Journal of Macromolecular Science, Part A

Kinetics, Mechanism, and Rheological Properties of the Copolymers of 2-Ethylhexylacrylate and Styrene

Neeta Srivastava[a]; J. S. P. Rai[a]

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

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KINETICS, MECHANISM, AND RHEOLOGICAL PROPERTIES OF THE COPOLYMERS OF 2-ETHYLHEXYLACRYLATE AND STYRENE

NEETA SRIVASTAVA* and J. S. P. RAI

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

ABSTRACT

Copolymerization of 2-ethylhexylacrylate (2-EHA) and styrene (Sty) initiated by α,α'-azobisisobutyronitrile (AIBN) was carried out at 60, 65, and 70 $\pm$ 0.1°C in bulk in the presence of zinc chloride ($ZnCl_2$). R_p was a direct function of [$ZnCl_2$] and temperature. R_p showed an initial increase with [monomers] followed by a subsequent decrease after a maximum was reached. The accelerating effect of $ZnCl_2$ was predicted by a lowering of the activation energy from 42.78 to 34.38 kJ·mol^{-1} and an increase in the specific rate constants ratio (k_p^2/k_t) from 4.64 to 5.83 L·mol^{-1}·s^{-1}. The product of the reactivity ratios of the two monomers was 0.018 and 0.648, favoring alternating and random copolymer structures, respectively. The copolymerization reaction mechanism was a radical complex. Rheological investigations favored Bingham and Ostwald models for the flow behaviors of alternating and random copolymers, respectively.

INTRODUCTION

Copolymers of 2-EHA and their methyl derivatives with vinyl chloride and methyl methacrylate were synthesized and characterized by Talamini et al. [1] and Verma et al. [2]. Different polymerization modes have been employed to synthesize adhesives from the copolymers of C_{4-12} alkyl acrylates [3–5] by several workers.

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The investigations regarding the formation of terpolymers of these acrylates have also appeared in the literature [6, 7]. A terpolymer of 2-hydroxymethyl methacrylate, methyl methacrylate, and methacrylic acid exhibiting the properties of a polyelectrolyte was synthesized by Wen et al. [8]. We earlier investigated the kinetics and mechanism of the copolymerization of styrene with lower C_{1-4} alkyl acrylates complexed by $ZnCl_2$ [9–13]. $ZnCl_2$ enhances the polarity difference between donor–acceptor monomers, and its complexation tendency increased with the size of the alkyl substituent in the acrylate monomer. The structure and composition of the copolymers as determined by NMR revealed an alternating tendency of the monomers in the copolymer with the reactivity ratio product approaching zero. In the present communication a study is made of the complexation behavior of a highly substituted acrylate, 2-ethylhexylacrylate (2-EHA), with $ZnCl_2$, and its kinetics and mechanism of copolymerization with styrene (Sty) monomer. The structure and rheological properties of the copolymers are reported as well.

EXPERIMENTAL

Reagent-grade monomers and AIBN were purified as reported earlier [9]. Anhydrous $ZnCl_2$ (Ranbaxy) was used without further purification, cautiously to avoid moisture absorption. Ethyl methyl ketone (E. Merck) and methanol (SDs), used as solvent and nonsolvent, respectively, were analytical-grade products.

The complex of 2-EHA with $ZnCl_2$ was prepared according to our earlier procedure [9] and characterized for its density and viscosity. The formation of the complex was characterized by infrared (IR) spectroscopy recorded on a 599-B Perkin-Elmer IR spectrometer.

The polymerization reactions were carried out in bulk at 60, 65, and 70 $\pm$ 0.1°C for 75 minutes under nitrogen atmosphere dilatometrically [10]. The progress of the reaction was monitored with the help of a cathetometer. The copolymers so formed were dissolved in ethyl methyl ketone and then precipitated with methanol followed by drying for 4–5 days at 20°C. The weight of the copolymers was utilized to prepare conversion–time plots.

The intrinsic viscosity, η_{int}, of the copolymers expressed in $dL \cdot g^{-1}$ was determined in ethyl methyl ketone at 20 $\pm$ 1°C. The structure and composition of the copolymers were analyzed by NMR spectrum recorded on a EM-390, 90 MHz NMR spectrometer using $CDCl_3$ as solvent and tetramethyl silane as the internal reference.

The rheological behavior of 40% copolymer solution in MEK was investigated by a Haake Rotovisco RV 20 coaxial cylinder viscometer with a MV-I sensor at shear rates ranging from 1 to 1000 s^{-1} at 20, 25, and 30°C. The sample loaded in the sensor was accelerated to the maximum shear rate in 5 minutes, and then maintained at that shear rate for 2 minutes, followed by a return to the zero shear rate in 5 minutes.

The zero shear viscosity (η_0) of all copolymer compositions was determined by direct extrapolation of low shear data from the viscosity–shear rate plots.

The zero shear viscosities (η_0) at low and high shear rates were also determined by the Cross equation [14, 15]:

$$\eta_a = \eta_\infty + \left[\frac{\eta_0 - \eta_\infty}{1 + \alpha D^{\frac{1}{3}}} \right]$$

where η_a is the apparent viscosity of the solution at a particular shear rate D, and α is a constant associated with rupture of the linkages. The activation energy (ΔE) for the viscous flow was determined at 20, 25, and 30°C by the WLF equation [16]:

$$E = \frac{R \, d\log \eta_a}{T} = \frac{4.12 \times 10^3 T^2}{(51.6 + T - T_g)^2}$$

where T is the temperature of the study and T_g is the glass transition temperature of the copolymer solution as determined by the mixture rule [17].

RESULTS AND DISCUSSION

The kinetics, characterization, mechanism, and rheological properties of the copolymers of 2-EHA and Sty initiated radically were investigated by varying the concentration of $ZnCl_2$, monomer, and temperature.

The IR spectra of 2-EHA monomer and of its complex with $ZnCl_2$ were studied, and a shift in the carbonyl group band from 1725 to 1745 cm^{-1} (Fig. 1) was observed. The shift in the carbonyl group band was due to the formation of a coordinate bond between zinc and the oxygen atom of the carbonyl group, confirming the formation of the complex shown on page 2052.
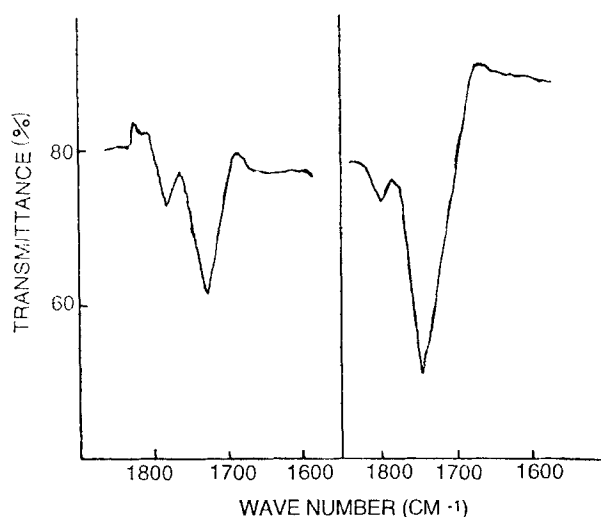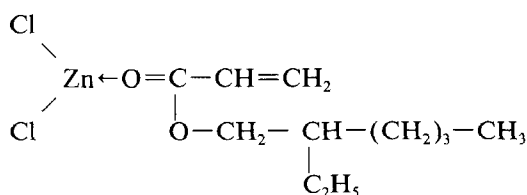

FIG. 1.   IR spectra of 2-ethylhexylacrylate (left) and of $ZnCl_2$:2-EHA complex (right).

$$
\begin{array}{c}
\mathrm{Cl} \\
\diagdown \\
\qquad \mathrm{Zn} {\leftarrow} \mathrm{O}{=}\mathrm{C}{-}\mathrm{CH}{=}\mathrm{CH_2} \\
\diagup \qquad\qquad | \\
\mathrm{Cl} \qquad\qquad \mathrm{O}{-}\mathrm{CH_2}{-}\ \mathrm{CH}{-}(\mathrm{CH_2})_3{-}\mathrm{CH_3} \\
\qquad\qquad\qquad\qquad | \\
\qquad\qquad\qquad\qquad \mathrm{C_2H_5}
\end{array}
$$

The viscosity and density of the complex at 300 K were 20 cP and 1.81 g·cm^{-3}, respectively. The stoichiometric composition of the ZnCl$_2$:2-EHA complex formed was 2:1 moles.

Effect of [ZnCl$_2$]

Table 1 illustrates the increase in percentage conversion (P_c) and the rate of polymerization (R_p) with [ZnCl$_2$] from 0.0 to 0.575 mol·L^{-1} at constant [AIBN], [Sty], and [2-EHA]. η_{int} showed an initial increase on addition of 0.503 mol·L^{-1} of ZnCl$_2$, followed by a constant value. Figure 2 shows a positive slope of log[ZnCl$_2$] vs R_p with an exponent value of 5.0, thereby indicating its accelerating effect.

Effect of [2-EHA]

The effect on R_p with a variation in 2-EHA concentration from 2.58 to 4.05 mol·L^{-1} at constant concentrations of AIBN, Sty, and ZnCl$_2$ is illustrated from a log R_p vs log 2-EHA plot (Fig. 3). An initial increase in R_p is observed with [2-EHA] from 2.58 to 2.94 mol·L^{-1}, followed by a gradual decrease up to 4.05 mol·L^{-1} [2-EHA]. The exponent values of the positive and negative slopes are 5.0 and 3.33, respectively. The initial increase in R_p is due to an increase in the [2-EHA] radical; in contrast, the decrease in R_p is probably due to the structure of complexed 2-EHA, Sty, and monomer.

Effect of [Sty]

The effect of [Sty] on R_p was studied by increasing its concentration from 1.35 to 4.04 mol·L^{-1} while [2-EHA], [ZnCl$_2$], and [AIBN] were kept constant. A logarithmic plot of [Sty] vs R_p, shown in Fig. 4, illustrates an increase in R_p with

TABLE 1.   Effect of Variation of [ZnCl$_2$] on the Copolymerization of 2-EHA with Sty[a]

[ZnCl$_2$], mol·L^{-1}	P_c, %	$R_p \times 10^3$ mol·L^{-1}·s^{-1}	$(\eta)_{int}$, dL·g^{-1}
0.000	39.0	07.692	0.25
0.503	40.5	08.772	0.40
0.525	45.8	10.593	0.41
0.538	55.0	12.023	0.41
0.550	61.3	14.125	0.40
0.575	77.5	16.670	0.40

[a][AIBN] = 9.38 × 10^{-3} mol·L^{-1}; [Sty] = 4.04 mol·L^{-1}; [2-EHA] = 2.58 mol·L^{-1}; T = 65°C; time = 75 minutes.
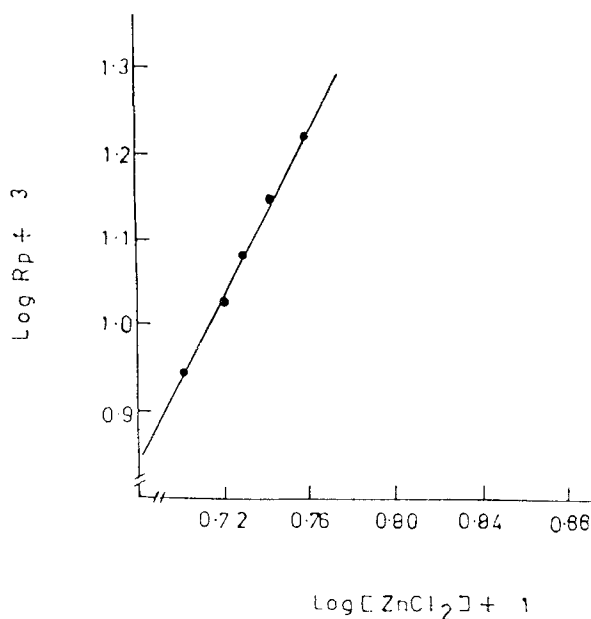
FIG. 2. Dependence between log R_p and log [ZnCl$_2$]: [AIBN] = 9.38 × 10^{-3} mol·L^{-1}, [2-EHA] = 2.58 mol·L^{-1}, [Sty] = 4.04 mol·L^{-1}, T = 65°C, time = 75 minutes.
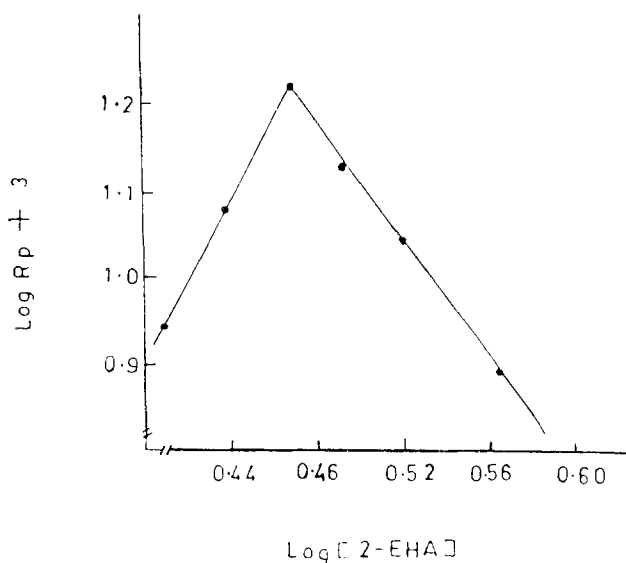
FIG. 3. Relationship between log R_p and log [2-EHA]: [AIBN] = 9.38 × 10^{-3} mol·L^{-1}, [ZnCl$_2$] = 0.50 mol·L^{-1}, [Sty] = 4.04 mol·L^{-1}, T = 65°C, time = 75 minutes.
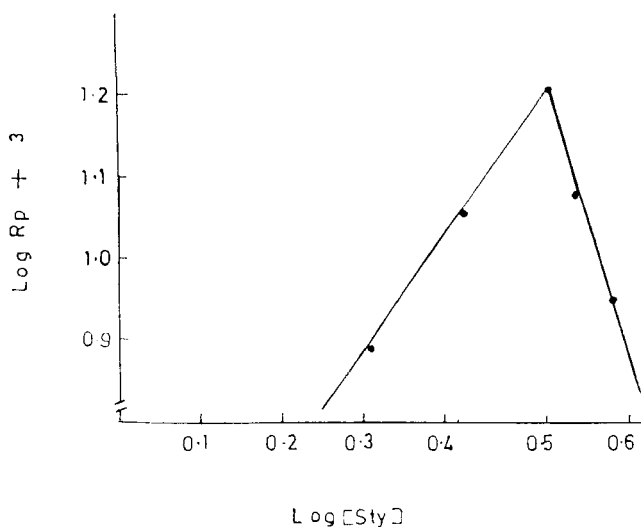
FIG. 4. Relationship between log R_p and log [Sty]: [AIBN] $= 9.38 \times 10^{-3}$ mol·L^{-1}, [ZnCl$_2$] $= 0.50$ mol·L^{-1}, [2-EHA] $= 2.58$ mol·L^{-1}, $T = 65°C$, time $= 75$ minutes.

[Sty] from 1.35 to 3.37 mol·L^{-1}, followed by a gradual decrease with [Sty] up to 4.04 mol·L^{-1}. The positive and negative slope exponent values are 1.4 and 4.0, respectively. The reason for the variation of R_p with [Sty] is discussed in an earlier section.

Effect of Temperature

The effect of temperature on R_p was studied in the absence and presence of ZnCl$_2$ at 60, 65, and 70 ± 0.1°C. The activation energy (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 complex was 42.78 and 34.38 kJ·mol^{-1}, respectively. The lowering of ΔE upon the addition of 0.503 mol·L^{-1} of ZnCl$_2$ indicates its accelerating effect.

The accelerating effect of ZnCl$_2$ may be due any one of the following reasons.

1. The rate of initiation R_i increases
2. The rate of propagation R_p increases
3. The rate of termination R_t decreases

The rate of decomposition of AIBN was unaffected on adding ZnCl$_2$, as no appreciable change was observed in the wavelength of maximum absorption (348 nm) [18].

A linear relationship was obtained between log R_p/R_{p_0} and log$(\eta)_{int}/(\eta_0)_{int}$ [where R_p and R_{p_0} are the rates of polymerization in the absence and the presence of ZnCl$_2$, and $(\eta)_{int}$ and $(\eta_0)_{int}$ are the corresponding intrinsic viscosities] as shown in Table 2, which explains why R_t is unaffected [10].
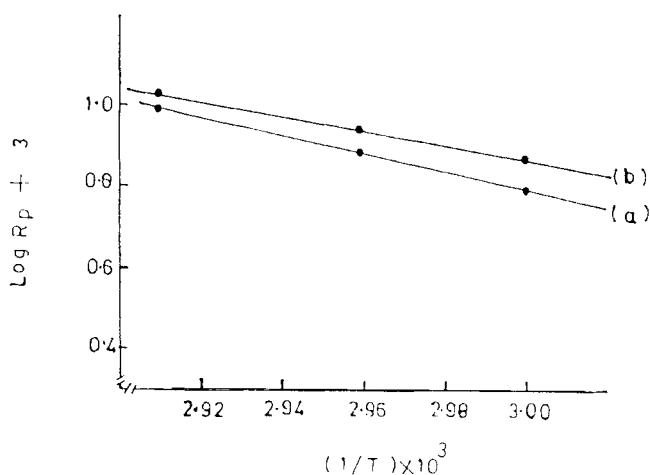
FIG. 5.   Dependence between log R_p and T^{-1} in the absence (a) and the presence (b) of ZnCl$_2$: [AIBN] = 9.38 × 10^{-3} mol·L^{-1}, [ZnCl$_2$] = 0.50 mol·L^{-1}, [2-EHA] = 2.58 mol·L^{-1}, [Sty] = 4.04 mol·L^{-1}, time = 75 minutes.

The ratio of propagation to termination rate constants in the presence/absence (Fig. 6a/b) of ZnCl$_2$ was determined from the slope of a plot of $1/(\eta)_{int}$ vs $R_p/$ [M]^2. k_p^2/k_t showed an increase from 4.64 to 5.83 L·mol^{-1}·s^{-1} upon the addition of 0.503 mol·L^{-1} ZnCl$_2$, confirming that the accelerating effect of ZnCl$_2$ is due to an increase in the rate of propagation.

CHARACTERIZATION

NMR Spectrum

Figure 7 shows a typical NMR spectrum of the copolymer. The aromatic protons peak appeared at 7.0-7.8 ppm. The aliphatic protons, i.e., methoxy protons, peak appeared at 3-3.7 ppm. The indistinguishable peak of methylene and

TABLE 2.   Relationship between log R_p/R_{p_0} and $\log(\eta)_{int}/(\eta_0)_{int}$ [a]

[ZnCl$_2$], mol·L^{-1}	log R_p/R_{p_0}	$\log(\eta)_{int}/(\eta_0)_{int}$
0.503	0.057	0.20
0.525	0.139	0.21
0.538	0.194	0.21
0.550	0.264	0.20
0.575	0.336	0.20

[a][AIBN] = 9.38 × 10^{-3} mol·L^{-1}; [Sty] = 4.04 mol·L^{-1}; [2-EHA] = 2.58 mol·L^{-1}; T = 65°C; time = 75 minutes.
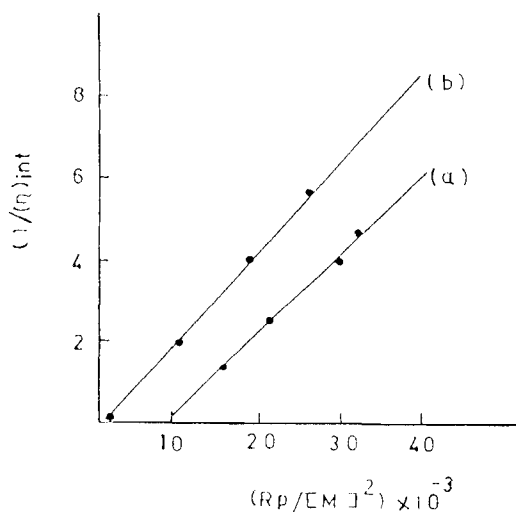
FIG. 6.   Plot of $1/(\eta)_{int}$ vs $R_p/[M]^2$ in the presence (a) and the absence (b) of $ZnCl_2$: 2-EHA complex: $[AIBN] = 9.38 \times 10^{-3}\,mol \cdot L^{-1}$, $[ZnCl_2] = 0.50\,mol \cdot L^{-1}$, $[2\text{-EHA}] = 2.58\,mol \cdot L^{-1}$, $[Sty] = 4.04\,mol \cdot L^{-1}$, $T = 65°C$, time = 75 minutes.

methine protons appeared in the 2–2.3 ppm region. The copolymer compositions [12] determined from the spectra are shown in Table 3. The reactivity ratios [19] of 2-EHA/Sty were 0.175/0.10, favoring an alternating copolymer structure, and 2.4/0.27, favoring a random copolymer structure. The product $r_1 r_2$ for an alternating
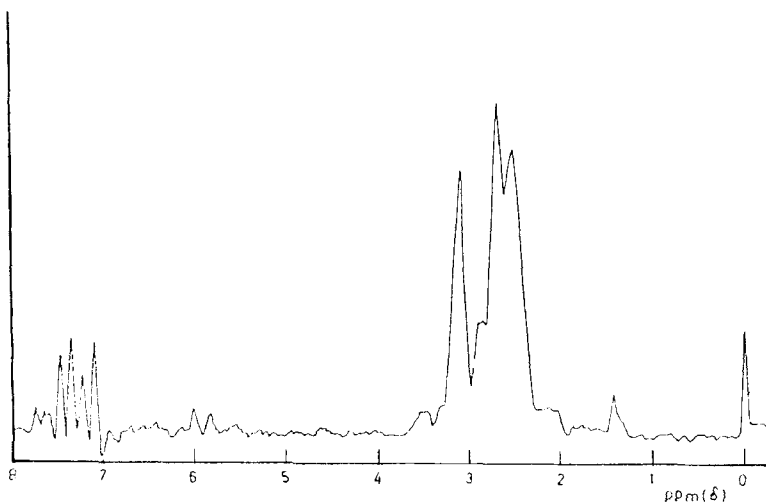

FIG. 7.   NMR spectrum of the copolymer of 2-EHA with Sty synthesized in the presence of $ZnCl_2$: $[AIBN] = 9.38 \times 10^{-3}\,mol \cdot L^{-1}$, $[ZnCl_2] = 0.50\,mol \cdot L^{-1}$, $[2\text{-EHA}]$ = $2.58\,mol \cdot L^{-1}$, $[Sty] = 4.04\,mol \cdot L^{-1}$, $T = 65°C$, time = 75 minutes.

copolymer approached zero whereas for a random copolymer it approached unity. On sequence distribution analysis, the probability of reacting Sty with 2-EHA varied from 0.891 to 0.803 with an increase in the feed ratio from 1.22 to 2.45 (Table 3), confirming the alternating structure of the copolymer. Similarly, the probability decreased from 0.675 to 0.645 with an increase in the feed ratio from 1.78 to 2.03, confirming the statistical tendency of the copolymer.

MECHANISM

The copolymerization of 2-EHA with Sty in the presence of $ZnCl_2$ may proceed via any of three mechanism:

1. Ternary molecular complex
2. Radical complex
3. Cross-propagation

The ternary molecular complex (TMC) mechanism is not operative in the present system as there is no sign of the formation of TMC. The graphical relationship between $[Sty]^2/R_p^2$ and $[Sty]/[ZnCl_2]$ with an increase in $[ZnCl_2]$ from 0.503 to 0.575 $mol \cdot L^{-1}$ is not quadratic, indicating that a cross-propagation mechanism is not operative in the present system. The linear relationship between $1/R_p$ and $1/[ZnCl_2]$ (Fig. 8) indicates that a radical complex mechanism is operative in the present system [12].

RHEOLOGICAL STUDIES

The relationship between viscosity and shear rate of the copolymers was investigated, and a typical logarithmic plot between viscosity and shear rate of alternating and random copolymers at 20°C is shown in Figs. 9 and 10, respectively. It is apparent from Fig. 9 that with an increase in acrylic content in the copolymer, the viscosity decreases at each shear rate. At a very low shear rate the viscosity seems to be highly dependent on the shear rate. A significant decrease in viscosity was ob-

TABLE 3. Effect of Copolymer Composition on Glass Transition Temperature and Energy of Activation for Flow

| Molar ratio in feed, Sty/EHA	Molar fraction in the copolymer		Glass transition temperature of copolymer solution,[a] K	Energy of activation ΔE (kcal/mol) at different temperatures, K		
	Sty	EHA		292	298	303
1.22	.42	.58	277	65.29	59.22	54.12
1.27	.39	.61	266	57.25	52.35	48.19
2.45	.29	.71	254	43.09	40.03	37.38
2.03	.16	.84	241	32.95	31.02	29.31
1.78	.11	.89	233	28.40	26.96	25.58

[a]Forty percent solution in methyl ethyl ketone.
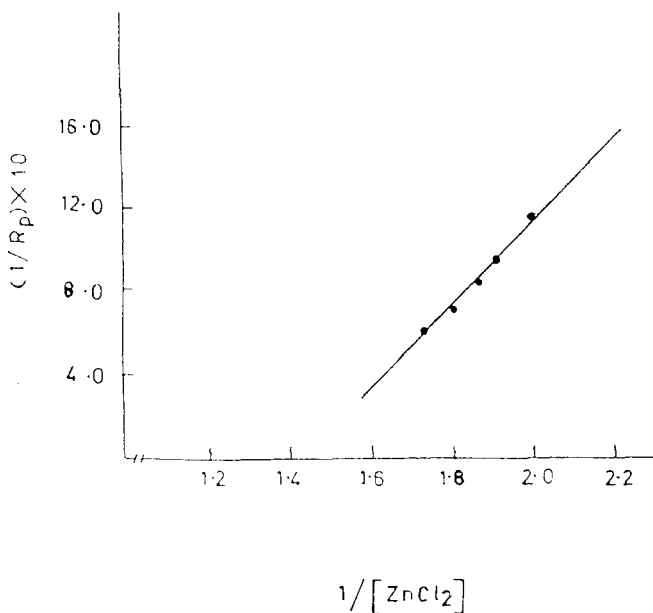
FIG. 8. $1/R_p$ vs $1/[ZnCl_2]$ for the copolymerization of 2-EHA with Sty at various [ZnCl$_2$]: [AIBN] = 9.38 × 10^{-3} mol·L^{-1}; [2-EHA] = 2.58 mol·L^{-1}, [Sty] = 4.04 mol·L^{-1}, T = 65°C, time = 75 minutes.
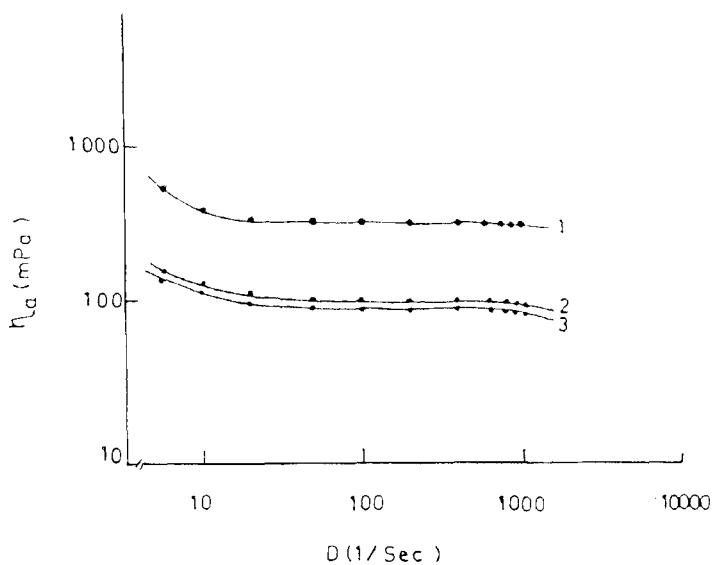

FIG. 9.   Plot between η_a and D for alternating copolymers of 2-EHA:Sty of composition (1) 58:42, (2) 61:39, and (3) 71:29.

served at 20 s^{-1} for all alternating copolymers; however, at higher shear rates the viscosity seems to be independent of it. Figure 10 illustrates that with an increase in acrylic content in the copolymer the viscosity decreases at each shear rate. At a very low shear rate the viscosity seems to be independent of the shear rate, but a significant decrease in viscosity is gradually observed at 100 and 20 s^{-1} shear rates for copolymers containing 84 and 89% acrylic content, respectively. At higher shear rates the viscosity is independent of shear rate, as in alternating copolymers.

The shear stress and shear rate data obtained at 20, 25, and 30°C were used to investigate the flow models of the copolymer solutions. The Bingham model fitted the data best for solutions of alternating copolymers. The equations at 25°C are $\tau = 3.928 + 0.2705D$ ($r = 1.00$); $\tau = 0.8697 + 0.09841D$ ($r = 1.00$), and $\tau = 1.264 + 0.07569D$ ($r = 1.00$) for alternating copolymers of 2-EHA:Sty with compositions of 58:42; 61:39, and 71:29, respectively. However, for random copolymers, the Ostwald model fitted the data best. The equations at 25°C are $t = 0.03113D^{1.034}$ ($r = 0.98$) and $t = 0.2947D^{0.9219}$ ($r = 0.98$) for random copolymers of 2-EHA:Sty with compositions of 89:11 and 84:16, respectively. It is obvious from shear stress and shear rate data that the structural arrangement of the monomer units in the copolymer has a direct influence on the flow model of copolymers.

The zero shear and infinite shear viscosities are shown in Table 4. It is apparent from the table that the values determined for η_0 by both methods (Cross equation and extrapolation) are in good agreement. A typical linear plot of $1/\eta_a$ vs $D^{2/3}$, shown in Fig. 11, gives the value of $1/\eta_0$ from the intercept. The intercept of the plot η_a vs $(\eta_0 - \eta_a)D^{-2/3}$, shown in Fig. 12, gives the value of η_∞.

ΔE determined at 20.25 and 30°C by the WLF equation is shown in Table 3. It is apparent from the table that ΔE decreases with an increase in temperature at any composition, while a corresponding increase in ΔE is observed with acrylic content at any temperature.
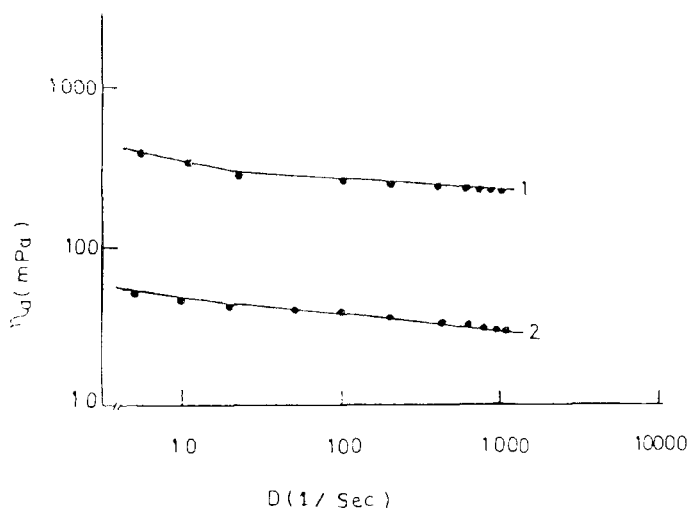

FIG. 10. Plot between η_a and D for random copolymers of 2-EHA:Sty of composition (1) 84:16 and (2) 89:11.

TABLE 4.   Zero Shear and Infinite Shear Viscosity

Molar ratio in copolymer Sty/EHA	Temperature, K								
	293 K			298 K			303 K		
	$\eta_0{}^a$	$\eta_0{}^b$	$\eta_\infty{}^b$	$\eta_0{}^a$	$\eta_0{}^b$	$\eta_\infty{}^b$	$\eta_0{}^a$	$\eta_0{}^b$	$\eta_\infty{}^b$
0.64	117.5	111.1	87.3	103.05	108.1	88.0	102.3	106.4	89.0
0.41	100.0	109.0	33.0	79.4	87.7	74.0	56.2	29.4	16.5
0.12	35.48	43.48	20.0	29.51	32.1	18.3	22.4	25.2	16.3

[a]Determined by the extrapolation method.
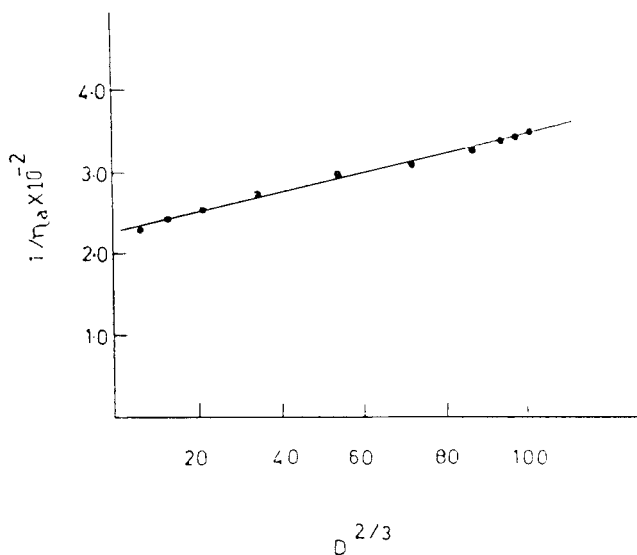[b]Determined by the Cross equation.

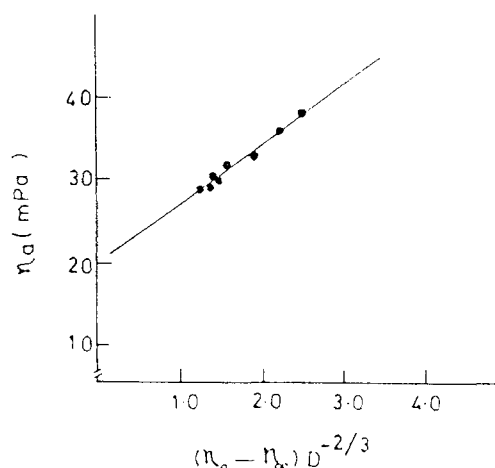FIG. 11.   Plot between $1/\eta_a$ and $D^{2/3}$ for copolymer of 2-EHA and Sty.

FIG. 12.   Relationship between η_a and $(\eta_0 - \eta_a)D^{-2/3}$ for copolymer of 2-EHA and Sty.

CONCLUSION

On the basis of above discussion, we conclude that $ZnCl_2$ acts as an accelerator by increasing the rate of propagation, resulting in the formation of alternating copolymer. The copolymerization reaction proceeds via a radical complex mechanism. Rheological studies favored Bingham and Ostwald models for alternating and random copolymers, respectively.

ACKNOWLEDGMENTS

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