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Neeta Srivastava^a; J. S. P. Rai^a

^a Department of Plastic Technology Harcourt, Butler Technological Institute, Kanpur, India

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RADICAL COPOLYMERIZATION OF ACRYLONITRILE WITH METHYL ACRYLATE COMPLEXED BY ZINC CHLORIDE

NEETA SRIVASTAVA and J. S. P. RAI*

Department of Plastic Technology
Harcourt Butler Technological Institute
Kanpur 208002, India

ABSTRACT

The kinetics of the radical copolymerization of acrylonitrile with methyl acrylate complexed by zinc chloride (ZnCl_2) in dimethylformamide (DMF) was investigated at 60, 65, and 70°C. The kinetic data revealed that R_p was an inverse function of ZnCl_2 concentration and directly related to monomers concentration. The increase in the activation energy from 11.85 to 19.25 $\text{kJ}\cdot\text{mol}^{-1}$ and the decrease in the value of the ratio of the propagation to termination rate constants (k_p^2/k_t) from 0.08 to 0.06 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ on the addition of ZnCl_2 indicated its retarding effect. The chain transfer constant of DMF for the system was 16.25×10^{-4} , accordingly the degree of polymerization decreased. The structure and composition of the copolymers determined by $^1\text{H-NMR}$ and elemental analysis was found to be alternating. The nonideal behavior of the glass transition temperatures determined by DSC also favors the alternation of monomer units in the copolymer. The reaction proceeds via a cross-propagation mechanism.

INTRODUCTION

Acrylonitrile (AN) copolymerizes readily with methyl acrylate (MA) but yields a random copolymer. The homopolymer fails in many applications due to its high melting point, its high melt viscosity, and its poor thermal stability. The copolymer-

ization of acrylonitrile with olefins and other acrylic monomers as initiated radically [1-3] or by lithium alkoxide [4, 5] or by complexes of ethyl aluminum dichloride [6] has been investigated by several workers. The effect of polar and nonpolar solvents [1, 2] on the copolymerization tendency of these monomers has also been studied. Radiation-induced copolymers of AN and MA with a composition of 0.50 ± 0.20 and a glass transition temperature below 80°C were recently synthesized by Shashidhar et al. [7]. We prepared the copolymers of methyl, ethyl and *n*-butyl acrylates with styrene [8-11] by complexing the acrylate monomer with ZnCl_2 . The structures of the copolymers were of the alternating type with a composition of 0.50 ± 0.20 and the product of reactivity ratio approached zero. In this paper we investigate the effect of ZnCl_2 on the kinetics, mechanism, structure, and composition of copolymers of AN and MA.

EXPERIMENTAL

Purification of AN (SDs) monomers was done by standard methods [8]. Dimethylformamide (DMF) (SDs) and extrapure petroleum ether (Poly pharma) were used without further purification. The radical initiator α, α' -azobisisobutyronitrile (AIBN) (mp 102°C) was recrystallized twice from ethanol. The anhydrous ZnCl_2 (Ranbaxy) was used as received.

The synthesis, composition, and characterization of the complex of ZnCl_2 with MA were reported in our earlier publications [8, 11]. The polymerization reactions were carried out at 60, 65, and 70°C dilatometrically [12] for 110 minutes under a nitrogen atmosphere. The progress of the reaction was monitored with a cathetometer by the meniscus movement (unit volume per unit time). The copolymer formed was precipitated from the reaction mixture with extrapure petroleum ether (bp $60\text{--}80^\circ\text{C}$) and dried to constant weight. The weight of the copolymer was used to calculate the percentage conversion (P_c). The rate of polymerization (R_p) was determined from the slope of a plot of P_c vs time.

The intrinsic viscosity $[\eta]$ of the copolymers, expressed in $\text{dL}\cdot\text{g}^{-1}$, was measured in DMF solution at $20 \pm 1^\circ\text{C}$ by using an Ubbelohde viscometer. The viscosity-average molecular weight (\overline{M}_v) was calculated by using the Mark-Houwink equation.

$$[\eta] = KM^\alpha$$

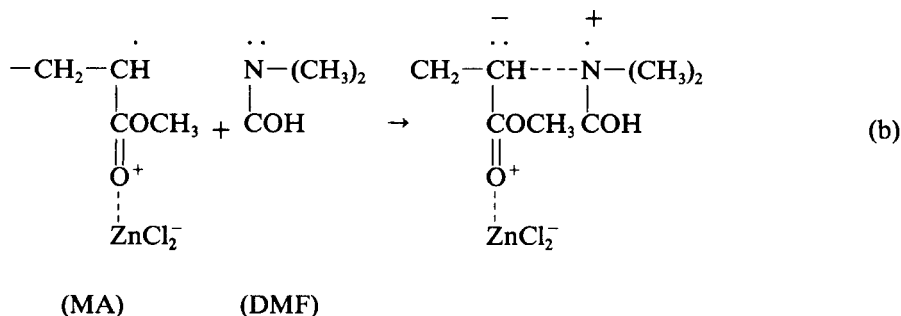
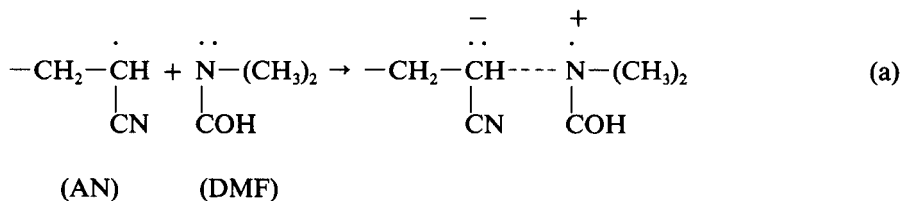
where the values [13] of K and α are 17.9×10^{-5} and 0.79, respectively. Further, the degree of polymerization (\overline{P}_n) was calculated from \overline{M}_v . The structure of the copolymers was established through the spectral records of an EM-390, 90 MHz, NMR spectrometer using CDCl_3 as the solvent and tetramethylsilane as the internal reference. The composition of the copolymers was determined by the NMR spectrum as well as by the percentage of elements as analyzed by a Heraeus CH N-O-Rapid Elemental Analyser. A Du Pont 910 Differential Scanning Calorimeter (DSC) with a 99XR Thermal Analyser was used to determine the glass transition temperature of the copolymers.

RESULTS AND DISCUSSION

The kinetics, characterization, and mechanism of the radically initiated copolymerization reaction of AN and MA were investigated by varying the concentration of ZnCl_2 , monomers, and temperature.

Kinetics

Effect of $[\text{ZnCl}_2]$. Table 1 shows the variation in percentage conversion (P_c), rate of polymerization (R_p), intrinsic viscosity (η) and degree of polymerization (\bar{P}_n) with an increase in $[\text{ZnCl}_2]$ from 4.95×10^{-2} to $14.90 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ at constant concentrations of initiator and monomers. It is apparent from the table that R_p and \bar{P}_n decrease with an increase in $[\text{ZnCl}_2]$. The retarding effect of ZnCl_2 on R_p is evident from Fig. 1 ($\log R_p$ vs $\log [\text{ZnCl}_2]$) which has a negative slope with an exponent value 0.42. The decrease in \bar{P}_n with a decrease in R_p , as is evident from Table 1, is contrary to that usually observed in free radical polymerizations. However, this is possible when termination occurs by chain transfer reactions. The present polymerization reaction was carried out in the solvent DMF, which might have acted as chain transfer agent [14]. The chain transfer constant of DMF as obtained from the slope of the plot of $1/\bar{P}_n - k_t/k_p^2 \cdot R_p/[M]^2$ vs $[\text{DMF}]/[M]$ (Fig. 2) was 16.25×10^{-4} , which was higher than that reported in the literature [15]. The chain transfer activity of DMF in the presence of the ZnCl_2 complexed acrylate monomer is probably due to the stabilization of the transition state in which partial charge transfer occurs between both the acceptor monomers and DMF, as shown below:



Effect of $[\text{MA}]$. The effect of $[\text{MA}]$ on R_p was studied by varying its concentration from 8.49×10^{-3} to $25.49 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and keeping the concentration

TABLE 1. Effect of $[\text{ZnCl}_2]$ on the Copolymerization of Acrylonitrile with Methyl Acrylate^a

$[\text{ZnCl}_2] \times 10^2$ $\text{mol} \cdot \text{L}^{-1}$	$P_c, \%$	$R_p \times 10^3$ $\text{mol} \cdot \text{L}^{-1} \cdot \text{S}^{-1}$	$\eta, \text{dL} \cdot \text{g}^{-1}$	$\bar{P}_n \times 10^{-2}$
4.95	60.00	8.33	1.62	7.3
5.89	58.00	8.04	1.41	6.2
7.08	47.00	7.33	1.32	5.7
9.91	46.05	6.67	1.10	4.5
11.48	40.50	5.96	0.98	3.9
14.90	28.50	5.21	0.73	2.7

^a $[\text{AIBN}] = 4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

$[\text{AN}] = 2.35 \text{ mol} \cdot \text{L}^{-1}$.

$[\text{MA}] = 16.99 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

$T = 70^\circ\text{C}$.

$t = 110 \text{ minutes}$.

$[\text{DMF}] = 7.5 \pm 0.3 \text{ mol} \cdot \text{L}^{-1}$.

of AIBN, ZnCl_2 , AN, and DMF constant. A logarithmic plot of R_p vs $[\text{MA}]$ (Fig. 3) is linear with a slope of 2.3 for a MA concentration from 8.49×10^{-3} to $16.99 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, indicating an increase in R_p with an $[\text{MA}]$ increase. The initial increase in R_p seems to be due to a lowering of steric hindrance caused by an increase in the concentration of uncomplexed MA monomer, a less stable MA

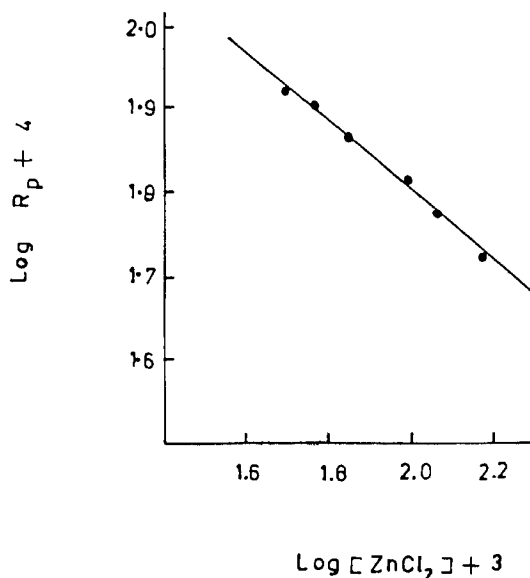


FIG. 1. Relationship between $\log R_p$ and $\log [\text{ZnCl}_2]$: $[\text{AIBN}] = 4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $[\text{DMF}] = 7.5 \pm 0.3 \text{ mol} \cdot \text{L}^{-1}$; $[\text{AN}] = 2.35 \text{ mol} \cdot \text{L}^{-1}$; $[\text{MA}] = 16.99 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

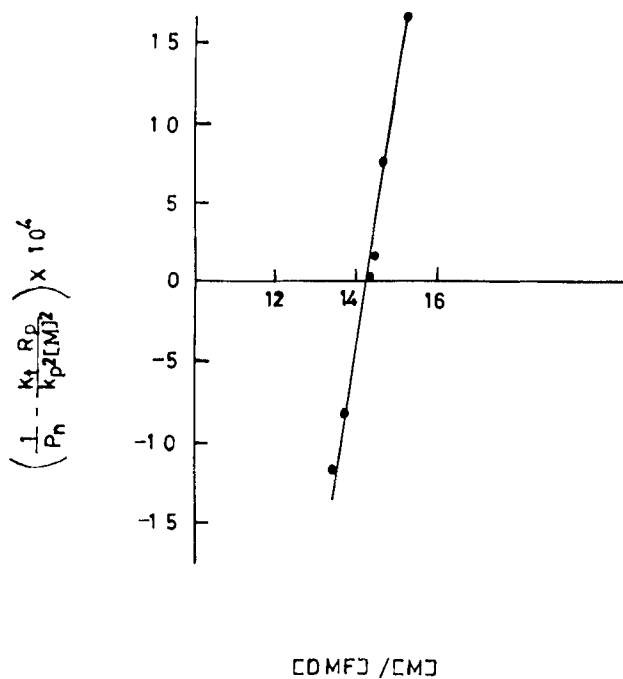


FIG. 2. Relationship between $(1/\bar{P}_n) - (k_t R_p/k_p^2 [M]^2)$ and $[DMF]/[M]$: $[AIBN] = 4.69 \times 10^{-3}$; $[ZnCl_2] = 9.91 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$; $[AN] = 2.35 \text{ mol}\cdot\text{L}^{-1}$; $[MA] = 16.99 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

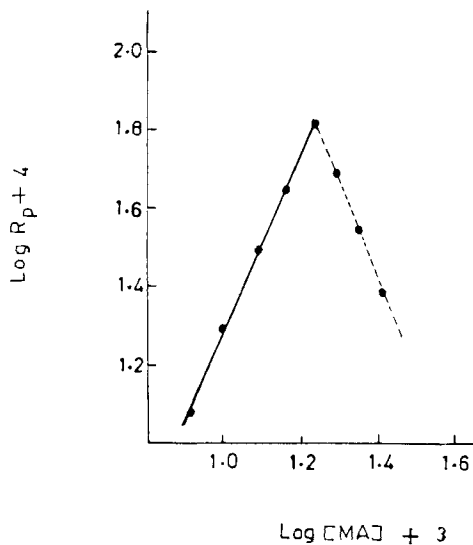


FIG. 3. Dependence of $\log R_p$ on $\log [MA]$: $[AIBN] = 4.69 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $[DMF] = 7.5 \pm 0.3 \text{ mol}\cdot\text{L}^{-1}$; $[AN] = 2.35 \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

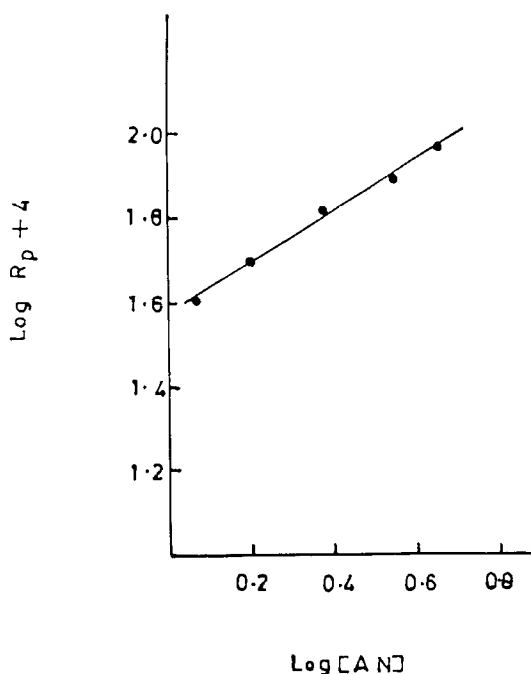


FIG. 4. Relationship of $\log R_p$ and $\log [AN]$: $[AIBN] = 4.69 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $[DMF] = 7.5 \pm 0.3 \text{ mol}\cdot\text{L}^{-1}$; $[MA] = 16.99 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

radical, and a lowering of the polarity difference between the two monomers. It is also apparent from the figure that for a further increase in $[MA]$ from 16.99×10^{-3} to $25.49 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ the slope of the plot is negative with an exponent value of 2.0, indicating that R_p decreases with an increase of $[MA]$, probably due to termination of primary radicals.

Effect of $[AN]$. The effect of AN concentration on R_p was studied while the other constituents in the reaction mixture were kept constant. Figure 4 is a logarithmic plot of $\log R_p$ vs $\log [AN]$. R_p was found to increase with an increase in $[AN]$ from 1.18 to $4.47 \text{ mol}\cdot\text{L}^{-1}$. The reaction order as determined from the slope of the plot was 0.6. The increase in R_p was due to an increase in the AN radical, which is comparatively unstable and more reactive.

Effect of Temperature. R_p was determined at 60, 65, and 70°C in the absence and presence of ZnCl_2 . The activation energies (ΔE) determined from the slope of the Arrhenius plot, $\log R_p$ vs $1/T$, in the absence (Fig. 5, Curve a) and presence (Fig. 5, Curve b) of the ZnCl_2 were 11.85 and $19.25 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. An increase in ΔE upon the addition of $9.91 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ ZnCl_2 indicated that ZnCl_2 retards the polymerization reaction.

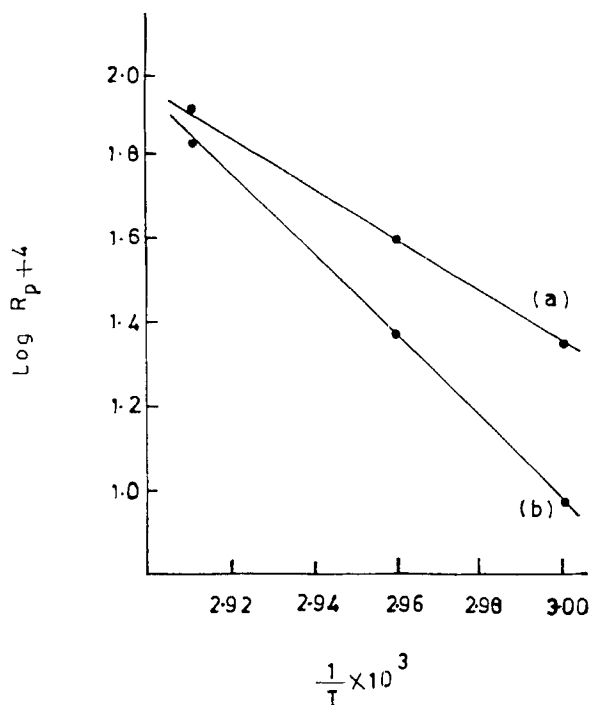


FIG. 5. Dependence between $\log R_p$ and $1/T$ in the absence (a) and presence (b) of the ZnCl_2 :MA complex: $[\text{AIBN}] = 4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $[\text{ZnCl}_2] = 9.91 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$; $[\text{DMF}] = 7.5 \pm 0.3 \text{ mol} \cdot \text{L}^{-1}$; $[\text{AN}] = 2.35 \text{ mol} \cdot \text{L}^{-1}$; $[\text{MA}] = 16.99 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

The retarding effect of the complex may be due to any one of the following reasons:

1. Rate of initiation (R_i) decreases.
2. Rate of propagation (R_p) decreases.
3. Rate of termination (R_t) increases.

The wavelength of maximum absorption (348 nm) of UV spectrum did not show an appreciable change when ZnCl_2 was added to the AIBN solution, indicating that ZnCl_2 does not effect the decomposition rate of AIBN, and therefore R_i is unaffected.

A logarithmic plot of R_p/R_{p_0} vs η/η_0 (where R_p and R_{p_0} are the rates of polymerization in the presence and absence of the complex, respectively, and η and η_0 are the corresponding intrinsic viscosity values) is shown in Fig. 6. The nonlinear relationship between $\log R_p/R_{p_0}$ and $\log \eta/\eta_0$ indicates that R_i is affected [16]. The influence on R_i is due to the chain transfer activity of DMF, as described earlier.

A plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ in the absence and presence of ZnCl_2 is shown in Fig. 7 (Curves a and b), respectively. The ratio of propagation to the termination rate constants k_p^2/k_t , as determined from the slope of the plot in the absence and presence of ZnCl_2 , was 0.08 and $0.06 \text{ L} \cdot \text{mol}^{-1} \cdot \text{S}^{-1}$, respectively. The decrease in

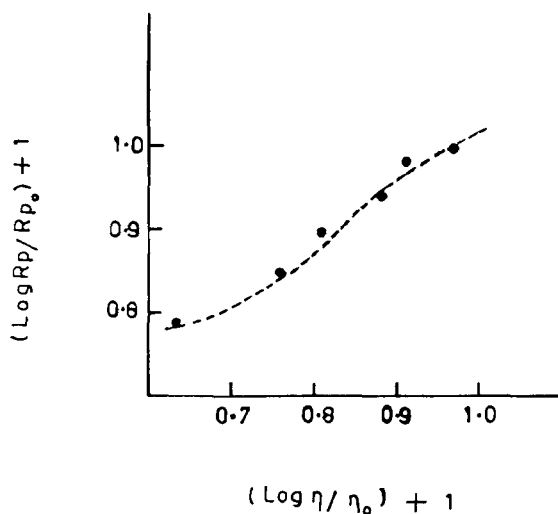


FIG. 6. Dependence between $\log R_p/R_{p_0}$ and $\log \eta/\eta_0$: $[\text{AIBN}] = 4.69 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $[\text{DMF}] = 7.5 \pm 0.3 \text{ mol}\cdot\text{L}^{-1}$; $[\text{AN}] = 2.35 \text{ mol}\cdot\text{L}^{-1}$; $[\text{MA}] = 16.99 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

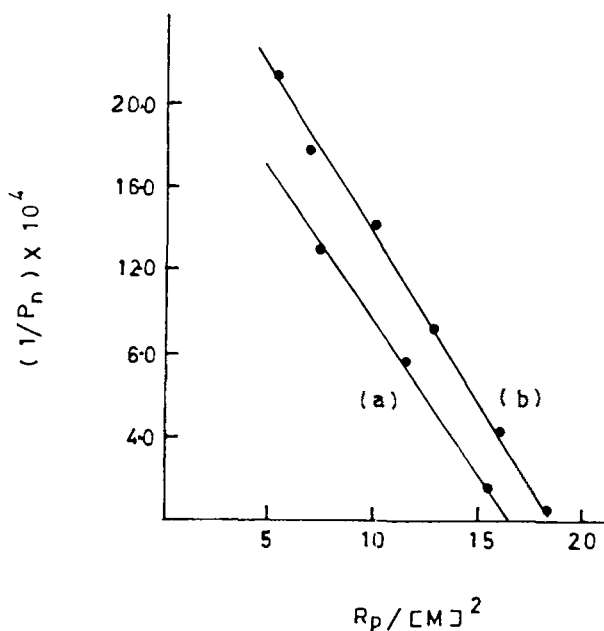


FIG. 7. Plot of $1/\bar{P}_n$ vs $R_p/[M]^2$ in the absence (a) and presence (b) of the ZnCl_2 :MA complex for the copolymerization of MA with styrene initiated by AIBN at 70°C : $[\text{ZnCl}_2] = 9.91 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$; $[\text{DMF}] = 7.5 \pm 0.3 \text{ mol}\cdot\text{L}^{-1}$; $[\text{AN}] = 2.35 \text{ mol}\cdot\text{L}^{-1}$; $[\text{MA}] = 16.99 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

k_p^2/k_t upon the addition of $ZnCl_2$ confirms that $ZnCl_2$ acts as a retarder. The retarding effect of $ZnCl_2$ is due to an increase in the polarity difference between the electron acceptor monomers by increasing the withdrawing tendency of MA monomers due to complexation with $ZnCl_2$. In our earlier investigation, $ZnCl_2$ behaved as an accelerator in the copolymerization of an electron donor monomer with a complexed acceptor monomer [8, 17].

Characterization

NMR Spectrum. Figure 8 shows the NMR spectrum of the AN-MA copolymer. The structural units in the AN-MA copolymer are as follows.

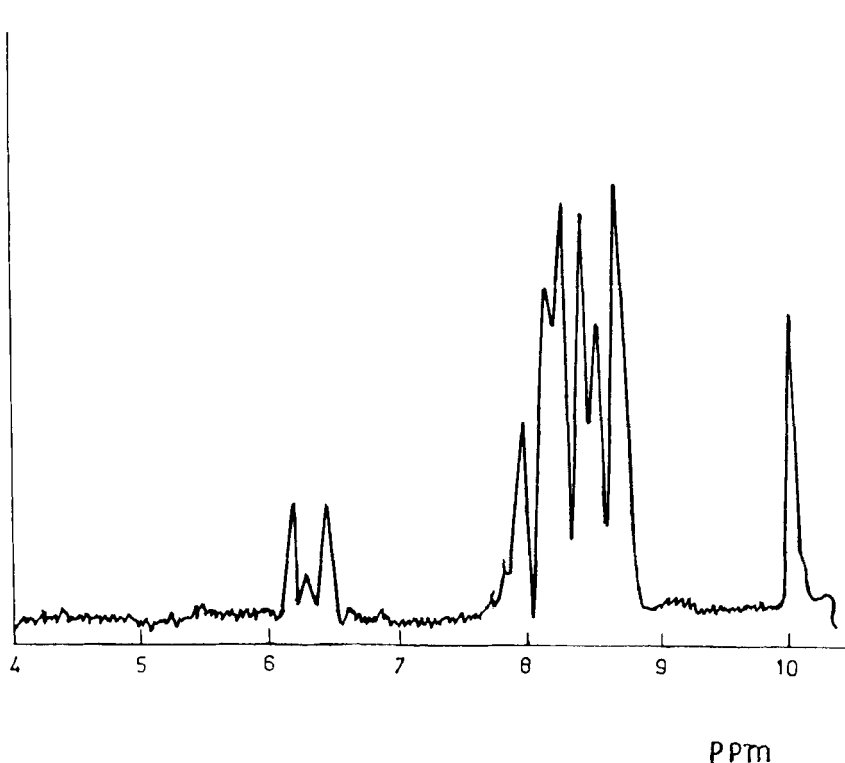
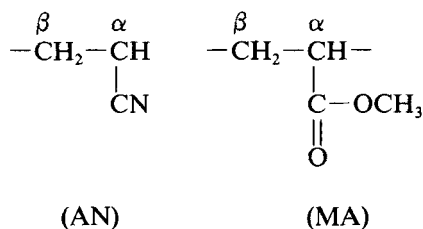


FIG. 8. NMR spectrum of AN-MA copolymer in the presence of the $ZnCl_2$:MA complex: $[AIBN] = 4.69 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $[ZnCl_2] = 9.91 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$; $[DMF] = 7.5 \pm 0.3 \text{ mol}\cdot\text{L}^{-1}$; $[AN] = 2.35 \text{ mol}\cdot\text{L}^{-1}$; $[MA] = 16.99 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

The chemical environments of methylene and methine protons of both monomers are similar, hence the peaks of these protons are identical and appear in the 7.8–8.8 τ region. The peaks of methoxy protons appeared as multiplets in the 6.2–6.7 τ region, indicating the formation of the copolymer, as a singlet peak which was observed when a homopolymer of MA was formed [18, 19]. The composition of the copolymers as determined by the ratio of methoxy protons to that of α, β -protons of the main chain and the reactivity ratios of the monomers calculated by the Fineman and Ross [20] method are shown in Table 2. The composition of the copolymers and the product of the reactivity ratio approaching zero predicts the alternating placement of AN and MA units in the copolymer.

Elemental Analysis. The observed values of the elements of the copolymer were C 60.1%, H 7.0%, N 10.02%, and O 22.88%. If the structure of the copolymer is assumed to be alternating, then its molecular formula should be $(C_7H_9O_2N)_n$ which corresponds to C 60.4%, H 6.47%, N 10.07%, and O 23.06%. The experimental and theoretically calculated values are in close proximity, and hence the copolymer structure can be considered to be an alternating one.

Glass Transition Temperature (T_g). The T_g s of the copolymers of different compositions obtained by variations of the amounts of the two monomers in the feed are shown in Table 2. It is apparent from the table that the T_g s of the copolymers decreased with a decrease in the molar fraction of acrylonitrile in the copolymer. A plot of the weight percent of AN vs the T_g of the copolymer is shown in Fig. 9. It is apparent from the figure that deviation of the observed values of T_g s from the line joining the T_g s of the two homopolymers explains its nonideal behavior, a characteristic of alternating copolymers [21].

TABLE 2. Composition and Glass Transition Temperature of MA-AN Copolymer in the Presence of $ZnCl_2^a$

Molar ratio in feed	Molar fraction in the copolymer		T_g , °K	r_1r_2
	MA	AN		
0.362	0.11	0.89	356	0.196
0.480	0.29	0.71	352	
0.723	0.32	0.68	330	
1.085	0.44	0.56	315	
1.439	0.33	0.67	318	

^a[AIBN] = $4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

$T = 70^\circ\text{C}$.

$t = 110$ minutes.

[DMF] = $7.5 \pm 0.3 \text{ mol} \cdot \text{L}^{-1}$.

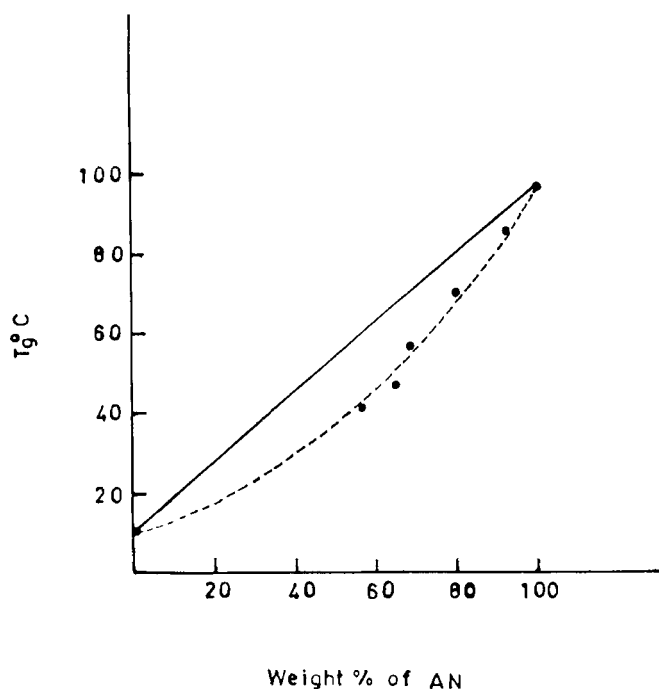


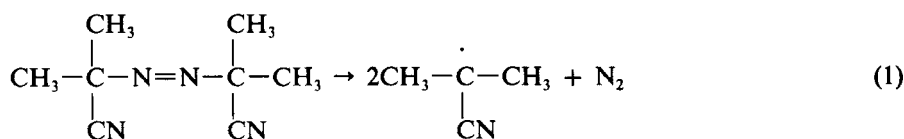
FIG. 9. Dependence of T_g on the weight percent of AN in the copolymers: $[AIBN] = 4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $[ZnCl_2] = 9.91 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$; $[DMF] = 7.5 \pm 0.3 \text{ mol} \cdot \text{L}^{-1}$.

Mechanism

The radical-initiated copolymerization of AN with complexed MA may proceed via any of three mechanisms: ternary molecular complex, cross-propagation, and radical complex.

According to our discussion in an earlier publication [11], the copolymerization of AN with MA does not proceed via a ternary molecular complex mechanism because the formation of an equimolar copolymer composition is not observed. The radical complex mechanism is not operative in the present system because a linear relationship is not obtained for $1/R_p$ vs $1/[ZnCl_2]$. However, the nonlinear relationship between $[AN]^2/R_p^2$ and $[AN]/[ZnCl_2]$ at a constant rate of initiation and constant $[AN]$ (Fig. 10) favors a cross-propagation mechanism which proceeds via three steps: initiation, propagation, and termination.

Initiation:



α, α' -Azobisisobutyronitrile

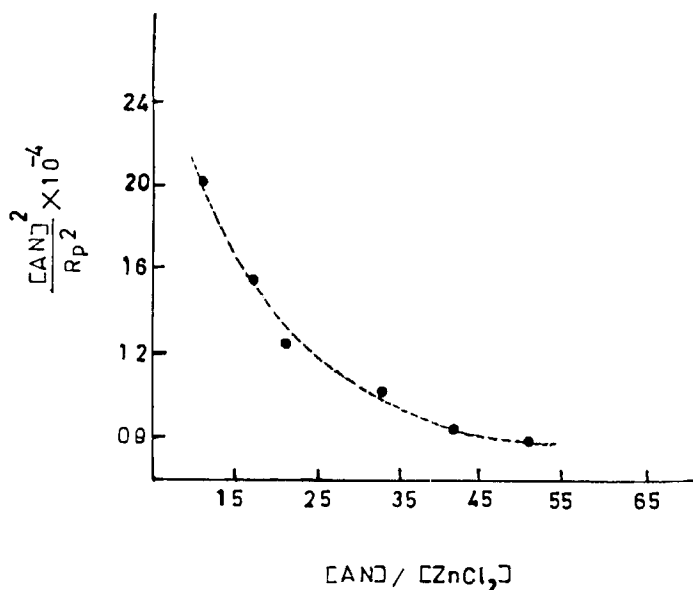
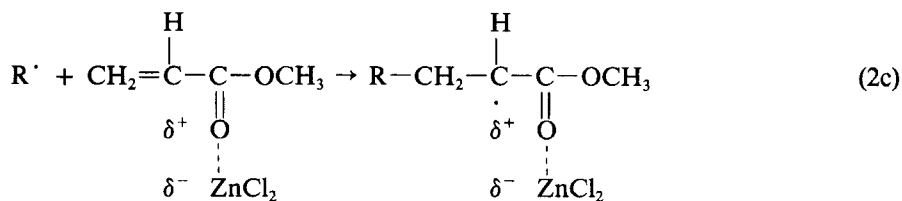
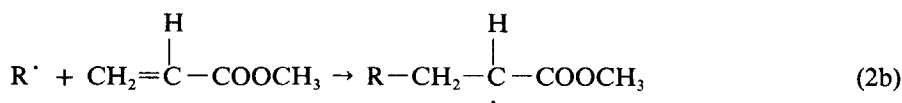
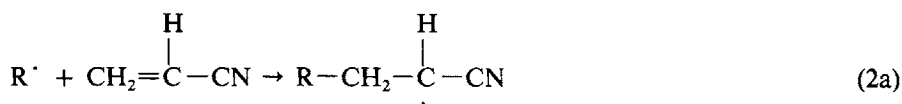


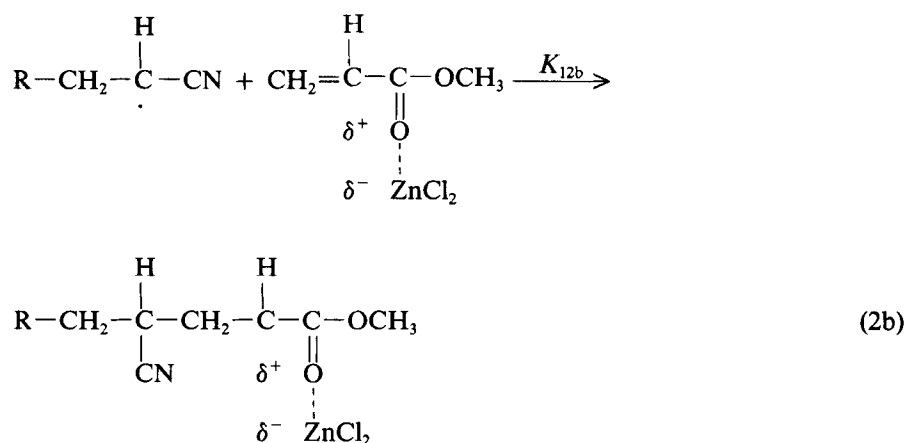
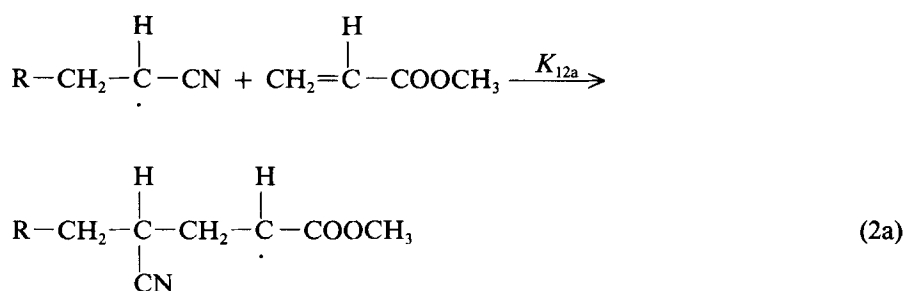
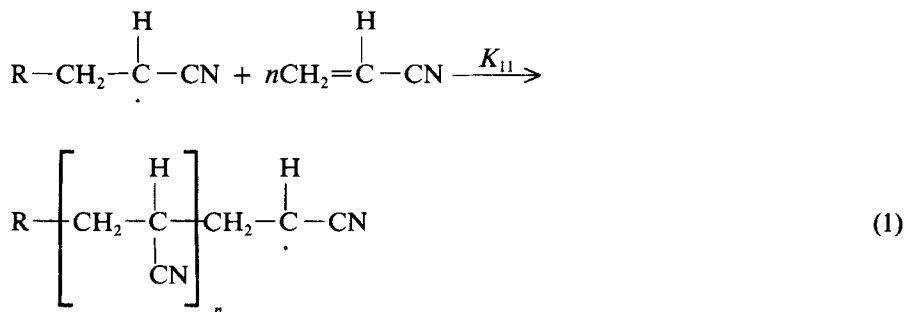
FIG. 10. Relationship between $([AN]/R_p)^2$ and $[AN]/[ZnCl_2]$; $[AIBN] = 4.69 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $[MA] = 16.00 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $T = 70^\circ\text{C}$; time = 110 minutes.

where $\left(\text{CH}_3 - \overset{\cdot}{\text{C}} - \text{CH}_3 \right) = \text{R} \cdot$
 $\quad \quad \quad |$
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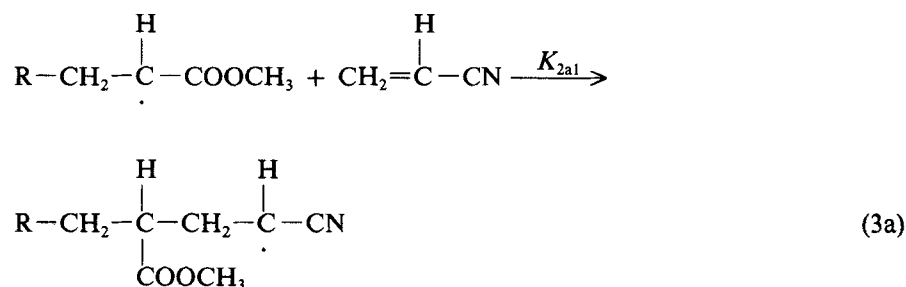


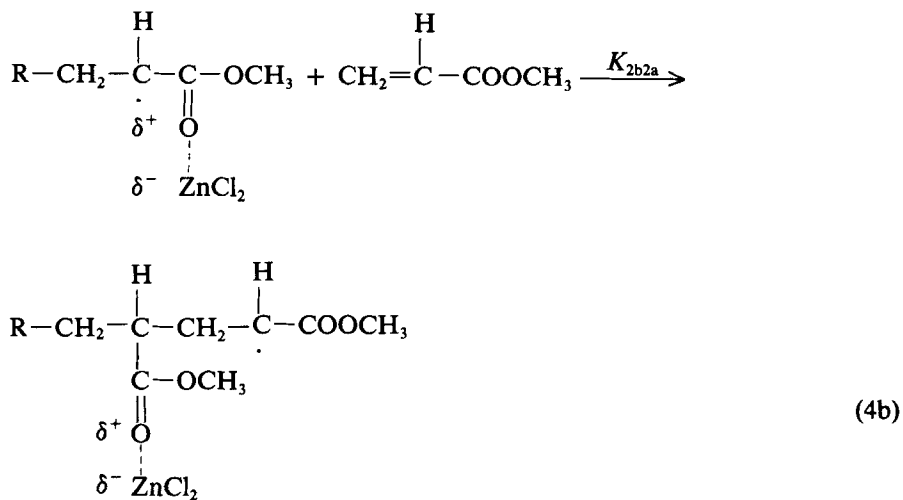
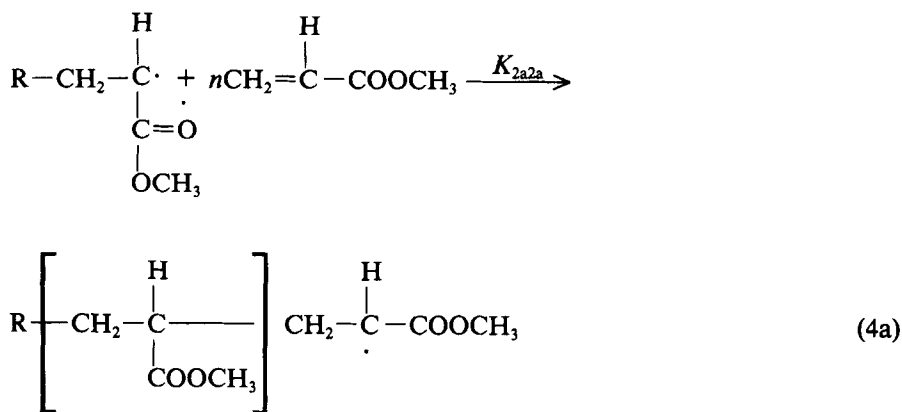
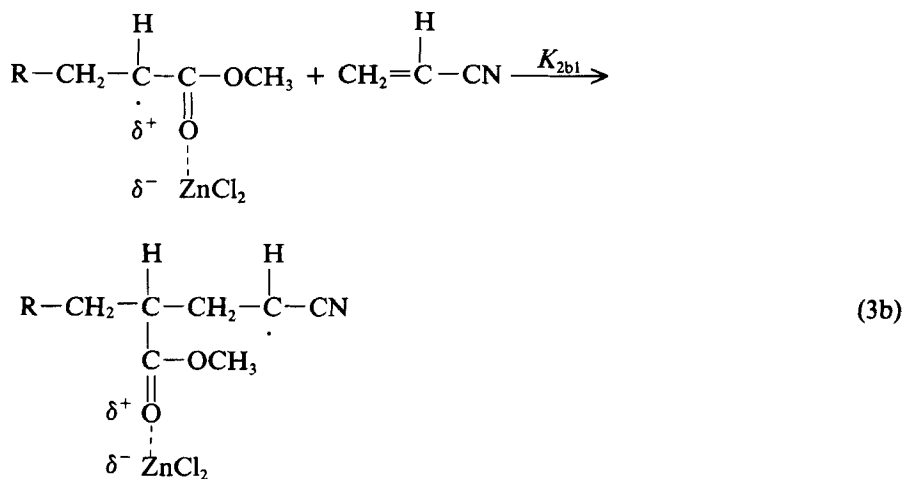
Binary complex

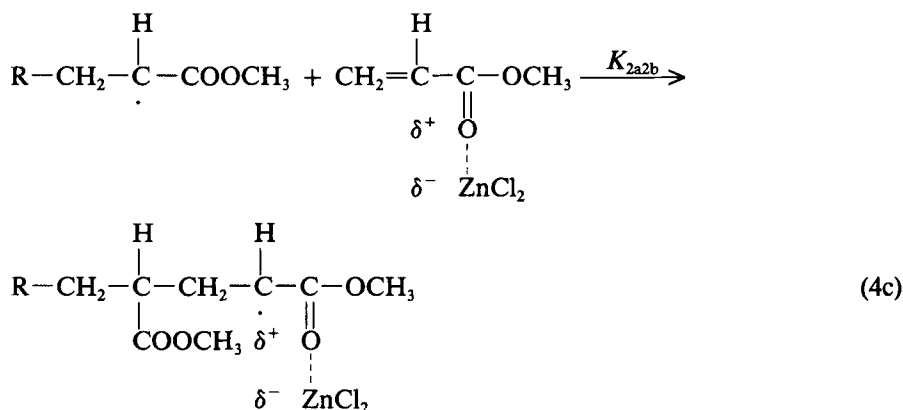
Propagation:



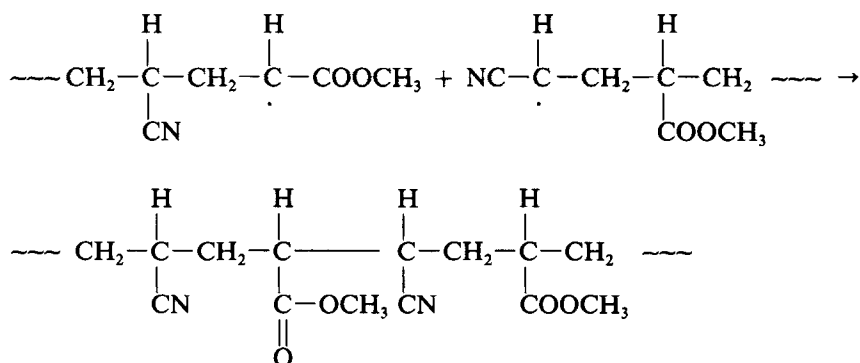
where 1 denotes AN and 2 is the MA monomer. The suffixes a and b are assigned for uncomplexed and complexed acrylate monomer, respectively.







Termination:



CONCLUSION

On the basis of the above discussion, we conclude that the ZnCl_2 complex retards the copolymerization of MA with AN by decreasing the rate of propagation, and the rate of termination is affected due to the chain transfer activity of DMF. The copolymer formed was alternating in nature, and the copolymerization reaction proceeds via a cross-propagation mechanism.

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