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Polymerization under magnetic field — II. Radical polymerization of acrylonitrile, styrene and methyl methacrylate

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Radical polymerization of acrylonitrile (AN), methyl methacrylate (MMA) and styrene (S) has been studied under magnetic field (MF) using an AIBN initiator. The effect of MF is observed on the polymerization of AN and not on MMA and styrene. This may be due to the heterogeneous polymerization of AN (occlusion theory). The MF increases the rate of AN polymerization and polymer (PAN) yield. The overall activation energy is not influenced by the MF; however, the MF helps to reduce the activation entropy of polymerization. The influence of MF alters the structure and properties of the polyacrylonitrile (PAN). The molecular weight (MW) of PAN prepared under MF is higher and the molecular weight distribution (MWD) is narrower than those obtained without MF. The syndiotactic stereoregularity and crystallinity of such PAN polymer is higher than that obtained without application of MF. Magnetic field enhances the thermostability and the dielectric property of PAN. © 1997 Elsevier Science Ltd.

(Keywords: radical polymerization; magnetic field (MF))

INTRODUCTION

Recently, the effect of magnetic field (MF) on the polymerization and the properties of polymers has attracted the interest of several group of workers[1]. Turro *et al.*[2] utilized the concept of radical pair mechanism for the emulsion polymerization of styrene initiated by an oil-soluble photoinitiator which produces triplet radical pairs. Due to the Zeeman splitting of the triplet state in the presence of MF, the intersystem crossing ($T_{\pm} \rightarrow S$) efficiency is hindered, and therefore the radical pair formed in the micelles (cages) cannot recombine easily. On the other hand, one partner of the geminate radical pair escapes out of the cage. Therefore, the isolated radical can grow uninterrupted in the micelles leading to greater polymer yields and higher molecular weights of polystyrene. Since this mechanism operates in a cage, various means have been utilized to create the cage effect in the polymerization systems. Huang *et al.*[3] added polymers, polyvinyl naphthalene and polyvinyl benzophenone to the photopolymerization system of MMA and styrene. In addition, acting as a cage the added polymers can also act as a triplet sensitizer to decompose the AIBN initiator. The effect of MF on the polymerization of MMA in the hydrophobic area formed by the added polymer, poly(2-hydroxyethyl methacrylate), has also been observed[4]. The influence of MF has been reported in the case of bulk polymerization of MMA initiated by the thermal decomposition of benzoyl peroxide[5].

In our earlier publication, the effect of MF on the radical polymerization of AN using AIBN initiator has been reported[6]. This paper reports the results of the detailed investigation of the MF effect on the kinetics of polymerization of AN as well as some other properties of the PAN polymer. The influence of MF on the polymerization of styrene and MMA has also been studied.

EXPERIMENTAL PROCEDURES

Materials

Acrylonitrile (AN) (S.D. Fine Chem.) was washed twice with 0.1 N H_2SO_4, followed by washing twice with 0.1 N aqueous NaOH solution and finally with water untill it was free from alkali, dried over fused $CaCl_2$ for 24 h and distilled under reduced pressure; the middle fraction of the distillate was collected and used for polymerization.

Methyl methacrylate (MMA) (Burgoyne, India) was washed twice with 5% aqueous NaOH solution and twice with water, dried over fused $CaCl_2$ for 24 h and distilled under reduced pressure; the middle fraction of the distillate was collected.

The purification of styrene (S) (Burgoyne, India) was carried out in similar fashion.

Toluene (S.D. Fine Chem.), N,N-dimethyl formamide (DMF) (E. Merck) and all other chemicals were purified according to standard procedures[7].

2,2′-Azobisisobutyronitrile (AIBN) (E. Merck) was recrystallized twice from cold methanol, dried in a vacuum desicator and stored in the dark at 5–10°C in a refrigerator.

Magnetic field

The magnetic field used for the copolymerization consists of an electromagnet with adjustable two poles and a power supply (model EM 150, Control Systems & Devices, India). The applied magnetic field strength can be varied by adjusting the distance between the two poles of the electromagnet and the supply of the current 0–40 A, 50 V DC. The minimum and maximum distances between the two poles are 1.0 and 10 cm, respectively.

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Polymerization

Polymerizations of AN, MMA and S were conducted under different conditions such as bulk, solution and at various temperatures ranging from 50 to 80°C with AIBN (0.1% w/w for S and MMA and 1% w/w for AN) as an initiator. The bulk polymerizations were carried out with about 4–6 ml monomer in a pyrex glass tube kept between the two poles of the electromagnet in a circulating oil thermostat (temperature controlled ± 1°C), at the desired temperature. The polymerization media, monomers and solvent were thoroughly flushed with dry and oxygen-free nitrogen and the polymerizations were continued for 30–60 min.

The polyacrylonitrile (PAN) obtained was purified by washing with cold water–acetone mixture, filtered in a gooch Crucible (G-4) and thoroughly washed with acetone. Finally PAN was purified by precipitation from DMF solution by acetone. Polystyrene (PS) and polymethyl methacrylate (PMMA) were purified by the repeated precipitation from toluene solution by methanol. All the polymers were dried at 50°C under vacuum to a constant weight.

Characterization

Viscosity measurements. Measurements of viscosity of the PAN solutions in DMF, and PS and PMMA solutions in toluene were carried out at 30°C using an Ubbelohde suspended level viscometer. Viscosity-averaged molecular weights ($\bar{M}_v$) of the PAN polymer were determined from its intrinsic viscosities in the DMF solvent[6].

GPC measurement. The molecular weight distribution (MWD) of the PAN polymers was carried out with a Waters liquid chromatograph fitted with a Waters 410 differential refractometer using polystyrene (PS) ultra styragel columns (10^3, 10^4, 10^5 and 10^6). The eluent used was DMF stabilized with 0.01% of LiBr at a flow rate of 1 ml min^{-1}. The GPC was calibrated with standard PS.

Density measurement. The densities of the powder PAN polymer samples were measured in benzene at 30°C using a pycnometer.

Dielectric measurement. The dielectric behaviour of the pellet polymer samples was measured with a capacitance measuring assembly (1620/AT, General Radio Company) within the frequency range of 10^2–10^4 Hz at room temperature.

X-ray diffractometry. Wide angle X-ray diffractographs for the powder polymer samples were recorded with a Phillips PW 1840 X-ray diffractometer using Ni-filtered CuKα (λ = 1.5418 Å) radiation at 40 kV–20 mA and scanning speeds of 3° min^{-1} and 1.2° min^{-1}.

RESULTS AND DISCUSSION

Rate and conversion

The effect of MF on the bulk polymerization of AN using AIBN initiator has been reported in our earlier publication[6]. The rate of AN polymerization increases under MF. The viscosity average MW of the PAN polymer obtained under MF is higher and increases with an increase in MF. However, the thermal bulk polymerizations of styrene and MMA are not affected by MF (*Table 1* and *Table 2*).

Table 1 Effect of MF on the polymerization of styrene[a]

MF (kg)	Time (min)	Yield (%)[b]	η_{inh}[c]
0	30	14.76	0.388
1.15	30	11.96	0.397
6.50	30	13.01	0.383

[a] Polymerization conditions: 6 ml styrene, 0.1% (w/w) AIBN, 80°C
[b] The values are the average of two measurements
[c] At 30°C, of 0.5% PS solution in toluene

Table 2 Effect of MF on the polymerization of MMA[a]

MF (kg)	Time (min)	Yield (%)[b]	η_{inh}[c]
0	30	17.14	0.161
1.15	30	17.89	0.168
6.50	30	16.78	0.159

[a] Polymerization conditions: 4 ml MMA, 0.1% (w/w) AIBN, 60°C
[b] The values are the average of two measurements
[c] At 30°C, of 0.5% PMMA solution in toluene

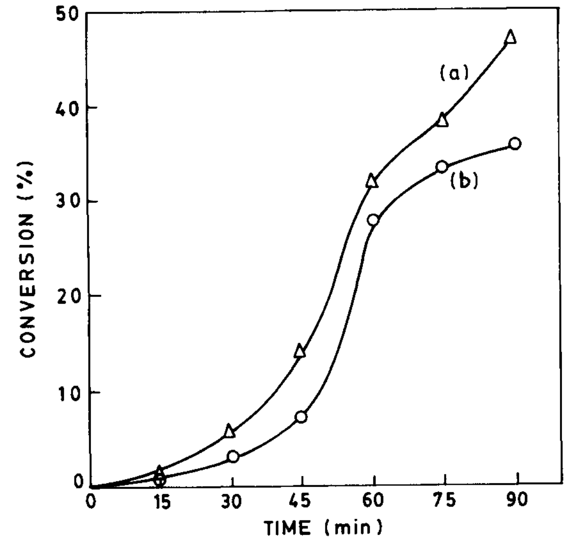

Figure 1 The conversion of solution polymerization of AN (a) with, and (b) without MF (1.15 kg); 2 ml AN, 1% (w/w) AIBN, 2 ml DMF, 60°C

Table 3 Effect of MF on the solution polymerization of AN[a]

MF (kg)	R_p (15)	R_p (30)	R_p (45)	R_p (60)	R_p (75)	R_p (90)
0	0.0167	0.1033	0.1638	0.4748	0.4530	0.3955
1.15	0.0273	0.1866	0.3324	0.5328	0.5066	0.5262
ΔR_p (%)	1.1	8.3	16.9	5.8	5.4	13.1

[a] Polymerization conditions: 2 ml AN, 1% (w/w) AIBN, 2 ml DMF, 60°C
$R_p(t)$ = rate (%yield/min) of polymerization at time t
ΔR_p (%) = $[R_p(H) - R_p(O)] \times 100$

There is also a positive MF effect on the rate and conversion in the moderately dilute solution polymerization of AN in DMF. The conversion *versus* time of polymerization of 2 ml AN in 2 ml DMF in the presence and absence of MF is shown in *Figure 1*. The nature of this curve is quite similar to the bulk polymerization of AN (see *Figure 1* of Ref. [6]). However, the extent of the MF effect is lower in the case of solution than in bulk polymerization. The rates in the presence and absence of MF and the increment of rate (ΔR_p%) by the application of MF is shown in *Table 3*.

The thermal decomposition of AIBN produces a singlet radical pair with Δg = zero. As a result, the singlet to triplet conversion due to the Δg-mechanism and/or the Zeeman splitting of the triplet state in the presence of MF does not arise. So, the number of initiating radicals available for such polymerization both in the presence and absence of MF are the same[8]. Therefore, the cause for increase in rate of polymerization under MF probably lies in the inherent nature of the AN polymerization which is absent in the case of styrene and MMA.

The speciality of AN polymerization in bulk over MMA and styrene polymerization is that it is heterogeneous in nature, with the polymer precipitating out of the monomer. Three polymerization loci were suggested for the heterogeneous polymerization of AN and vinyl chloride[9,10], namely the monomer phase, the polymer phase and also the polymer–monomer interface. Although in both homogeneous and heterogeneous polymerization the phenomenon of autoacceleration is a consequence of diffusion controlled termination reactions, the situation is more complex when the polymer pricipitates from its monomer in heterogeneous polymerization (the occlusion theory)[11]. It may be pointed out here that Mayo *et al.*[12] demonstrated the restriction of the translational movement of adsorbed radicals on the silica gel. The environments which restrict the translational movements of radicals are reaction spaces that are suited for the observation of magnetic field effect on radical reaction[13]. Therefore it may be assumed that the effect of MF may be due to trapped (occluded) radicals in the heterogeneous polymerization of AN. In the polymer phase, the termination by combination of macro-radicals is affected by MF due to restricted translational movement of macro-radicals as they precipitate out. The radicals at the interface, having a somewhat more restricted motion, are also likely to possess a more favourable condition for the MF effect. It may also be assumed that as macro-radicals precipitate out due to restricted translational movement, MF may be able to orient the spin moments of the electrons of macro-radicals in the same direction. As a result, the termination of the precipitated macro-radicals is hindered, resulting in a higher rate of polymerization.

Moreover, the effect of MF is lower in solution rather than bulk polymerization and the extent of the MF effect decreases when the mobility of the macro-radical is enhanced and/or occlusion is disrupted by dilution. This has been reflected in the plot of the difference of conversion (X) with and without MF against volume of DMF added to the polymerization medium (*Figure 2*). This effect perhaps varies with degrees of occlusion (*Figure 2*) and attains maximum at a certain degrees of occlusion (*Figures 3* and *4*). At extreme degree of occlusion, the effect tends to zero (*Figures 3* and *4*). On the other hand, in the case of homogeneous polymerization of MMA and styrene the rate and conversion are unaffected under MF.

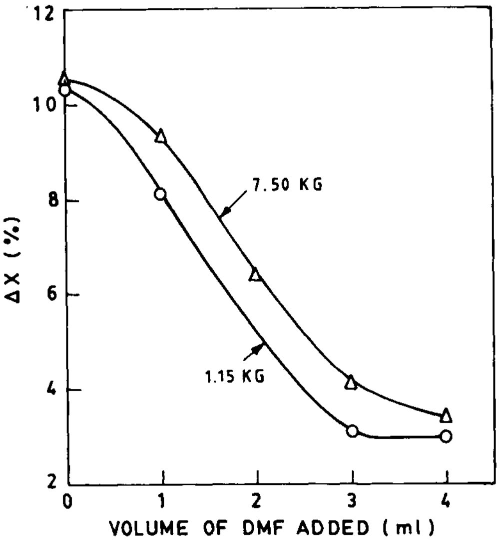

Figure 2 The influence of MF on AN polymerization with dilution of the reaction mixture; 2 ml AN, 1% (w/w) AIBN, 60°C, 45 min

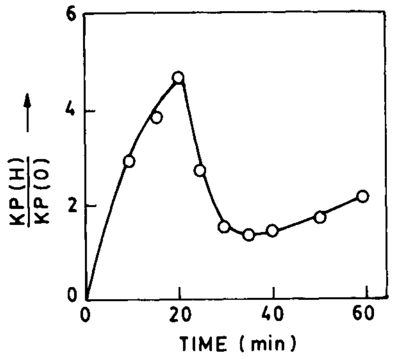

Figure 3 The influence of MF on the kinetic parameter (KP) of bulk polymerization of AN; based on *Table 1* of Ref. [6]

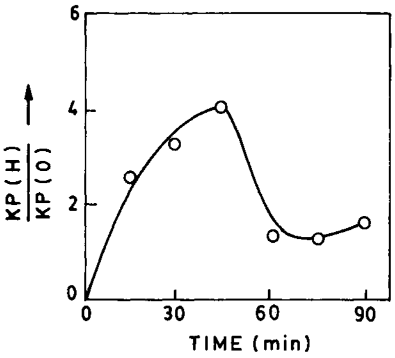

Figure 4 The influence of MF on the kinetic parameter (KP) of solution polymerization of AN; based on *Table 3*

Although the effect of the magnetic field may be attributed to the occlusion phenomenon arising due to the heterogeneous polymerization of AN, the polarity of the monomer under test is also responsible. It has already been observed that in the copolymerization of styrene and acrylonitrile under the magnetic field the monomer reactivity of AN is higher than that of S and the resulting copolymer SAN is rich in the AN content[8]. This has been discussed elsewhere[14].

Kinetic parameter (k_p^2/k_t)

The kinetic parameter (KP) may be calculated from the rate of polymerization. The relative kinetic parameter in the presence and absence of MF may be obtained as

$$\frac{KP(\mathrm{H})}{KP(\mathrm{O})}=\frac{R_p^2(\mathrm{H})}{R_p^2(\mathrm{O})} \qquad (1)$$

For the bulk polymerization of AN the ratio of KP is plotted against time (*Figure 3*, based on the result of *Table 1* of Ref. [6]). The nature of this curve indicates that the MF effect increases with time, attains a maximum and then decreases to a limiting value. A similar trend is also observed for the solution polymerization of AN (*Figure 4*). However, the

Table 4 Influence of MF on the kinetic parameter

Polymer code[a]	MF (kg)	$\bar{M}_n$[b]	$\bar{X}_n$	$KP(H)/KP(O)$
$14a_1$	0	609 500	11 500	1.426
$14b_1$	1.15	727 800	13 732	
$41a_3$	0	173 600	3275	1.109
$41b_3$	1.15	182 800	3449	

[a] Polymer code 14 means PAN polymer obtained by bulk polymerization of AN (as in *Table 1* of Ref. [6]) for 30 min. Polymer code 41 means PAN polymer obtained by solution polymerization of AN (as in *Table 3*) for 60 min

[b] Determined by GPC measurement

Table 5 Influence of MF on the MW and polydispersity of PAN prepared in bulk and solution polymerization

Polymer code[a]	MF (kg)	$\bar{M}_w \times 10^5$	$\bar{M}_n \times 10^5$	$\bar{M}_w/\bar{M}_n$ (PDI)	$\phi_{\bar{M}_n}$[b] (%)	ϕ_{PDI}[b] (%)
$14a_1$	0	40.00	6.09	6.57	+ 19.4	− 42.8
$14b_1$	1.15	27.36	7.27	3.76		
$41a_3$	0	3.04	1.73	1.76	+ 5.8	− 3.9
$41b_3$	1.15	3.09	1.83	1.69		

[a] As in *Table 4*

[b] Calculated using equations (3) and (4)

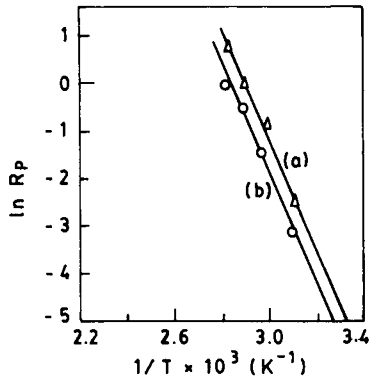

Figure 5 Arrhenius plots for the polymerizations of AN in (a) the presence and (b) absence of MF (1.15 kg); 2 ml AN, 0.1% (w/w) AIBN, 8 ml H_2O, 45 min

time to attain the maximum is longer in the case of polymerization of AN in a small (2 ml) amount of DMF than in the neat polymerization (*Figures 3* and *4*). This trend may be explained due to the precipitation of macro-radicals as it grows. However, KP(H)/KP(O) is always greater than unity, indicating the MF effect on KP.

The kinetic parameter (KP) can also be calculated based on the degree of polymerization (X_n). The relative kinetic parameter in the presence and absence of MF, i.e. KP(H)/KP(O) may be obtained as follows:

$$\frac{KP(\mathrm{H})}{KP(\mathrm{O})} = \frac{\bar{X}_n^z(H)}{\bar{X}_n^z(0)} \tag{2}$$

The MF effect on the kinetic parameter as determined by the number average molecular weight is shown in *Table 4*. The values of KP(H)/KP(O) obtained from equation (2) are quite close to those values obtained from equation (1).

Activation energy

Arrhenius plots of ln R_p *versus* $1/T$ of the bulk polymerization of AN are shown in *Figure 5*. The overall activation energies for the polymerization of AN with and without MF were determined to be 22.92 and 23.33 kCal - mol^{-1}, respectively, indicating that the MF has little influence on the activation energy. Simionescu *et al.*[5], however, observed that the MF reduces the activation energy for the thermal polymerization of MMA by BPO. On the other hand, no effect of the MF on the activation energy was reported by Ouchi *et al.*[4] for the thermal polymerization of MMA in the hydrophobic area of poly (2-hydroxyethyl methacrylate) (PHEMA) initiated by PHEMA itself. Similarly, Hanabusa *et al.*[15] observed no effect of the MF on the activation energy for the polymerization of γ-benzyl-L-glutamate N-carboxy anhydride. Interestingly, the strongest external magnetic field of 100 KG can induce at most energy changes of 0.03 kCal mol^{-1}, even in paramagnetic molecules[16]. It is therefore more likely that MF cannot reduce the activation energy of polymerization. Since it is observed that the rate of AN polymerization increases in presence of MF, it is suggested that the MF influences the activation entropy and not the activation energy for polymerization.

Molecular weight and molecular weight distribution

The variation of viscosity average molecular weight (MW) of PAN with MF was discussed in an earlier report. The MW increases with the MF strength[6]. The molecular weight distribution (MWD) of PAN polymer is determined by GPC measurements. The MWD of the PAN prepared under MF is narrower than the PAN prepared without MF. The polydispersity index (PDI), i.e. $\bar{M}_w/\bar{M}_n$, of PAN is shown in *Table 5*. The increase of MW by the application of MF has also been reported in photopolymerization of styrene[2,3]. The MWD in these cases also became narrower by the application of MF[2,3]. The MW has additionally been reported to increase under MF in the case of MMA polymerization initiated by the thermal decomposition of benzoyl peroxide[5].

The fluctuation of the lifetime of propagating AN macroradicals is smaller because of the orientation of their spin moments under MF and hence the MWD is much narrower. Again, the $\bar{M}_n$ of PAN prepared under MF is higher because the diffusion controlled termination by coupling is hindered due to the restricted translational movement of the propagating macroradicals.

Now let us define $\phi_{\bar{M}_n}$ and ϕ_{PDI} as

$$\phi_{\bar{M}_n} = \frac{\bar{M}_n(\mathrm{H}) - \bar{M}_n(\mathrm{O})}{\bar{M}_n(\mathrm{O})} \times 100\% \tag{3}$$

and

$$\phi_{PDI} = \frac{\mathrm{PDI(H) - PDI(O)}}{\mathrm{PDI(O)}} \times 100\% \tag{4}$$

where (H) and (O) indicate the presence and absence of MF. Both the values of $\phi_{\bar{M}_n}$ and ϕ_{PDI} are higher in the case of bulk polymerization than in the solution polymerization (*Table 5*). This also supports the occlusion theory for the MF effect. In case of solution polymerization the PAN produced is soluble in the medium and hence the MF effect due to occlusion is relatively lower than that in case of bulk polymerization of AN.

Tacticity

The tacticity of the PAN polymer samples were determined by $^{13}C-NMR$ (400 MHz) analysis. The syndiotactic content increased by about 5% by the application of MF of 1.15 kg[6] However, it increases about

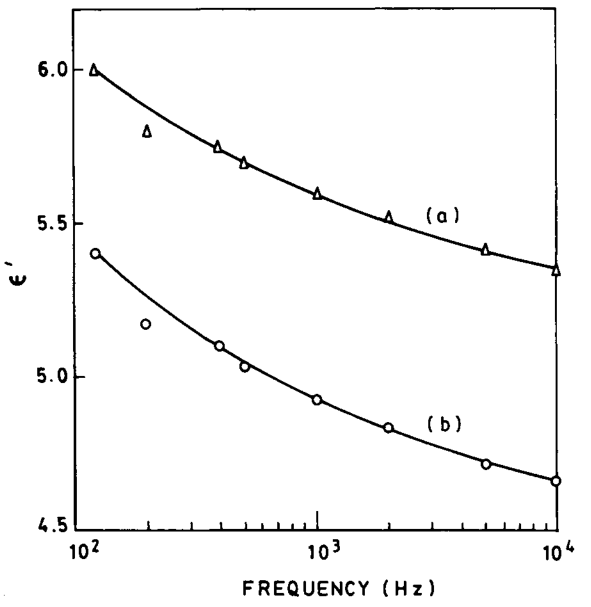

Figure 6 Variation of dielectric permittivity (ε') with frequency at room temperature of PAN samples prepared (a) with, and (b) without MF (1.15 kg)

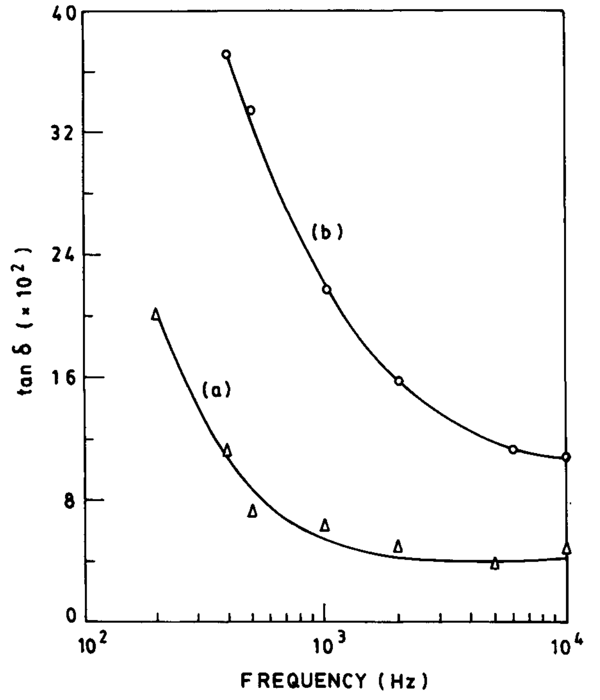

Figure 7 Variation of dielectric loss (tan δ) with frequency of PAN samples prepared (a) with, and (b) without MF (1.15 kg)

6–7% under a MF of 5.90 kg. However, the isotactic content of the polymer remains unaffected.

Density

The density of the powder PAN prepared with and without MF are 1.29 and 1.11 g cm^{-3}, respectively, against the reported value of 1.17–1.18 g cm^{-3} for PAN flake samples[17]. Thus, by the application of MF the density of PAN increases, perhaps due to the degree of regularity of the structural units, the degree of orientation of the macrochains and crystallinity.

Dielectric properties

The dielectric constant (relative permittivity) and dielectric loss (tan δ) of pellet samples of PAN prepared with and without MF were measured at room temperature within the frequency range of 10^2–10^4 Hz. The dielectric constant and also dielectric loss values of the PAN samples are on a par with the reported values[17]. The variation of dielectric constant (ε') and loss factor (tan δ) with frequency is shown in *Figures 6* and *7*, respectively. The dielectric constant is higher, whereas the loss is lower for the PAN sample prepared under MF. This dielectric behaviour of PAN samples can be explained on the basis of their structures. It has been observed that the density of PAN prepared under MF is higher, resulting in a greater number of polar cyanide groups per unit volume sample. The PAN prepared under MF is, therefore, a better dielectric material than that normally obtained.

Crystallinity

PAN has been considered as a polymer which exhibits at least only two-dimensional (lateral) order. Sharp reflections are obtained only on the equator of fibre patterns[18]. The X-ray diffractographs of powder PAN prepared with and without MF are shown in *Figure 8*. Two peaks appear at around 2θ values of 16.8 and 29.5°. From the diffractographs the particle size is calculated using the following two equations.

$$t_{hkl}^{1/2} = \frac{K\lambda}{\beta_{1/2}\cos\theta} = \frac{0.9 \times 1.542}{\beta_{1/2}\cos\theta}\,\text{Å} \qquad (5)$$

and

$$t_{hkl}^{i} = \frac{K\lambda}{\beta_i\cos\theta} = \frac{1 \times 1.542}{\beta_i\cos\theta}\,\text{Å} \qquad (6)$$

where θ is the peak position, β_i is the area of the peak/maximum intensity in radians and $\beta_{1/2}$ is the width of a peak at half maxima.

The '*d*' spacings have been calculated using the following equation:

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \qquad (7)$$

Table 6 Results of XRD analysis of PAN prepared under MF

PAN[a]	MF (kg)	x_c (%)	Peak I (*hkl* = 400) 2θ (°)	*d* (Å)	$t_{400}^{1/2}$	t_{400}^{i}	Peak II (*hkl* = 620) 2θ (°)	*d* (Å)	$t_{400}^{1/2}$	t_{400}^{i}
$14a_1$	0	53	16.7	5.31	69.4	39.3	29.5	3.03	28.3	21.3
$14b_1$	1.15	58	16.8	5.28	61.8	33.6	29.4	3.04	30.4	22.5
$14c_1$	5.90	69	16.8	5.28	59.2	31.4	29.4	3.04	31.6	25.2
$14a_7$	0	55	16.8	5.28	64.3	45.1	29.5	3.03	32.9	23.8
$14b_7$	1.15	61	16.5	5.32	61.8	34.3	29.3	3.05	34.3	27.1

[a] PAN ($14a_1$, $14b_1$, $14c_1$) and PAN ($14a_7$, $14b_7$) obtained for 30 and 50 min, respectively, in the same polymerization condition as in *Table 1* of Ref. [6]

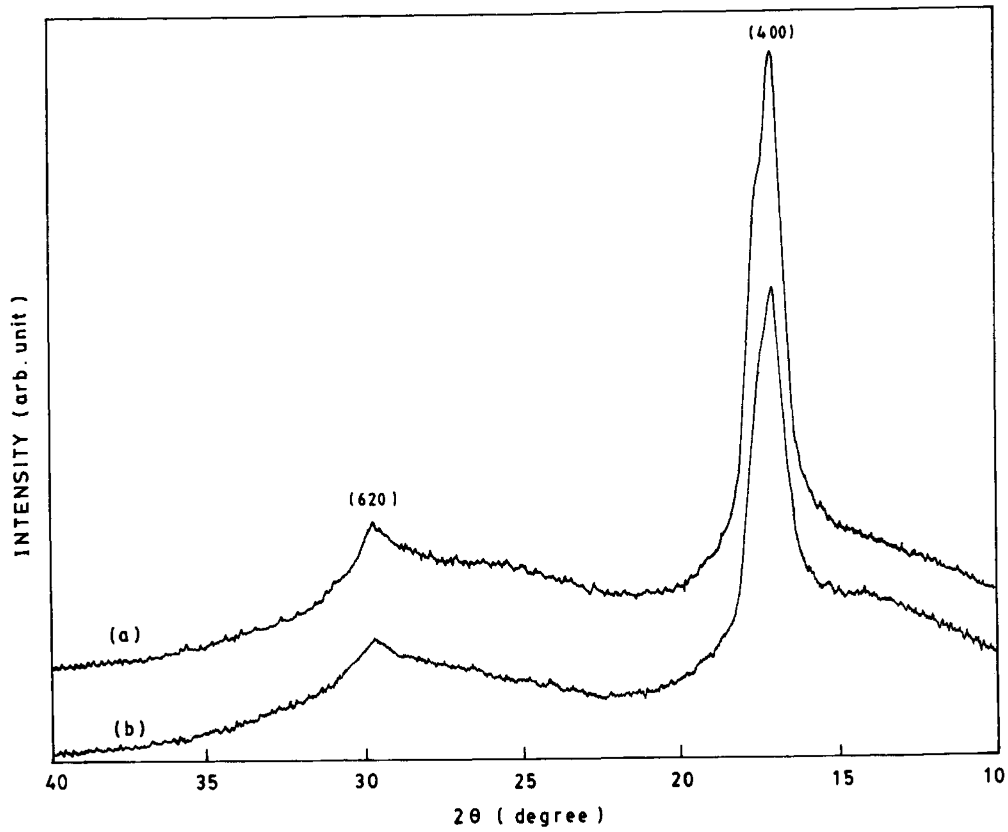

Figure 8 X-ray diffractographs ($CuK_{\alpha,\lambda}$ = 1.5418 Å, rate = 1.2° min^{-1}) of PAN prepared (a) with, and (b) without MF (5.90 kg)

The percentage crystallinity was calculated by the relation

$$x_c = \frac{A_c}{A_c + A_\alpha} \times 100\% \qquad (8)$$

where A_c and A_α are the areas under the crystalline and amorphous portion of the X-ray diffractographs.

Table 6 lists the X-ray data with particle size and percentage crystallinity. The '*d*' values agree well with the reported experimental values for the PAN samples which are 5.31 and 3.03 Å corresponding to *hkl* 400 and 620, respectively[19].

However, the particle size in the 400 plane decreases whereas it increases along the 620 plane when PAN is prepared under MF. The crystallinity is marginally higher for PAN prepared under MF. This may be due to the orientation of the highly polar cyanide groups and polar PAN chains in the presence of MF. This observation is also supported by the density measurements.

CONCLUSION

The influence of magnetic field (MF) is observed on the thermal radical bulk polymerization of acrylonitrile (AN) and not on the polymerization of styrene and MMA. This is due to the heterogeneous nature of AN polymerization, where the polymer precipitates out from its monomer. As a result, the diffusion controlled termination by combination is hindered and is pronounced in the presence of MF due to restricted translation movement of the growing macroradicals. The MF effect is lower in the case of solution polymerization of AN. Moreover, it decreases with dilution. The overall activation energy is barely influenced by the MF. However, the MF helps reduce the activation entropy of polymerization. Therefore the rate, polymer yield and also the molecular weight of the polymer increase in the presence of MF. The molecular weight distribution of the PAN polymer prepared under MF is narrower because the fluctuation of the lifetime of the propagating radicals is lower in the presence of MF.

The syndiotactic content of such polymer is higher and the isotactic content remains the same compared to that obtained without application of MF. Therefore, the polymer obtained under MF is more stereoregular and more crystalline. The density of PAN polymer prepared under MF is also higher. The PAN prepared under MF possesses better dielectric charateristics.

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