

Synthesis of polyacrylonitrile (PAN) catalyzed by Ni(II)/glycine chelate complex through emulsion polymerization initiated by monopersulphate

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A radical polymer of acrylonitrile (AN) was prepared using a non-conventional complex initiating system Ni(II)/Glycine/KHSO₅ in the absence of an added emulsifier. The polymerization reaction was also carried out in the presence of various divalent transition metal salts, certain amino acids and their chelate complexes in atmospheric oxygen. The metal salts and amino acids with free amino and carboxyl groups have a retarding effect on the polymerization reaction while their chelate complexes have catalytic effect. From among the data, NiCl₂/glycine chelate complex was chosen for detailed kinetic study of acrylonitrile polymerization. The stirring of solution produces dispersion of the insoluble monomer in the continuous phase. The rate of polymerization (R_p) was studied for varying concentration of monomer, initiator, glycine, NiCl₂ and solvents over a temperature range of 40-70°C. The polymers were characterized by molecular weight determination by GPC and viscosity methods. The overall activation energy was computed to be 5.35 kcal mol⁻¹. From kinetic and spectrophotometric study, the mechanism of KHSO₅ decomposition by Ni(II)/glycine complex and initiation of polymerization was suggested.

Emulsifier-free emulsion polymerization of vinyl and acrylic monomers have received much attention because of both practical and academic interests¹⁻¹⁰, and also with a view to synthesize commercial polymers for biomedical, coating and adhesive applications. Several studies were carried out in the field of emulsion polymerization of various monomers using different redox pairs¹¹⁻¹⁴ and metal ions but most of these are performed at high temperature over 70°C under oxygen-free (inert) atmosphere. In previous communications¹⁵, the emulsifier-free emulsion polymerization of acrylonitrile (AN) initiated by KHSO₅ in the presence of inorganic¹⁵ salts CaSO₃ and BaSO₄ and Cu(II)/glycine chelate complex¹⁶ in N₂ atmosphere has been reported. In the present topic more attention has been given to develop a non-conventional initiating system to investigate the emulsifier-free emulsion polymerization of AN in atmospheric oxygen initiated by KHSO₅ catalyzed by *in situ* developed Ni(II)/glycine complex. Aqueous polymerization of AN in oxygen atmosphere¹⁷ has been attempted because of its low cost polymerization technique and wide industrial application in surface coatings technology¹⁸.

Experimental Procedure

Acrylonitrile (AN) from BDH was purified as reported earlier¹⁶. Potassium monopersulphate (KHSO₅) was a gift sample from Du Pont Co., USA and was used as such. Glycine, alanine, leucine were from E. Merck and were used as such. All other reagents were of BDH (AR) grade and were used after purification.

The polymerization experiments were carried out in round bottomed flask containing known concentration of monomer (AN), NiCl₂ and glycine, alanine or leucine. For comparison, a set of experiments with monomer variation was done under N₂ atmosphere. The solution was stirred at 400-600 rpm that is average and has no remarkable effect on the rate of polymerization. A requisite amount of initiator (KHSO₅) was carefully added after 5 min. The pH of the system was found to be 2.8 prior to polymerization. It is found that the agitation produces dispersion of the insoluble monomer in the continuous phase. The reaction is terminated after 180 min by keeping the flask in ice-cold water and by addition, of a known excess of Fe(II) solution, which spontaneously consumed unreacted KHSO₅¹⁹. The precipitated polymers were filtered, washed repeatedly with water and absolute alcohol and dried to constant weight at 60°C. The % conversion and rate of polymerization were calculated gravimetrically. The visible spectra of

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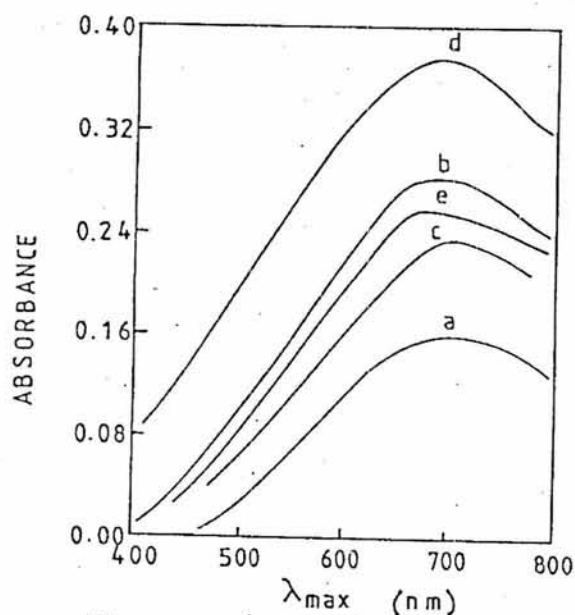


Fig. 1—Spectral evidence for the interaction of NiCl₂ with gly, AN, KHSO₅ at [NiCl₂] = 10.0×10⁻³ mol. dm⁻³, [gly]=10.0×10⁻³ mol.dm⁻³ [AN] = 1.517 mol.dm⁻³, [KHSO₅] = 12.9×10⁻³ mol. dm⁻³ (a) NiCl₂, (b) NiCl₂ + gly, (c) NiCl₂ + gly + KHSO₅, (d) NiCl₂ + gly + AN, (e) NiCl₂ + gly + AN + KHSO₅.

Ni(II), Ni(II)/Glycine complex, Ni(II)/Glycine/AN, Ni(II)/Glycine/KHSO₅ and Ni(II)/Glycine/AN/KHSO₅ were studied by Perkin-Elmer UV-Visible spectrophotometer. The number average (\bar{M}_n) and viscosity average (\bar{M}_v) molecular weights of the purified polymers were determined respectively by Gel Permeation Chromatography (GPC) and Viscosity method in pure DMF at 30°C using the relationship of Shibukawa *et al.*²⁰

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

Results and Discussion

The study of polymerization rate (R_p) and % conversion in AN polymerization catalyzed by various transition metal/glycine chelate complex, initiated by KHSO₅ are presented in Table 1. The results of the studies on the AN polymerization initiated by KHSO₅ catalyzed by Ni(II) salts, amino acids and Ni(II)/amino acid complex in atmospheric O₂ and in N₂ atmosphere are also presented in Table 2. From the result, it is clear that Ni(II)/glycine chelate complex has pronounced catalytic effect than other Ni(II)/amino acid complex. Again

Table 1—Rate of polymerization (R_p) and % conversion in AN polymerization catalyzed by various transition metal/glycine chelate complexes initiated by potassium monopersulphate (KHSO₅)

Transition Metal(II) Salts	Percent Conversion	$R_p \times 10^5$ mol.dm ⁻³ s ⁻¹
Zn(II) SO ₄	36.77	5.16
Cu(II) SO ₄	85.42	12.0
Ni(II) Cl ₂	52.68	7.40
Co(II) SO ₄	58.38	8.26
Mn(II) SO ₄	44.84	6.2

[gly] = 10.0×10⁻³ mol.dm⁻³, [AN] = 1.517 mol.dm⁻³, [KHSO₅] = 12.9×10⁻³ mol.dm⁻³

[M (II)] = 10.0×10⁻³ mol.dm⁻³ at 50°C.

Table 2—Rate of AN polymerization (R_p) catalyzed by various Ni (II) salts, amino acids and Ni(II)/amino acid complex initiated by KHSO₅ at [Ni(II)]=10.0×10⁻³mol.dm⁻³, [Amino acid]=10.0×10⁻³ mol.dm⁻³, [AN]=1.517 mol.dm⁻³, [KHSO₅]=12.9×10⁻³ mol.dm⁻³ at 50°C

Amino acids	$R_p \times 10^5$ mol.dm ⁻³ s ⁻¹			
	NiCl ₂	Ni SO ₄	Ni (OAC) ₂	No Ni(II) Salts
No amino acid				1.65
Glycine	7.40	7.18	6.54	2.69
Alanine	5.84	6.08	5.36	4.12
Leucine	4.96	5.32	4.76	4.97

with glycine, it was found that: R_p [AN/KHSO₅/Gly/Ni(II)] > R_p (AN/KHSO₅) + R_p [AN/KHSO₅/Ni(II)] + R_p (AN/KHSO₅/Gly). Further, NiCl₂/glycine complex has more activation effect as compared to other Ni(II)/glycine complexes. From the value of R_p , NiCl₂ has poor activation, glycine has moderate activation and NiCl₂/gly complex has pronounced activation effect, which is five times greater than the non-catalyzed system.

Fig. 1 shows the visible spectra of various mixtures like Ni(II), Ni(II)/gly, Ni(II)/gly/KHSO₅, Ni(II)/gly/AN, Ni(II)/gly/AN/KHSO₅, measured to obtain complete picture of the interaction between the reacting components and their relationship with the R_p data. The high % conversion and R_p values with Ni(II)/gly couple may be due to the high rate of production of initiating radical by the facile homolysis of the initiator bound by the transient complex Ni(II)/gly, where the internal energy is transferred to the initiator. The novel non-conventional complex initiating system leads to stabilize the emulsion latex to high conversion in absence of an added emulsifier.

Table 3—Effect of concentration of AN, KHSO₅, NiCl₂ and glycine on % conversion, R_p and viscosity average molecular weight (\bar{M}_v) of PAN at 50°C

[AN] mol.dm ⁻³	[KHSO ₅] ×10 ³ mol.dm ⁻³	[Gly] ×10 ³ mol.dm ⁻³	[NiCl ₂] ×10 ³ mol.dm ⁻³	Percent conversion	R _p ×10 ⁵ mol.dm ⁻³	mol.wt \bar{M}_v ×10 ⁴	Percent conversion	R _p ×10 ⁵ mol.dm ⁻³	Mol. wt \bar{M}_v ×10 ⁴
				in atmospheric O ₂			in N ₂ atmosphere		
1.517	12.9	10.0	10.0	52.68	7.40	4.48	58.73	8.18	4.97
1.896	12.9	10.0	10.0	50.18	8.81	5.78	57.16	9.75	6.40
2.276	12.9	10.0	10.0	47.63	10.03	6.62	53.34	12.14	7.82
2.655	12.9	10.0	10.0	43.74	10.75	7.04	49.28	12.97	8.10
3.034	12.9	10.0	10.0	39.34	11.05	7.14	44.54	13.37	8.61
1.517	16.12	10.0	10.0	55.62	7.81	4.98	—	—	—
1.517	19.35	10.0	10.0	59.26	8.32	5.57	—	—	—
1.517	22.57	10.0	10.0	62.14	8.72	5.68	—	—	—
1.517	25.8	10.0	10.0	68.74	9.65	6.23	—	—	—
1.517	12.9	5.0	10.0	44.37	6.23	3.63	—	—	—
1.517	12.9	7.5	10.0	49.28	6.93	4.18	—	—	—
1.517	12.9	12.5	10.0	48.25	6.77	4.06	—	—	—
1.517	12.9	15.0	10.0	42.73	6.00	3.42	—	—	—
1.517	12.9	10.0	5.0	36.56	5.13	3.03	—	—	—
1.517	12.9	10.0	7.5	43.78	6.15	3.59	—	—	—
1.517	12.9	10.0	12.5	46.72	6.56	3.96	—	—	—
1.517	12.9	10.0	15.0	38.43	5.39	3.14	—	—	—
1.517	12.9	10.0	17.5	34.14	4.79	2.91	—	—	—
1.517	12.9	10.0	20.0	30.72	4.31	2.76	—	—	—

Effect of [Monomer]—The rate of polymerization and conversion were found to increase with increasing concentration of monomer [AN] (1.517-3.034 mol.dm⁻³) at fixed concentration of NiCl₂ (10.0×10⁻³ mol dm⁻³), glycine (10.0×10⁻³ mol.dm⁻³), KHSO₅ (12.9×10⁻³ mol.dm⁻³) at 50°C, under atmospheric O₂ and N₂ atmosphere (Table 3). From the double logarithmic plot of rate versus [AN], it has been found that the rate depends on 0.89 power of monomer concentration. The slight deviation from 1st order dependence on [monomer] may be ascribed to more active participation of the monomer in the initiation step that is evident from the decrease of the absorbance of 0.375 (λ_{\max} =685 nm) in NiCl₂/gly/AN to 0.258 (λ_{\max} = 665 nm) in NiCl₂/gly/AN/KHSO₅ (Figs 1d, e). The molecular weights \bar{M}_v and \bar{M}_n of the PAN determined by viscosity and GPC methods increase from 4.48×10⁴-7.14×10⁴ and 4.12×10⁴-6.95×10⁴, respectively with increasing [AN] from 1.517 - 3.034 mol. dm⁻³.

Effect of [Initiator]—The effect of [KHSO₅] on the R_p and % conversion has been studied by varying concentration in the range 12.9×10⁻³ - 25.8×10⁻³ mol. dm⁻³ (Table 3). With increase in monopersulphate concentration in the above range, the maximum conversion and R_p are found to increase due to increase in concentration of active species²¹ resulting in smaller oligomers with higher critical micelle con-

centration (CMC). Therefore, the number of particles will increase, thus increasing the chance of diffusion of the monomer in the particles, as a result, increasing polymerization rate. The overall rate is found from plot of log R_p versus log[KHSO₅] to be 0.46 order dependent on initiator concentration, which is in agreement in normal half order dependence of the rate in conventional free radical polymerization.

Effect of [NiCl₂]—Effect of [NiCl₂] on the R_p and % conversion has been studied by varying its concentration in the range of 5.0-20.0×10⁻³ mol.dm⁻³ (Table 3). Plot of log R_p versus log[NiCl₂] indicated the overall rate to be half (0.5) order dependent on [NiCl₂]. The rate of polymerization was found to be maximum at 10.0×10⁻³ mol. dm⁻³ NiCl₂ and then decreases. The increase in rate may be due to increasing catalysis, since an appropriate mole ratio of Ni(II) to glycine in solution favours the formation of an activated complex, which actively interacts with the peroxo bridge orbital, resulting in cleavage of O-O bond in a sequential fashion. This was evident from the decrease in absorbance from 0.295 (λ_{\max} = 680 nm) for NiCl₂/gly to 0.235 (λ_{\max} = 690 nm) for NiCl₂/gly/KHSO₅ (Figs 1b, c). The decrease in rate may be due to the retardation effect of the transition metal ion, i.e. Ni(II) ion. Further at higher Ni(II) concentration, the decrease in rate may be due to prema-

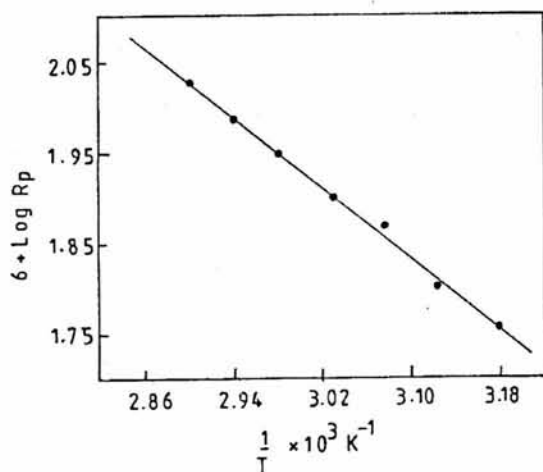


Fig. 2—Arrhenius plot of $\log R_p$ versus $1/T$: $[\text{NiCl}_2] = 10.0 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{gly}] = 10.0 \times 10^{-3} \text{ mol.dm}^{-3}$, $[\text{AN}] = 1.517 \text{ mol.dm}^{-3}$, $[\text{KHSO}_5] = 12.9 \times 10^{-3} \text{ mol.dm}^{-3}$, and temperature = 40 - 70°C.

ture termination of the growing radicals by Ni(III) produced during the reaction.

Effect of [Glycine]—The initial rate of polymerization and the % conversion are found to increase with increasing the concentration of glycine (5.0×10^{-3} – $10.0 \times 10^{-3} \text{ mol. dm}^{-3}$) and then decrease. The overall rate was found to be 0.43 order dependant on [glycine] as calculated from the plot of $\log R_p$ versus $\log [\text{glycine}]$. The enhancement of rate may be due to increase in concentration of Ni(II)/glycine complex, which causes a ready decomposition of initiator to produce initiating radicals at a much greater rate. It may be noted that the catalytic activity of Ni(II) in cleaving the peroxo bond is enhanced by coupling the metal ion with chelating glycine ligand, where a competitive coordination between Ni(II) ion, KHSO_5 and glycine takes place. Because of this competition, the stability of Ni(II)-glycine complex is distorted towards Ni(II)- HSO_5^- interaction and the internal energy of the complex is released in the direction of the peroxo bond, resulting in its breakage. The decrease in absorbance on addition of KHSO_5 to Ni(II)/glycine system may support the explanation (Fig. 1).

Effect of organic solvents—The addition of 20% (v/v) water miscible organic solvents such as methanol and acetic acid to the reaction mixture retarded the conversion % and R_p , then with DMSO the rate and conversion are negligible. The retardation of the reaction in presence of these solvents may be due to (i) solvation of Ni(II) ions, lessening its complex forming ability with glycine, (ii) simultaneous oxida-

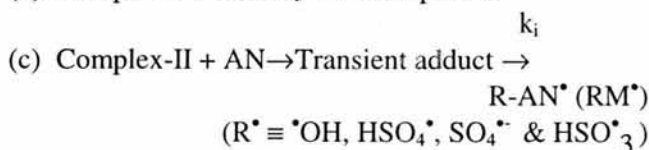
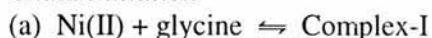
tion of the additives by KHSO_5 , thus reducing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer. The oxidation of compounds such as ethyl alcohol to ethyl acetate and acetic acid to glycolic acid has been established²² (iii) premature termination of growing polymer chains resulting from activity transfer to these solvents.

Effect of temperature and Arrhenius plot—The R_p and % conversion have been investigated by varying the temperature in the range 40–70°C. The result shows with increase in temperature both R_p and % conversion increase. From the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 2) the overall activation energy of polymerization was found to be $5.35 \text{ kcal mol}^{-1}$ ($20.48 \text{ kJ mol}^{-1}$).

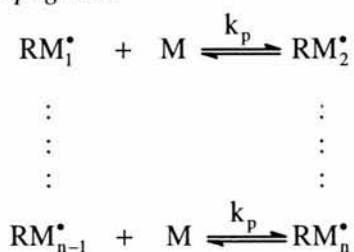
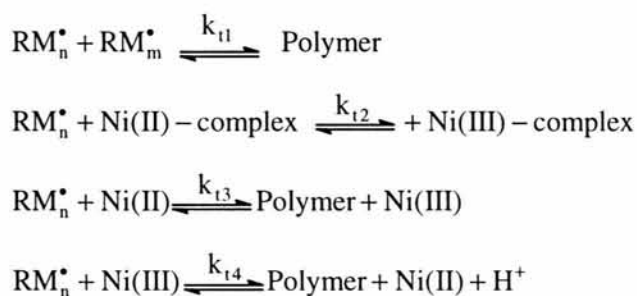
Mechanism—The mode of initiator decomposition, chain initiation and termination mechanism of polymerization involving a novel tricomponent activator system Ni(II)/gly/ KHSO_5 can be explained from the proportionalities obtained between measurable parameters and variables ($R_p \propto [\text{Ni(II)}]^{0.50} [\text{gly}]^{0.43} [\text{KHSO}_5]^{0.46} [\text{AN}]^{0.89}$).

The reaction involves a complex initiation mechanism, which can be interpreted as proceeding through a novel catalytic path induced by the transient 1:1, Ni(II):Gly complex. The initiation is a surface catalysis with adequate energy transfer from the complex to the initiator molecule. Also the complex stabilizes the emulsion latex leading to high conversion even without an added emulsifier.

Chain Initiation



Out of the free radicals produced above as reported elsewhere, the actual initiating species may be proposed as HSO_3^{\bullet} which is not inhibited by O_2 in the atmosphere. This has been reported by Bajpai¹⁷. This has been further indicated by the detection of SO_3^- end-groups. The other radicals OH^{\bullet} , HSO_4^{\bullet} and $\text{SO}_4^{\bullet-}$ formed may be inhibited by O_2 because the R_p , conversion and \bar{M}_n of the polymers were found to decrease by 10–15% in comparison under N_2 atmosphere (Table 3).

Propagation**Termination****Conclusion**

The most interesting and significant outcome of the paper is the conversion of inhibitors/retarders (metal ions and O₂) into accelerators of polymerization by the *in situ* developed complex of NiCl₂/amino acid. The results indicate that the new novel non-conventional complex initiating system is able to stabilize the emulsion latex²³ leading to high conversion in much the same way as a polymerizable surfactant/emulsifier.

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