

Emulsifier-Free Emulsion Polymerization of Acrylonitrile: Effect of *In Situ* Developed Cu(II)/Glycine Chelate Complex Initiated by Monopersulfate

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ABSTRACT: The catalytic effect of various Cu(II) salts and Cu(II) chelate complexes of certain amino acids on the emulsion polymerization of acrylonitrile in the absence of added emulsifier was investigated in experiments. The CuSO_4 /glycine chelate complex was chosen for a detailed kinetic study of acrylonitrile polymerization. The polymerization was studied at varying concentrations of initiator, monomer, Cu(II), glycine, solvents, and TiO_2 over a temperature range of 30–60°C. The overall activation energy and the viscosity average molecular weight of the polymer were computed. From the kinetic and spectrophotometric studies, the mechanism of KHSO_5 decomposition by the Cu(II)/glycine complex and initiation of polymerization was suggested. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2785–2790, 1999

Key words: emulsifier-free emulsion; chelate complex; kinetics; complex initiation

INTRODUCTION

Emulsifier-free emulsion polymerization of vinyl and acrylic monomers has received much attention because of practical and academic interests^{1–12} and to synthesize polymers for biomedical, coating, and adhesive applications. In recent years, several studies were carried out in the field of emulsion polymerization of various monomers using different redox pair initiation systems^{13–19} and metal ions, but most of these were performed at temperatures over 70°C. Sahoo et al.²⁰ recently reported the emulsifier-free emulsion polymerization of acrylonitrile (AN) that was initiated by an acidic peroxy salt, potassium monopersulfate (KHSO_5), in the presence of inorganic powders (CaSO_3 and BaSO_4). Prior to this Sahoo et al.^{21–24} studied the effect of a Cu(II)/phenols chelate com-

plex on the KHSO_5 initiated vinyl polymerization of AN. However, no report seems to be available on the emulsifier-free emulsion polymerization of AN initiated by KHSO_5 catalyzed by a newly *in situ* developed metal salts/amino acid chelate complex. The present study describes the development of a novel initiating system comprising KHSO_5 –Cu(II)–glycine to obtain a stable emulsion of high conversion in the absence of an added emulsifier and the effect of some solvents and inorganic substances on the rate of polymerization. Another advantage of the complex initiating system is to design a simple and low cost polymerization technique suitable for commercial purposes.

EXPERIMENTAL

Potassium monopersulfate (KHSO_5) was a gift from Du Pont and was used as received. A stock solution of 0.129M of the initiator was used. AN was purified as reported earlier.²² All other re-

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Table I Rates of AN Polymerization (R_p) Catalyzed by Various Cu(II) Salts, Amino Acids, and Cu(II) Amino Acid Couple Initiated by KHSO_5

| Amino Acids | $10^5 \times R_p$ ($\text{mL}^{-1} \text{s}^{-1}$) | | | | |
|-------------|--|----------------------------|-----------------|---------------------------|----------------|
| | CuSO_4 | $\text{Cu}(\text{NO}_3)_2$ | CuCl_2 | $\text{Cu}(\text{OAc})_2$ | No Cu(II) Salt |
| None | 2.49 | 2.30 | 7.02 | 11.85 | 1.65 |
| Glycine | 12.0 | 7.22 | 5.78 | 10.31 | 2.69 |
| Alanine | 16.63 | 9.35 | 8.23 | 14.55 | 4.12 |
| Leucine | 14.61 | 8.61 | 6.29 | 13.20 | 4.97 |

[Cu(II)] = 0.015M, $[\text{KHSO}_5]$ = 0.0129M, [AN] = 1.517M, and [amino acid] = 0.03M at 50°C; R_p = $1.65 \times 10^{-5} \text{ mL}^{-1} \text{ s}^{-1}$ for control.

agents were AR grade and were used after purification.

The polymerization experiments were carried out in a round bottomed flask with inlet and outlet tubes for passing oxygen-free nitrogen. The reaction flasks containing known concentrations of monomer, CuSO_4 , and glycine/alanine/leucine were deaerated by passing them through purified nitrogen; the mixtures were stirred at 400–600 rpm. The speed was in the range where the agitation had no remarkable effect on the rate of polymerization. A requisite amount of the initiator (KHSO_5) solution was carefully injected. The reaction was arrested by the addition of a known excess of Fe(II), which spontaneously consumed the unreacted KHSO_5 .

The precipitated polymers were filtered, washed repeatedly with water and absolute alcohol, and dried to constant weight at 60°C. Conversion and rate were determined gravimetrically. The visible spectra of Cu(II) and Cu(II)/amino acid chelate complexes with monomer (AN) and initiator (KHSO_5) were studied with a Perkin Elmer UV-visible spectrophotometer. The viscosity average molecular weight (\bar{M}_v) of the purified polymers were determined in purified DMF at 30°C using the relationship of Shibukawa et al.²⁵

$$[\eta] = 3.335 \times 10^{-4} \bar{M}_v^{0.72}$$

RESULTS AND DISCUSSION

The emulsion polymerization of AN was carried out using KHSO_5 as the initiator with Cu(II) salts and Cu(II)/amino acid complex as the catalysts. Reference experiments were performed. The possibility of a Cu(II)/amino acid complex initiating the polymerization was excluded by the fact that

no polymer was formed after 48 h in the absence of KHSO_5 . The results of these preliminary studies are recorded in Table I.

From Table I it is evident that with CuSO_4 , which has a feeble activating effect on the course of potassium monopersulfate decomposition, the addition of glycine, alanine, and leucine greatly activates the rate of KHSO_5 decomposition and hence the rate of initiation of polymerization. From the results with glycine it was found that the rate of polymerization (R_p) of ($\text{KHSO}_5/\text{CuSO}_4/\text{glycine}$) > [R_p (KHSO_5) + R_p ($\text{KHSO}_5/\text{CuSO}_4$) + R_p (KHSO_5/Gly)]. Further, CuSO_4 alone has poor activation, glycine has moderate activation, and the $\text{CuSO}_4/\text{glycine}$ complex has pronounced activation effects on the R_p , which is about 7 times greater than the noncatalyzed system.

The poor activation rate with CuSO_4 might be due to weak interaction of the vacant d orbital of the Cu(II) ion with the bridged peroxy orbital of KHSO_5 , generating initiating radicals at a low rate. This was confirmed by the visible spectra of the Cu(II) SO_4 solution and Cu(II)/ KHSO_5 mixture that absorbs at the same wavelength (λ_{max} = 800 nm) with different absorbances. Figure 1 shows the visible spectra of various mixtures like Cu(II)/Gly, Cu(II)/Gly/AN, Cu(II)/Gly/ KHSO_5 , and Cu(II)/Gly/AN/ KHSO_5 that were measured to obtain a complete picture of the interaction between the reacting components and their relationship with the rate data. The tridentate ligand character of glycine in conjunction with colored cations like Cu(II) to form a complex in an acidic medium (pH 2.7) is well recognized,^{26–28} where the metal-ligand stability constants $\log k_1$, $\log k_2$, and $\log \beta_2$ were found to be 8.48, 7.10 and 15.83, respectively. The high R_p value with the $\text{CuSO}_4/\text{glycine}$ couple may probably be attributed to the high

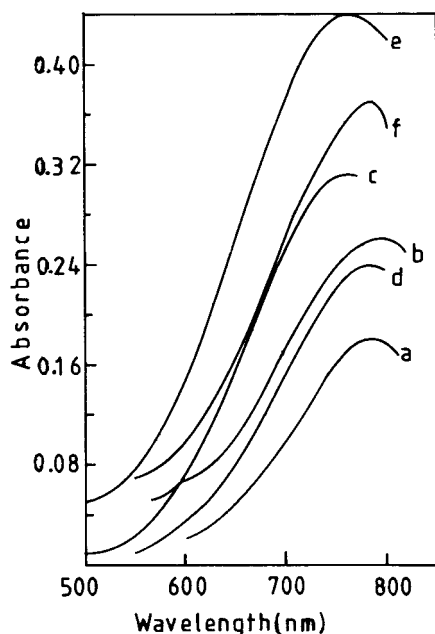


Figure 1 Visible spectra of (a) CuSO_4 , (b) $\text{CuSO}_4 + \text{KHSO}_5$, (c) $\text{CuSO}_4 + \text{Gly}$, (d) $\text{CuSO}_4 + \text{Gly} + \text{KHSO}_5$, (e) $\text{CuSO}_4 + \text{Gly} + \text{AN}$, (f) $\text{CuSO}_4 + \text{Gly} + \text{AN} + \text{KHSO}_5$ at $[\text{CuSO}_4] = 0.02M$, $[\text{Gly}] = 0.03M$, $[\text{KHSO}_5] = 0.0129M$, and $[\text{AN}] = 1.517M$.

rate of production of initiating radicals generated by the facile homolysis of the initiator bound by the transient complex of Cu(II) -glycine, where the internal energy is transferred to the initiator.

The polymerization was studied at various concentrations of the reaction components to establish the relationship between the catalytic influence and mole ratios of the donor-acceptor entities.

Influence of Initiator Concentration

The initial rate of polymerization and maximum conversion were increased on increasing the concentration of KHSO_5 (0.00645–0.0226M) at fixed concentrations of CuSO_4 (0.01M), glycine (0.03M), and AN (1.517M) at 50°C. Plots of R_p versus $[\text{KHSO}_5]$ and $\log R_p$ versus $\log [\text{KHSO}_5]$ (Fig. 2) indicate the overall rate to be first-order dependent on initiator concentration. This deviates from the normal half-order dependence of the rate on initiator concentration in conventional free-radical polymerization. This deviation may be attributed to the complexation of the initiator with the Cu(II) ion in the Cu(II) -glycine complex, resulting in selective stereochemical initiation involving a cis-attack on the bound monomer.

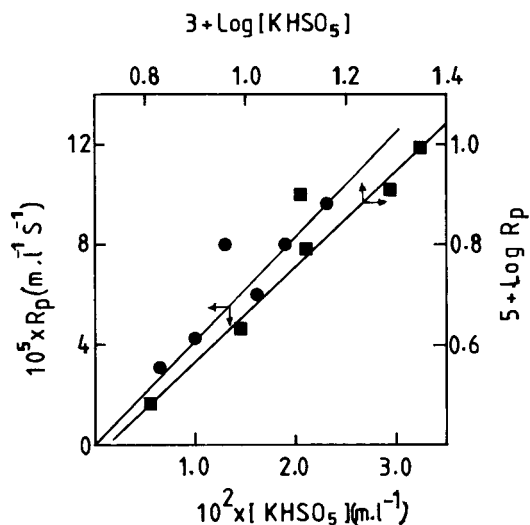


Figure 2 Variation in R_p with $[\text{KHSO}_5]$: $[\text{CuSO}_4] = 0.015M$, $[\text{Gly}] = 0.03M$, and $[\text{AN}] = 1.517M$ at 50°C. (●) $(10^2 \times [\text{KHSO}_5])$ vs. $(10^5 \times R_p)$, (■) $(3 + \log [\text{KHSO}_5])$ vs. $(5 + \log R_p)$.

Influence of CuSO_4 Concentration

The variation of the R_p with CuSO_4 concentration (0.01–0.0175M) is shown in Figure 3. The maximum conversion was found to be at 0.015M CuSO_4 . The arbitrary increase and decrease in rate within the above range of CuSO_4 concentration may be due to increasing catalysis because

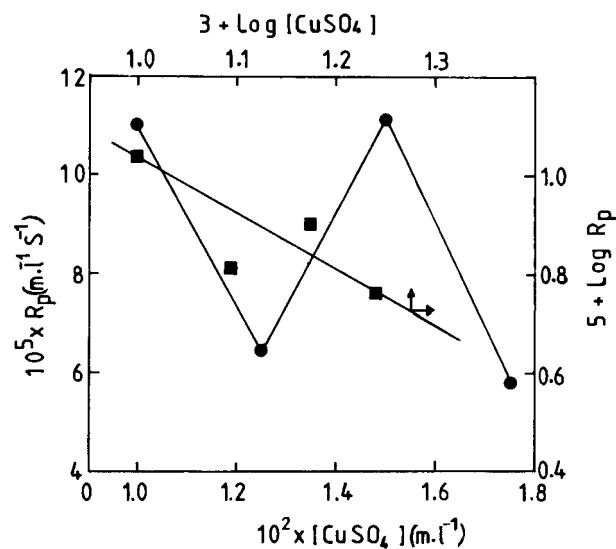


Figure 3 Variation in R_p with $[\text{CuSO}_4]$: $[\text{KHSO}_5] = 0.0129M$, $[\text{AN}] = 1.517M$, and $[\text{Gly}] = 0.03M$, at 50°C. (●) $(10^2 \times [\text{CuSO}_4])$ vs. $(10^5 \times R_p)$, (■) $(3 + \log [\text{CuSO}_4])$ vs. $(5 + \log R_p)$.

an appropriate mole ratio of Cu(II) to glycine in solution favors the formation of an activated complex that actively interacts with the peroxy bridge orbital, resulting in rupture of the O—O bond in a sequential fashion. This, in turn, influences the rate of the initiation of polymerization. The rate was dependent on the 1.09 power of Cu(II).

Influence of Glycine Concentration

The initial R_p and the maximum conversion were found to increase with an increasing concentration of glycine (0.015–0.045M) and then decreased at a fixed concentration of CuSO_4 (0.015M), AN (1.517M), and KHSO_5 (0.0129M) at 50°C. The overall slope was found to be 0.87 from the plot of $\log R_p$ versus $\log [\text{glycine}]$ (Fig. 4). The enhancement of rate may be due to an increase in the concentration of the Cu(II)/glycine complex that causes ready decomposition of the initiator to produce initiating radicals at a much greater rate. It may be noted that the catalytic activity of Cu(II) in cleaving the peroxy bond is enhanced by coupling the metal ion with chelating glycine molecules in which a competitive coordination among the Cu(II) ion, KHSO_5 , and glycine takes place. Due to this competition, the stability of the Cu(II)/glycine complex is distorted toward Cu(II)- KHSO_5 interaction and the internal energy of the complex is released in the direction of the peroxy bond, resulting in its breakage. The de-

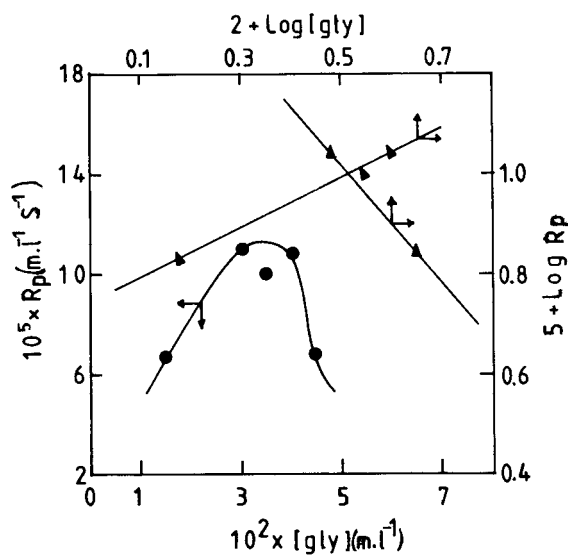


Figure 4 Variation in R_p with [glycine] : $[\text{KHSO}_5] = 0.0129M$, $[\text{AN}] = 1.517M$, and $[\text{CuSO}_4] = 0.015M$ at 50°C. (●) $(10^2 \times [\text{Gly}])$ vs. $(10^5 \times R_p)$, (▲) $(2 + \log[\text{Gly}])$ vs. $(5 + \log R_p)$.

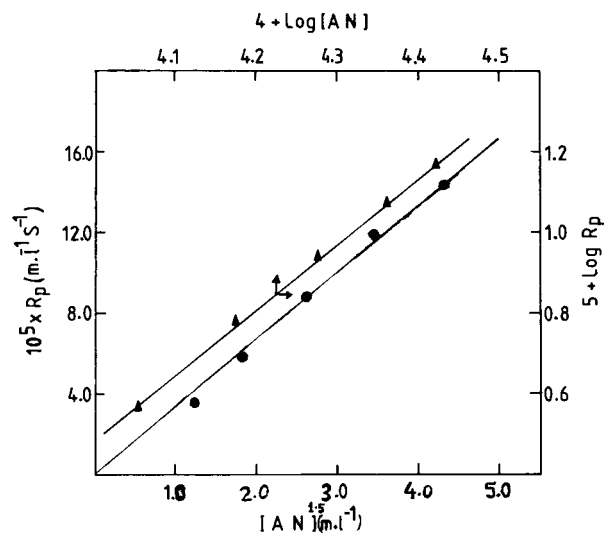


Figure 5 Variation in R_p with [monomer] : $[\text{KHSO}_5] = 0.0129M$, $[\text{CuSO}_4] = 0.015M$, and $[\text{Gly}] = 0.03M$ at 50°C. (●) $[\text{AN}]^{1.5}$ vs. $(10^5 \times R_p)$, (▲) $(4 + \log[\text{AN}])$ vs. $(5 + \log R_p)$.

crease in absorbance from 0.31 for Cu(II)/Gly to 0.23 on the addition of KHSO_5 may support the explanation (Fig. 1).

Influence of Monomer Concentration

The R_p increases with an increase in the concentration of AN (1.138–2.655M) at fixed concentrations of CuSO_4 (0.01M), Gly (0.03M), and KHSO_5 (0.0129M) at 50°C. A plot of R_p versus $[\text{AN}]^{1.5}$ was linear and passed through the origin (Fig. 5). Figure 5 also includes the double logarithmic plot of rate versus $[\text{AN}]$ with a slope of 1.54, which indicates the rate to be dependent on a 3/2 power of the monomer concentration.

This order may be attributed to the greater rate of participation of the monomer in the initiation step. This is evident from the decrease of the absorbance of 0.44 of the Cu(II)/Gly/AN to 0.35 of Cu(II)/Gly/AN/ KHSO_5 (Fig. 1). The molecular weights of the polymer increased (3.7×10^5 – 5.6×10^5) with increasing $[\text{AN}]$ from 1.138 to 2.276M and then remained constant at 5.6×10^5 at increasing $[\text{AN}]$. This result can be attributed to the excess of monomer acting as a good solvent for the polymer and was explained by Norrish and Smith²⁹ as the action of a good solvent decreasing the mobility of the growing chains, thus decreasing the probability of the binary collision necessary for termination.

Influence of Solvent Concentration

The addition of 20% (v/v) water miscible organic solvents such as acetone, acetic acid, and DMSO to the reaction mixture retarded the initial rate and maximum conversion and then with DMSO the rate and conversion were negligible. Figure 6 shows the effect of acetic acid variation on the rate and percent conversion. The retardation of the reaction in the presence of these solvents may be due to solvation of Cu(II) ions that lessens its complex forming ability with glycine, the net effect of which is a reduction of complex catalysis in the decomposing peroxy orbital; or simultaneous oxidation of the additives by KHSO_5 , thus reducing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer; or premature termination of growing polymer chains resulting from activity transfer to these solvents. The oxidation of compounds such as ethyl alcohol to ethyl acetate and acetic acid to glycolic acid has been established.³⁰

Influence of TiO_2 Percent

TiO_2 is used as a white pigment for the polymer emulsion latexes in surface coating technology; hence, it is very essential to study the effect of the

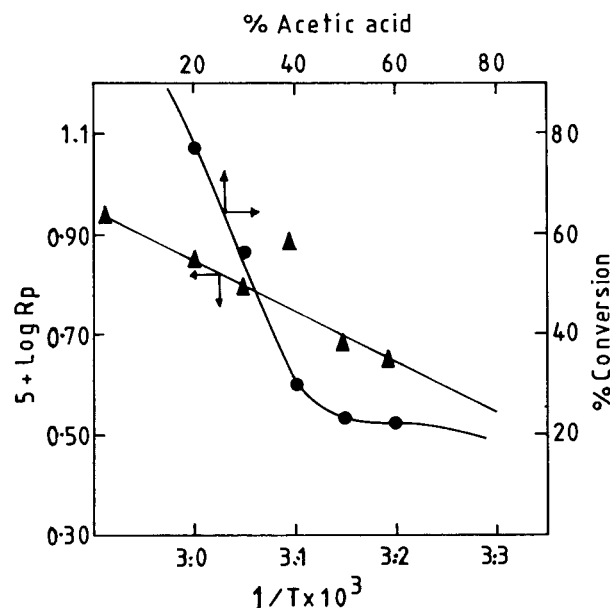


Figure 6 (▲) Arrhenius plot for acrylonitrile polymerization initiated by the Cu(II)/Gly/ KHSO_5 system: (●) variation in conversion % with acetic acid % at $[\text{AN}] = 1.517M$, $[\text{KHSO}_5] = 0.0129M$, $[\text{CuSO}_4] = 0.015M$, and $[\text{Gly}] = 0.03M$ at 50°C .

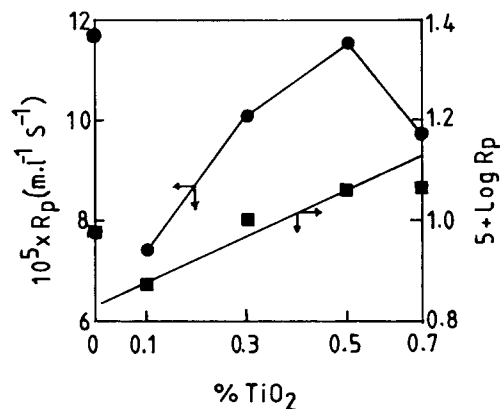


Figure 7 Variation in R_p with $\text{TiO}_2\%$: $[\text{KHSO}_5] = 0.0129M$, $[\text{CuSO}_4] = 0.015M$, $[\text{Gly}] = 0.03M$, and $[\text{AN}] = 1.517M$ at 50°C . (●) $\% \text{TiO}_2$ vs. $(10^5 \times R_p)$, (■) $\% \text{TiO}_2$ vs. $(5 + \log R_p)$.

presence of TiO_2 in the polymerization process medium. The polymerization of AN was carried out at different percentages of TiO_2 (0.1–0.7%) at fixed concentrations of CuSO_4 (0.015M), KHSO_5 (0.0129M), glycine (0.03M), and AN (1.517M) at 50°C for 180 min and the results are plotted in Figure 7. It was found that the rate of polymerization decreased with the addition to TiO_2 because of fewer free radicals formed in its presence. The rate was half-order dependent on the percent TiO_2 .

The Arrhenius plot of $\log R_p$ versus $1/T$ is linear (Fig. 6), giving the activation energy as $4.5 \text{ kcal mol}^{-1}$ (19.1 kJ mol^{-1}), which is much lower than the O—O bond energy in KHSO_5 (34 kcal mol^{-1}), and it should be thermally catalyzed to undergo decomposition at elevated temperature. However, at a low temperature the molecule decomposes because of excess energy released by the Cu(II)–glycine interaction.

Mechanism of Polymerization

The mode of initiator decomposition and the chain initiation and termination mechanism of polymerization involving the novel tricomponent activator system Cu(II)/glycine/ KHSO_5 can be interpreted and explained as below:

1. chain initiation:



