

ON THE KINETICS AND MECHANISM OF THE COPOLYMERIZATION OF ACRYLONITRILE WITH STYRENE IN THE PRESENCE OF COPPER CHLORIDE

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Abstract The copolymerization of styrene (St) and acrylonitrile (AN) complexed with CuCl_2 monomer by a free radical mechanism was performed using benzoyl peroxide as an initiator at 65°C under N_2 atmosphere for 150 min. The rate of polymerization (R_p) was found to increase linearly with the concentration (in mol/L) of CuCl_2 , AN and St through scaling relations. The activation energy of the copolymerization process in the presence and absence of CuCl_2 was found to be 46.5 kJ/mol and 102 kJ/mol, respectively. The viscosity average molecular weight of the copolymer and the k_p^2/k_t ratio were determined to further assess the accelerating effect of CuCl_2 on the copolymerization process. The copolymerization process in the presence of CuCl_2 has a radical complex mechanism.

Keywords Rate of polymerization (R_p), Scaling relations, Viscosity average molecular weight, Radical complex mechanism.

INTRODUCTION

Investigation of the alternating copolymerization of acrylonitrile (AN) with styrene (St) and different conjugate diene monomers by kinetic treatment has been a subject of interest for many authors^[1–5]. In the copolymerization process of AN with St some ylides were used as initiators^[6, 7], or accelerators^[8]. Thermo oxidative degradation kinetics were also investigated^[9]. Srivastava *et al.*^[10–12] studied the copolymerization kinetics and mechanism of acrylates with St in the presence of Lewis acid complexes. The copolymerization of St with AN complexed with ZnCl_2 ^[13] was investigated to explain the role of ZnCl_2 in accelerating the copolymerization process. In the light of these publications, we think it is important to study the effect of CuCl_2 on the copolymerization process, and extract the important role of metal halides in the copolymerization process of St with AN monomers.

EXPERIMENTAL

Materials and Characterization

AN (99 %, Fluka) and St (99 %, Aldrich) monomers were washed three times with 5% NaOH, purified by vacuum distillation at 45°C , and kept at -10°C until used. Benzoyl peroxide (> 98%, Merck) was twice purified by recrystallization using a mixture of chloroform and methanol, and dried at 50°C . Anhydrous CuCl_2 (99%, Acros) was used without further purification. Methanol (99.8%, HPLC grade), and cyclohexane (99%, Scharlau) solvents were used as received.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 analyzer (Japan) under N_2 atmosphere at a heating rate of 10 K/min. A Nicolet (avator-360, USA) FTIR spectrometer was used to record the IR spectra of AN and complex monomers. The molecular weight of the copolymer was determined in terms of viscosity average molecular weight (M_v), in which tetrahydrofuran (THF) was used as the solvent at 25°C , using an Ubbelohde viscometer and is expressed in deciliters per gram. The Mark-Houwink equation was used for this purpose^[14].

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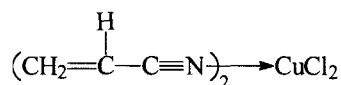
Polymerization Method

The polymerization process was performed in two steps, first the complex of AN and CuCl_2 was formed by adding a certain amount of CuCl_2 to an excess amount of AN with continuous stirring, then the solution was kept overnight at 0°C . The formed complex was placed in a polymerization ampoule, treated with the required amount of St monomer without any solvent, and sealed under N_2 atmosphere. The bulk polymerization was carried out under N_2 atmosphere at 65°C for 150 min in a water thermostat shaker (GFL-1083, Germany). The composition of the complex was determined gravimetrically by the addition of silver nitrate and the precipitation of silver chloride. After the completion of polymerization (*i.e.* every 30 min), the polymerization mixture was poured into a large amount of methanol, and the resulting precipitate was filtered and dried to constant weight. The gross copolymer was purified from homopolymers using cyclohexane by soaking and washing several times, and then dried to constant weight. The rate of polymerization (R_p) was calculated from the slope of the curve of % conversion versus time, and was related to the concentration (in mol/L) of CuCl_2 , AN and St, respectively, by lg-lg scaling relations.

RESULTS AND DISCUSSION

Complex Formation

The composition of the AN/ CuCl_2 complex was followed gravimetrically by the addition of AgNO_3 and precipitation of AgCl . It was found that the ratio of AN to CuCl_2 in the complex is 2:1, where the Cu binds to the N atom of the nitrile group as follows



The formation of the above complex was identified by comparing the FTIR spectra of AN monomer with the complexed monomer (Fig. 1), because it can be observed that there exists a shift in the absorption band of nitrile group from 2228 cm^{-1} to 2273 cm^{-1} .

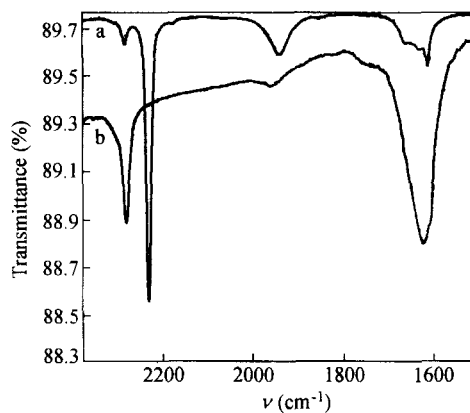


Fig. 1 FTIR spectra of (a) AN monomer and (b) Complexed monomer ($\text{CuCl}_2(\text{AN})_2$)

Effect of Concentration of Monomers on R_p

The change of concentration of CuCl_2 , AN, and St (in mol/L) with rate of polymerization (R_p) was studied in the form of lg-lg relations. Figure 2 shows the variation of concentration of CuCl_2 within the range of 0.38–1.90 mol/L (10 mol%–50 mol% with respect to AN monomer) at constant Bz_2O_2 concentration, AN and St monomers. The rate of polymerization was found to increase as the concentration of CuCl_2 increases to the power of 1.5 according to the scaling relation:

$$R_p \sim [\text{CuCl}_2]^{1.5} \quad (1)$$

At a fixed concentration of AN monomer, Bz_2O_2 , CuCl_2 and a varying concentration of St monomer from 2.18 mol/L to 4.70 mol/L, the (R_p) was found to increase linearly with the concentration of St monomer to the power of 1.4 (Fig. 3), according to the scaling relation;

$$R_p \sim [\text{St}]^{1.4} \quad (2)$$

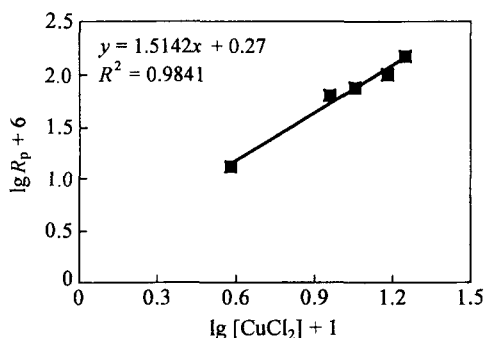


Fig. 2 Scaling relation of R_p and concentration of CuCl_2 at $[\text{AN}] = 3.8 \text{ mol/L}$, $[\text{St}] = 4.7 \text{ mol L}^{-1}$, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

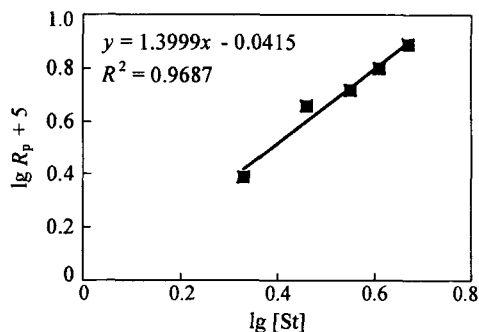


Fig. 3 Scaling relation of R_p and concentration of styrene at $[\text{CuCl}_2] = 0.38 \text{ mol L}^{-1}$, $[\text{AN}] = 3.8 \text{ mol L}^{-1}$, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

In Fig. 4, (R_p) was studied as a function of AN at constant concentration of Bz_2O_2 , St monomer, and CuCl_2 . The (R_p) increased as the concentration of AN increased from 3.8 mol/L up to 7.6 mol/L to the power of 0.70 according to the scaling relation:

$$R_p \sim [\text{AN}]^{0.70} \quad (3)$$

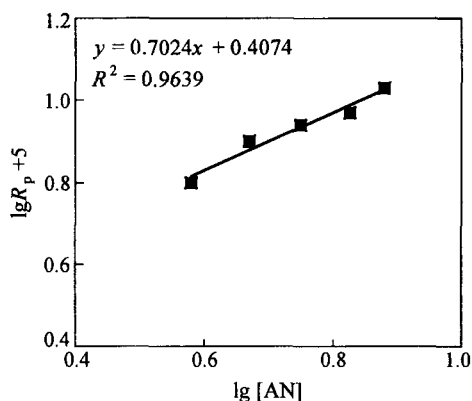


Fig. 4 Scaling relation of R_p and concentration of acrylonitrile at $[\text{CuCl}_2] = 0.38 \text{ mol L}^{-1}$, $[\text{St}] = 4.7 \text{ mol L}^{-1}$, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

From Eqs. (1) and (3) one can further deduce a new relationship between R_p and $[\text{CuCl}_2(\text{AN})_2]$ as

$$R_p \sim [\text{CuCl}_2(\text{AN})_2]^{1.5} \quad (4)$$

where the (R_p) increased as the concentration of the complex increases to the power of 1.5. The alternating copolymerization behavior of St with AN^[1, 2, 13] could be seen in the presence of CuCl_2 from Eqs. (2) and (4), where (R_p) increases with nearly similar changes of St monomer and complexed monomer. This behavior implicitly states that the consumption of the complexed monomer and St monomer throughout the polymerization

time is the same, which provides an alternating behavior. From Eq. (3) one can say that the introduction of AN monomer is slower than that of the others and that can produce some random structure among the chains throughout the copolymerization process.

Accelerating Effect of CuCl_2 on the Copolymerization of AN and St

The role of CuCl_2 in the copolymerization of AN with St can be regarded as that of supplier of copper electrons to the nitrile group of the AN monomer, which is reflected on the ease of opening of the aliphatic double bond. This effect can be followed through monitoring the rate of polymerization in the absence and the presence of CuCl_2 in the copolymerization process. This could be seen from Fig. 2, but for more detailed investigation the overall activation energy, molecular weight and k_p^2/k_t in the absence and the presence of CuCl_2 should be determined.

Activation energy

The effect of temperature on the R_p in the temperature range of 60–70°C was studied. The calculated R_p values were correlated with the reciprocals of the polymerization temperature. Figure 5 is the Arrhenius plot which shows that the relationship between $\lg R_p$ and $1/T$ in the temperature range of 60–70°C is a straight line and from the slope of this line one can calculate the overall activation energy (E_a) for the polymerization process. The values of E_a in the presence and absence of the complex were 46.5 kJ/mol and 102 kJ/mol, respectively.

Molecular weight and k_p^2/k_t calculations

Table 1 shows the influence of CuCl_2 concentration on the rate of propagation, M_v , $\lg R_p/R_{p0}$ and $\lg \eta/\eta_0$ (where R_p and R_{p0} are the rate of polymerization in the presence and the absence of $\text{CuCl}_2(\text{AN})_2$ complex, and η and η_0 are the corresponding intrinsic viscosities).

Table 1. Influence of CuCl_2 concentration on rate of propagation and M_v

CuCl_2 (mol/L)	$R_p \times 10^5$ (mol $\cdot$ L $^{-1}$ $\cdot$ s $^{-1}$)	$M_v \times 10^{-6}$	$[\eta]$ (dL $\cdot$ g $^{-1}$)	$\lg(R_p/R_{p0})$	$\lg(\eta/\eta_0)$
0.00	0.16	0.610	1.910	0.00	0.000
0.38	1.41	0.625	1.950	0.92	0.009
0.76	6.33	0.641	1.982	1.60	0.016
1.14	7.50	0.655	2.010	1.67	0.022
1.52	10.20	0.661	2.022	1.80	0.025
1.90	14.80	0.685	2.073	1.97	0.035

Reaction conditions: $[\text{AN}] = 3.8$ mol/L, $[\text{St}] = 4.7$ mol/L, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2}$ M, $T = 65^\circ\text{C}$, $t = 150$ min

It can be clearly seen that the decrease in the overall activation energy in the presence of $\text{CuCl}_2(\text{AN})_2$ complex and the linear relationship between $\lg R_p/R_{p0}$ and $\lg \eta/\eta_0$ illustrates the accelerating effect of CuCl_2 on the rate of polymerization. k_p^2/k_t for copolymerization processes can be determined [13,15,16] from the relation

$$1/M_v = k_t/k_p^2 R_p/[M]^2 \quad (5)$$

where $[M]$ is the total monomer concentration. According to Fig. 6, the k_p^2/k_t value in the absence and in the presence of CuCl_2 was found to be 0.4 and 2.6 L mol $^{-1}$ $\cdot$ s $^{-1}$ respectively. The large increase in rate of propagation in the presence of CuCl_2 with respect to rate of termination confirms the accelerating effect of CuCl_2 on the rate of polymerization. It further indicates the big increase of rate of polymerization as the concentration of CuCl_2 increases as shown in Table 1. Ref. [13] has reported similar work but using ZnCl_2 . The rate of polymerization in our case is found to be higher than that of ZnCl_2 . This can be attributed to the high formation constant (K_f) of $\text{CuCl}_2(\text{AN})_2$ complex compared with $\text{ZnCl}_2(\text{AN})_2$ complex. The high formation constant of $\text{CuCl}_2(\text{AN})_2$ complex is due to the $d^9 \text{Cu}^{2+}$ that have Jahn-Teller distortion causing a high stability for the nitrogen copper bond, which is then reflected in the ease of opening the double bond of acrylonitrile, and the consequent drastic change in the rate of copolymerization^[17].

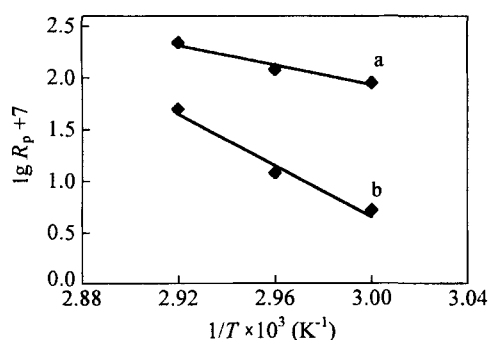


Fig. 5 Relationship between $\lg R_p$ and $1/T$
 (a) In the presence of the complex; (b) in the absence of the complex at $[\text{CuCl}_2] = 0.38 \text{ mol/L}$, $[\text{St}] = 4.7 \text{ mol L}^{-1}$, $[\text{AN}] = 3.8 \text{ mol L}^{-1}$, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

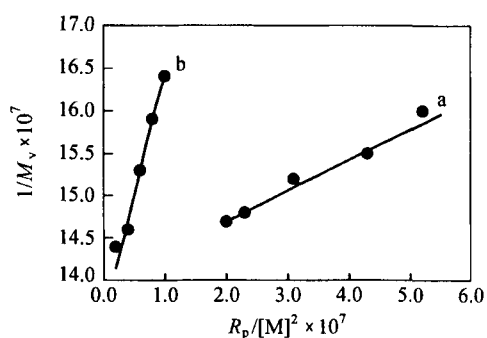


Fig. 6 Plot of $1/M_v$ versus $R_p/[M]^2$
 (a) In the presence of complex; (b) In the absence of the complex at $[\text{CuCl}_2] = 0.38 \text{ mol L}^{-1}$, $[\text{St}] = 4.7 \text{ mol L}^{-1}$, $[\text{AN}] = 3.8 \text{ mol L}^{-1}$, $[\text{Bz}_2\text{O}_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

Thermogravimetric Analysis (TGA)

Figure 7 shows the TGA profiles of St-AN copolymer in the absence and the presence of CuCl_2 . It can be seen that the copolymer in the absence of CuCl_2 exhibits only one thermal degradation process in the temperature range of $386\text{--}428^\circ\text{C}$ with a total weight loss of 94.6%. In contrast the copolymer in the presence of CuCl_2 exhibits two thermal degradation processes in the temperature range of $67\text{--}113^\circ\text{C}$ and $375\text{--}500^\circ\text{C}$, where the weight losses are 19.85% and 26.12% respectively. There is a small decline of weight (*ca.* 11.60%) in the range of $114\text{--}374^\circ\text{C}$. Thus, the total weight loss in the presence of CuCl_2 (*i.e.* 57.5%) is much less than in the absence of CuCl_2 (*i.e.* 94.6%). The existence of $\text{CuCl}_2(\text{AN})_2$ complex can make it possible for AN to react from both sides of the complex (*i.e.* act as a crosslinker) that binds different chains together to form some three dimensional networks. These networks increase the resistance to degradation at elevated temperatures. Furthermore, the fast propagation step due to the existence of CuCl_2 (*i.e.* $R_p \sim [\text{CuCl}_2(\text{AN})_2]^{1.5}$) and the relatively flexible AN group binding to CuCl_2 make it possible for both AN groups to react with each other, forming small cyclic oligomers which have low degradation temperatures. These small oligomers were probably responsible of the first thermal degradation process in the range of $67\text{--}113^\circ\text{C}$.

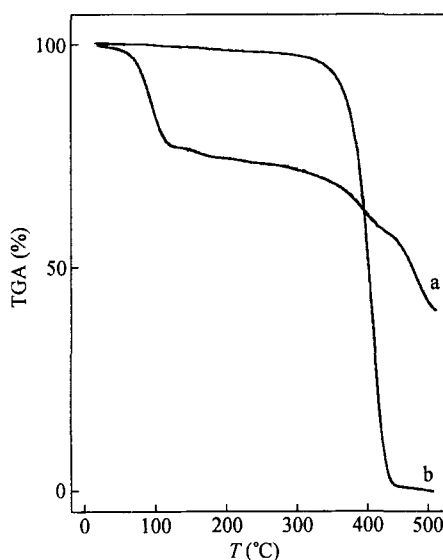


Fig. 7 TGA profiles of St-AN copolymers
 (a) In the presence of the complex; (b) in the absence of complex

Mechanism

Hirae *et al.*^[18] proposed that if a linear relationship is obtained when plotting $1/R_p$ versus $1/[CuCl_2]$, then the copolymerization is of radical complex mechanism type.

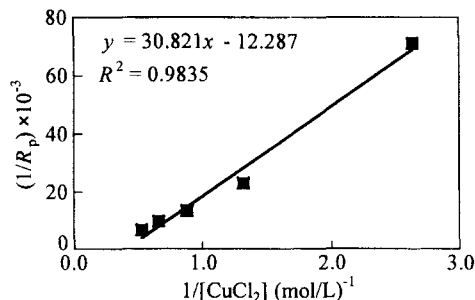
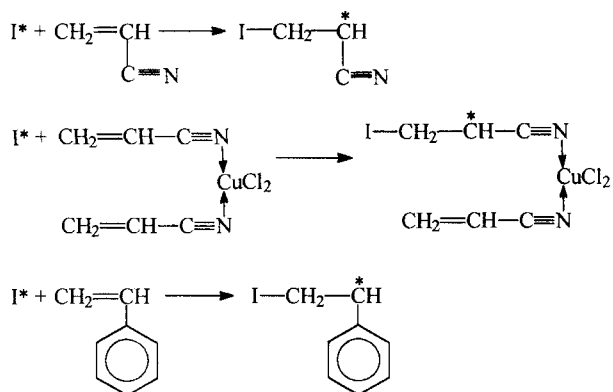


Fig. 8 Relationship of $1/R_p$ versus $1/[CuCl_2]$ at $[St] = 4.7 \text{ mol L}^{-1}$, $[AN] = 3.8 \text{ mol L}^{-1}$, $[Bz_2O_2] = 4.25 \times 10^{-2} \text{ mol L}^{-1}$, $T = 65^\circ\text{C}$, $t = 150 \text{ min}$

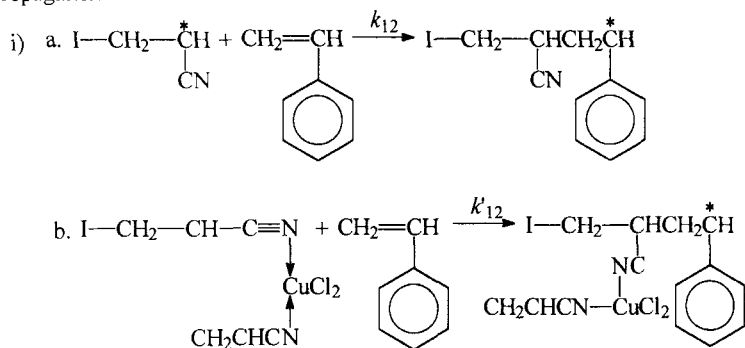
Thus the copolymerization process proceeds in three steps; initiation, propagation and termination.

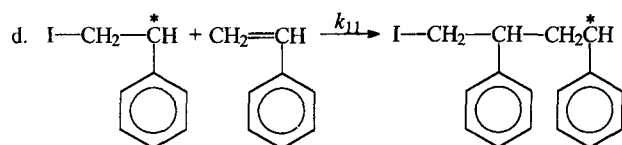
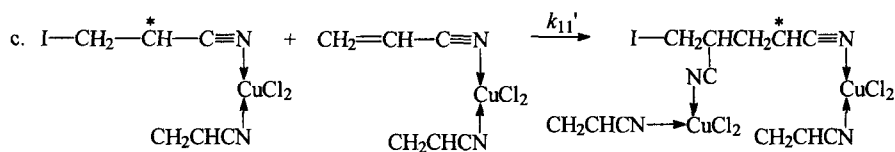
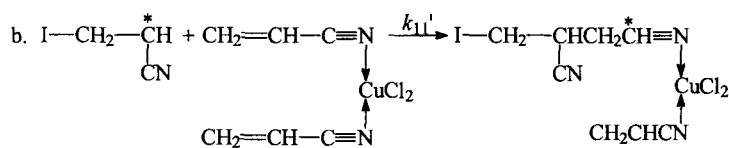
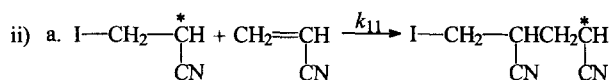
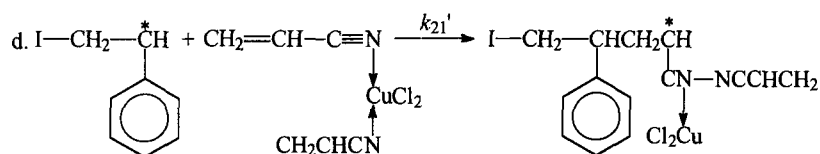
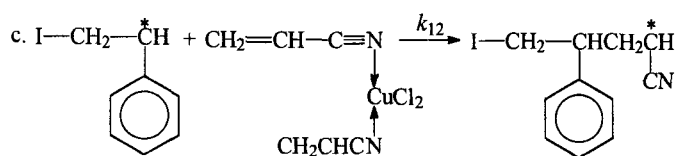
a) Initiation



Benzoyl peroxide radical = I^*

b) Propagation





Where the subscripts 1, 1', and 2 refers to acrylonitrile, complex, and styrene respectively.

c) Termination

