitrene. So, crosslinking occurs through the triplet nitrene. And the decrease in the rate of ISC ($T \rightarrow S$) of ${}^3RN: \rightarrow {}^1RN:$ by the influence of MF is also expected to increase the efficiency of photocrosslinking. Another possibility of crosslinking is through the H-abstraction by 3SH from the polymer like (a) (Fig. 7) but it is a minor process.

ii. In the direct excitation of the polymer (RN_3 or PH) having photoactive groups⁵⁴ (e.g., azido group in AZMS), the singlet nitrene (${}^1RN:$) is produced from the singlet excited polymer (1RN_3) (step 2). The singlet nitrene abstracts a H-atom from the polymer and forms the singlet radical pair, ${}^1(RNH \cdot P)$ (step 3). The singlet radical pair easily produces recombination product (crosslinking of two polymers, step 4). The ISC rate of the singlet radical pair to triplet (step 5) is decreased under MF. So, photocrosslinking under MF decreases (step 8). Although the possibility of ISC of the singlet nitrene to the triplet nitrene (step 6) to generate triplet radical pair, ${}^3(RNH \cdot P)$ (step 7) cannot be excluded completely, it is a minor process.

iii. In the crosslinking of polymer (PH) by the photolysis of ketonic initiator⁵⁶ (R_1-CO-R_2), the triplet radical pair, ${}^3(R_1CO \cdot R_2)$ is produced (steps 1 to 3). Under the influence of MF, the rate of triplet to singlet ISC (step 4) is reduced due to the Zeeman splitting of the triplet states (T_+ , T_0 , T_-) and hence, with a longer life time, the triplet pair undergoes less cage recombination yielding more free radicals for crosslinking (step 5).

Miscellaneous polymerizations under magnetic field

Synthesis of magnetic polymers

Now-a-days, one of the frontier investigations in the polymer field is magnetic polymers, which involves synthesis of conjugated stable polyradicals with long range magnetic ordering among the spins. The net moment of the spinning electrons is responsible for the magnetic properties. Now, the net magnetic moment will be enhanced if all the radical centers i.e., spins in the molecules, are aligned in the same direction under MF. Ota *et al.*⁵⁷ prepared a thermosetting resin composed of triarylmethane structure (COPNA) by heating at 130–140°C for 1 h a mixture of terephthalaldehyde (TPA) and pyrene (molar ratio = 1.25:1) blended with 5 wt % *p*-toluene sulfonic acid in argon atmosphere under a MF of 0.44 KG or 0.88 KG, and the product resin exhibited ferromagnetic characteristics. This resin prepared under ordinary conditions is diamagnetic. However, the ferromagnetism of the resin disappeared after pulverization into a fine powder suggesting that stacking and orientation of the constituent molecules in the resin is responsible for ferromagnetism.

Synthesis of conducting polymers

One classical route to electrical conducting polymer is to bound the ferromagnetic and electri-

cally conducting filler with a hardenable organic adhesive. Salyer *et al.*⁵⁸ prepared conducting phenolic resins by curing them thermally under MF (4 KG) with 5-60% ferromagnetic and electrically conducting fillers such as Fe, Co, Ni, Gd and alloys that were coated with metals like Cu, Al, Zn or Cr. During curing, interface of the layer was maintained normal to the lines of force of the MF so that the filler particles are oriented to form an electrically conducting bridge between the units. Positive conductivity of the filled materials was observed as compared to the zero conductivity when cured in the absence of MF. Makarov *et al.*⁵⁹ examined the change in the volume resistivity of ED-20 epoxy resin on crosslinking under an external constant MF. Since the constant MF has a directional effect, an anisotropy in volume resistivity of ED-20 was observed with respect to the strength and direction of the MF. The decrease in resistivity of ED-20 in the field direction during the initial stage of crosslinking suggested an increased generation and mobility of ionic formations due to a rupture of α -oxide groups in the polymer molecule.

For preparation of conducting polyacetylene (PA) various new methods have been used during the process of polymerization in order to produce highly oriented PA. One such method is polymerization under high MF where the polymerization catalyst molecules are oriented along with the orientation of the liquid crystal (LC) medium in a preferred direction. Thus, PA with higher anisotropy is obtained. Aldissi⁶⁰ polymerized acetylene under MF (4 KG) at 25°C with Ziegler-Natta catalyst, $[\text{Ti}(\text{OBU})_4/\text{AlEt}_3]$ using (4-methoxybenzylidene)-4-*n*-butylaniline nematic LC as the medium instead of toluene. Similarly, Tsuji *et al.*⁶¹ polymerized acetylene under MF of 8 KG in the presence of the above catalyst utilizing equimolar mixture of two different kinds of nematic LCs, 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene and 4-(4-*trans*-4-*n*-propylcyclohexyl)butoxybenzene as the medium. PA obtained under MF exhibits a high electrical anisotropy with a preferred orientation of the polymer chains and a more ordered fibrillar structure. But the *cis-trans* composition and its density are similar to those obtained when toluene is used as solvent. Previously, the reaction temperature was above 273 K to keep two component of LC mixture in the nematic phase. But polymerization at lower reaction temperature down to 233 K or even lower and using suitable five- or six-component LC mixtures aligned under MF results in *cis*-rich PA films (90% *cis*-content)^{62,63}. EPR measurement of pure PA pre-

pared under MF (3 KG), by the Shirakawa technique has been reported⁶⁴. The spin mobility in the sample prepared under MF decreased.

Biopolymerization

Torbet *et al.*⁶⁵ investigated a biological polymerization process under a strong MF. The slow rate of polymerization of fibrinogen under MF obtains oriented fibrin fiber. The orientation during polymerization is explained due to the diamagnetic anisotropy of aggregated fibrinogen, and is examined by magnetically induced birefringence measurement^{65,66} and also by light transmissivity and degree of polarization of transmitted light^{67,68} as a function of polymerization time. Neutron diffraction and scanning electron microscopy were utilized to distinguish the surface morphology of sample prepared with and without MF. At the beginning of polymerization because of a small diamagnetic anisotropy of small fibrinogen molecules and fibrin monomers, the magnetic orienting energy is much less than the thermal energy (kT) and consequently the orientation is poor. The upsurge in the birefringence commences with polymerization as many monomers come together in an ordered way. This is because the diamagnetic anisotropy of the aggregates is many times that of a monomer and the magnetic orienting energy is sufficiently large to allow a high degree of orientation. It may be mentioned here that the orientation is relatively poor even in the strongest MF and the production of oriented fibrin network under MF is different from the production of oriented polymer during polymerization of LC monomers which are oriented before polymerization. Other investigations on biomolecules including the growth of the living cell under the influence of MF have been reviewed⁶⁹.

Radiation induced solid state and plasma polymerization

Mori *et al.*⁷⁰, while studying radiation induced solid state polymerization of acrylonitrile (AN) at 77 K, observed an increase in the initial rate with increasing MF which become maximum at 4 KG. The MW was, however, unaffected by MF. But in the case of radiation induced solid state polymerization of acetaldehyde a decrease of yield was observed⁷¹ if MF was applied.

Plasma polymerization is a general term to include plasma deposition of organic and inorganic materials. However, the plasma deposition of vinyl monomers produces the deposited polymers usually in the form of thin films on the substrate. So, only the plasma polymerizations of vinyl mon-

omers associated with the influence of MF are included here. The influence of MF on the plasma polymerization of tetrafluoroethylene (TFE) was observed in a capacitively coupled system with internal electrodes using radio-frequency (13.56 MHz)⁷², audio-frequency (10 KHz), AC discharge⁷³, and in a magnetron glow discharge electrode⁷⁴. In the absence of MF, the most active zone of the plasma is the centre of the interelectrode gap whereas the influence of MF moves this active zone closer to the electrodes^{72,73}. The MF influences the deposition rate. The chemical characteristics of the deposited polymers as revealed by electron spectroscopy for chemical analysis (ESCA) are also changed by the influence of MF⁷²⁻⁷⁴. The reduction of breakdown voltage at a particular pressure with increasing MF strength was also reported for the plasma polymerization of ethylene (C_2H_4) and fluoroethylene (C_2H_3F)⁷⁵.

Conclusion

The magnetic field (MF) can exert great influences on chemical reactions including polymerization/crosslinking reactions, as light, pressure and heat do. Though in some cases the influence of MF on kinetics of polymerization is contradictory²⁰⁻²², the influence of Zeeman splitting of the triplet states (T_+ , T_0 , T_-) and the singlet $\leftrightarrow$ triplet intersystem crossing due to Δg - and hfi-mechanism explain some of the observations reasonably⁷⁻¹⁷. However, depending upon the systems, the polymer yield and molecular weight (MW) can be increased under magnetic field, mainly, in radical polymerization^{7,14-16,21,22,25} and crosslinking reactions^{52,53,56}. Wide molecular weight distribution (MWD) for radical polymerization in general, may also be made narrower under the influence of magnetic field^{8,10,15,16}. The properties of polymers such as crystallinity, chain flexibility, solubility and thermal behaviour can also be controlled by the application of magnetic field. The microstructure of the polymer chain, mainly tacticity, monomer sequence in copolymer etc. may be altered under magnetic field³⁴. The extent of grafting³¹⁻³² and the composition of copolymer³⁴ can also be modified by the application of magnetic field.

The demand for orientated liquid crystal polymer may be partially fulfilled by polymerizing relevant monomers under magnetic field where *in situ* oriented^{35,36,38-40,45,47} liquid crystal polymer is formed which is much more stable and ordered than that obtained without magnetic field or even those oriented by other external forces^{39,48}. The ordered structure in the liquid crystal polymers

may also be locked by crosslinking such system under magnetic field⁴⁷⁻⁴⁹.

Synthesis of magnetic polymers⁵⁷ and conducting polyacetylene⁶⁰ under magnetic field is a remarkable achievement. This novel route appears to be promising for such syntheses in near future.

Acknowledgement

The authors wish to thank the CSIR (India) for award of a fellowship to DSB.

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