Cobalt(III)-Mediated Microemulsion Polymerization of Acrylonitrile: Kinetics and Particle Morphology

Prafulla K. Sahoo,[1] Bijayashree Samal,[1] Sarat K. Swain[2]

[1]Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751004, India
[2]ICFAI Institute of Science & Technology, Fortune Tower, Chandrasekharpur, Bhubaneswar 751023, India

ABSTRACT: The catalytic effect of *trans*-dichloro-bis(ethylenediamine)cobalt(III) chloride (*trans*-[Co(en)$_2$Cl$_2$]Cl) complex on the microemulsion polymerization of acrylonitrile, in the absence of added emulsifier, was investigated. Polymerization was studied at varying concentrations of initiator, monomer, complex, and solvent over the temperature range of 30–70°C. The overall activation energy (E_a, 39.26 kJ/mol), energy of dissociation of initiator (E_d, 61.62 kJ/mol), number of micelles (0.122 × 10^{18}), and viscosity average molecular weight of the polymer were computed. The distribution of particle sizes was determined by transmission electron microscopy (TEM). It was found that the oil-in-water microemulsion polymerization was stabilized by the presence of the Co(III) complex, reducing the particle size into the nano range. The average diameters of PAN nanoparticles, obtained by TEM, were in the range of 50–150 nm at maximum conversion. The experimental particle size was mainly dependent on the concentration of complex and temperature. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3120–3126, 2004

Key words: microemulsion; Co(III) complex; nanoparticle; kinetics; TEM

INTRODUCTION

In a conventional emulsion process, the presence of absorbed surfactant gives rise to somewhat variable properties and applications. The use of a non-conventional process, in the absence of surfactant or emulsifier, will help in eliminating the complicated, costly, and time-consuming process of removal of surfactants. Emulsifier-free emulsion polymerization of vinyl and acrylic monomers has received much attention because of both practical and academic interests,[1–10] and also with a view to synthesize commercial polymers for biomedical, coatings, and adhesive applications. Again, microemulsion polymerization has gained its importance in past years[11–13] because the microemulsion medium allows polymerization of various monomers, which differ appreciably in their polarity and reactivity. Use of a microemulsion controls the macromolecular characteristics and later particle morphology.

In our earlier publications, we reported on the kinetics of emulsifier-free emulsion polymerization of acrylonitrile initiated by KHSO$_5$ in the presence of in situ developed complexes of transition metals and amino acids, viz. Cu(II)/glycine,[14] Ni(II)/glycine,[15] Co(II)/glycine,[16] and Cu(II)/H$_2$salen.[17] The present research work relates to the development of a new catalyst of freshly prepared *trans*-[Co^{III}(en)$_2$Cl$_2$]Cl on microemulsion polymerization of acrylonitrile initiated by ammonium persulfate. The new Co(III)-complex system is not only found to stabilize the emulsion latex leading to high conversion in the absence of any added emulsifier but also is successful in decreasing the size of the particles to the nano range. This interesting findings prompted us to make use of the Co(III) complex over our previous Co(II)/glycine system.[16] Further, this has come as an advantage over the developed PMMA nano composites by conventional emulsion method with the use of emulsifier and silicate additives.[18] Another advantage of this emulsifier-free microemulsion polymerization is explained by the fact that a high concentration of surfactant/emulsifier is considered as one of the main drawbacks of microemulsion polymerization due to difficulties in removing the residual emulsifier from the nanoparticle surfaces.[19]
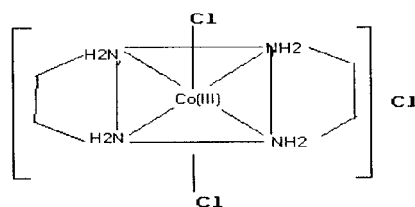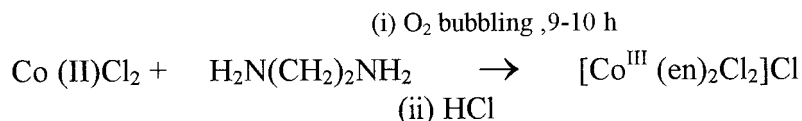
EXPERIMENTAL

Acrylonitrile of BDH (AR) grade was purified as reported earlier.[20] Ammonium persulfate [APS], cobalt(II) chloride, ethylene diamine, and other reagents were of BDH (AR) grade and used after purification.

(i) O_2 bubbling, 9-10 h

$$Co(II)Cl_2 + H_2N(CH_2)_2NH_2 \quad \rightarrow \quad [Co^{III}(en)_2Cl_2]Cl$$

(ii) HCl

Scheme 1

Preparation of the complex trans-[Co^{III}(en)$_2$Cl$_2$]Cl

The complex was prepared by treating Co(II) chloride hexahydrate (CoCl$_2$ · 6H$_2$O) with a 10% solution of ethylene diamine according to the literature method.[21] A solution of ethylene diamine hydrate in water was slowly added with stirring to a solution of Co(II) chloride hexahydrate in water and air-oxidized vigorously for 9–10 h; concentrated HCl was then added to the oxidized solution. The mixture was evaporated on a steam bath until a crust formed over its surface. This was then cooled and allowed to stand overnight, when bright green platelets of the hydrochloride of the complex were separated out. The crystals were filtered off, washed with ether, recrystallized in presence of concentrated HCl, and then dried at 110°C until a solution of the complex in distilled water was neutral to litmus. The formation of the complex [Co^{III}(en)$_2$Cl$_2$]Cl was confirmed by UV-spectral analysis (Scheme 1).

Polymerization

The polymerization experiments were carried out in a round-bottomed flask containing known concentrations of monomer (AN), Co(III)-complex solution in water under nitrogen atmosphere. A required amount of initiator (APS) solution was carefully added after maintaining constant temperature. The pH of the solution was found to be 4.2, before and after the polymerization, with an E-Merck (Germany) digital pH meter. After the desired time of 4–4.5 h, the polymerization was terminated by keeping the flask in ice-cold water and by adding a known excess of ferrous ammonium sulfate solution, which spontaneously consumed unreacted initiator.[22] The precipitated polymers were filtered, washed repeatedly with distilled water and absolute alcohol, and then dried to constant

weight at 60°C. The percent conversion and rate of polymerization were calculated gravimetrically. The UV–visible spectra of trans-[Co(en)$_2$Cl$_2$)Cl] complex, complex/AN, complex/AN/APS, and AN/APS were studied using a Perkin-Elmer UV–vis spectrophotometer.

Characterization

The viscosity average molecular weights of the purified polymers were determined by using a Ubbelohde viscometer in pure DMF at 30°C, with the equation[23]

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

Particle size was investigated by TEM (Joel JEM 2000-Ex11). Samples were prepared by dropping highly diluted latex on a carbon-coated copper grid and dried in a desiccator at room temperature.

RESULTS AND DISCUSSION

From the series of experiments, it was found that the isolated complex trans-[Co(en)$_2$Cl$_2$]Cl had a pronounced catalytic effect on the polymerization reaction of AN initiated by APS as compared to the noncatalyzed system (Table I). The possibility of Co^{III}-complex initiated polymerization was excluded by the fact that no polymer was precipitated in absence of APS even after 48 h. Figure 1 shows the UV–visible spectra of various mixtures like CoCl$_2$ (a), trans-[Co^{III}(en)$_2$Cl$_2$]Cl complex (b), complex/APS (c), and complex/AN/APS (d), measured to obtain a complete picture of the interaction between reacting components and their relationship with the rate data. The high conversion may be ascribed to the high rate of production of initiating radicals by facile homolysis of

TABLE I
Effect of Concentration of AN, $(NH_4)_2S_2O_8$, and $[Co^{III} (en)_2Cl_2]Cl$ on % Conversion, R_P, and Viscosity Average Molecular Weight (Mv) of PAN at 50°C

[AN] (mol dm^{-3})	$[(NH_4)_2S_2O_8]$ ($\times 10^3$ mol dm^{-3})	$[[Co^{III} (en)_2Cl_2]Cl]$ ($\times 10^3$ mol dm^{-3})	% Conversion	$R_p \times 10^5$ (mol dm^{-3} S^{-1})	Mol wt 10^4
1.51	10	0.0	8.1	0.8	1.78
0.759	10	10	12.40	2.43	2.30
1.51	10	10	15.2	6.08	3.24
2.27	10	10	29.04	25.40	4.14
3.03	10	10	90.40	14.66	5.14
3.79	10	10	41.68	14.36	
4.53	10	10	34.03	3.26	
1.51	15	10	23.20	4.12	
1.51	20	10	27.23	5.0	
1.51	25	10	36.54	7.46	
1.51	30	10	53.03	7.7	
1.51	10	15	55.21	8.1	
1.51	10	20	61.3	8.9	
1.51	10	25	48.3	7.01	
1.51	10	30	40.6	5.8	

the initiator bound by the transient complex *trans*-$[Co^{III}(en)_2Cl_2]Cl$, where the internal energy is transferred to the initiator. The new non-conventional complex initiating system helps stabilize the emulsion latex to a high conversion level in the absence of added emulsifier.

A preliminary study on the particle morphology was carried out by TEM micrographs. Average particle sizes (diameters) of the nanoparticles were calculated by evaluating micrographs containing about 300–450 particles. Again, it is observed in Table II that the particle size distribution decreases with increasing
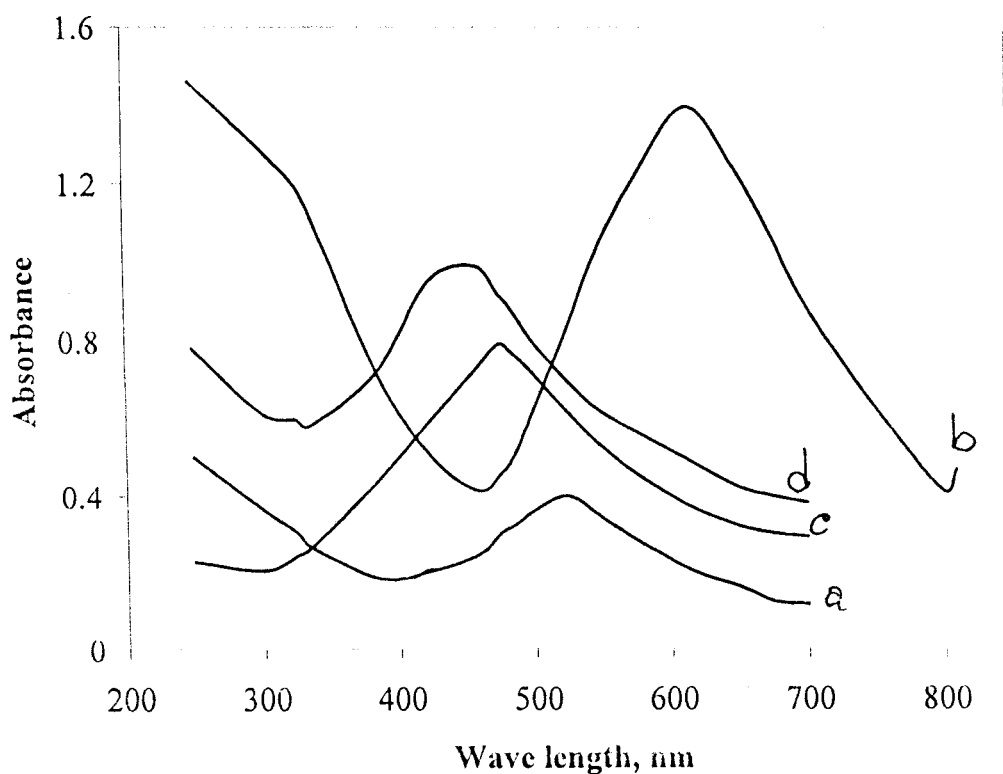

Figure 1 Spectral evidence for the interaction of $[Co^{III}(en)_2Cl_2]$ Cl with acrylonitrile, APS at $[Co^{III}(en)_2Cl_2]Cl = 10 \times 10^{-3}$ mol dm^{-3}, [AN] = 1.51 mol dm^{-3}, [APS] = 10.0×10^{-3} mol dm^{-3} (a) CoCl$_2$, (b) $[Co^{III}(en)_2Cl_2]Cl$, (c) $[Co^{III}(en)_2Cl_2]Cl$ + APS, (d) $[Co^{III}(en)_2Cl_2]Cl$ + AN + APS.

TABLE II
Variation of Particle Size and % Conversion at Different Temperatures and Concentrations of Complex at [AN] = 1.51 mol dm⁻³, [APS] = 10.0 × 10⁻³ mol dm⁻³

[[Co^{III} (en)$_2$Cl$_2$]Cl] ($\times 10^3$ mol dm^{-3})	Temperature, (°C)	% Conversion	Diameter of particle (nm)
10	50	15.20	67
15	50	55.21	82
20	50	61.30	98
25	50	48.30	122
30	50	40.60	148
10	55	39.12	57
10	60	53.66	48
10	65	56.42	42
10	70	72.98	34

This is attributed to the increase in concentration of active species resulting in smaller oligomers with higher critical micelle concentration (CMC). The rate of polymerization depends on the number of primary free radicals generated from initiator decomposition and hence with the increased initiator concentration, the number of primary free radicals, and R_P increase. Therefore, the number of particles will increase, thereby increasing the chance of diffusion of the monomer in the particles: as a result, the rate of polymerization increases. The overall rate is found from the plot of log R_P versus log [APS] to be 0.94-order dependent on [initiator], which is near to first-order dependence on the rate in the conventional free radical polymerization.

Effect of organic solvents

The addition of concentrated organic solvents such as acetic acid, acetone, and benzene to the reaction mixture retarded the percent conversion and R_P. In fact,
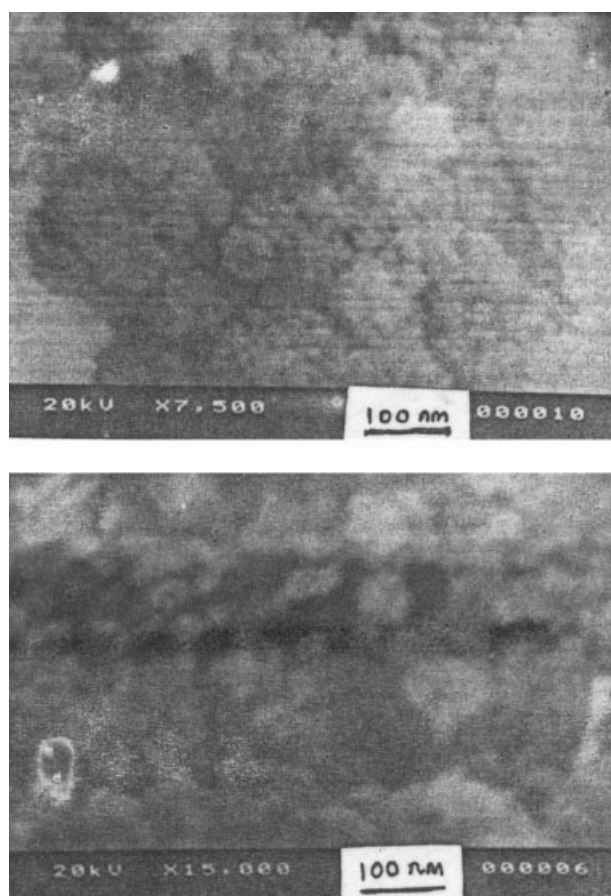
temperature, and the result is in good agreement with the literature.[24] Also, the average diameter of particles as determined from TEM (Fig. 2) at different conversions is in the range 50–150 nm (Table II).

It was found that the conversion was strongly affected by the monomer, initiator, complex concentrations, and also by the reaction time and temperature.

Effect of monomer concentration

The polymerization of AN with monomer variation (0.759–4.53 mol dm^{-3}) clearly indicates that the rate of polymerization and conversion increase with increase in monomer concentration at fixed concentration of complex trans-[Co^{III}(en)$_2$Cl$_2$]Cl (10.0 × 10^{-3} mol dm^{-3}), APS (10.0 × 10^{-3} mol dm^{-3}) at 50°C under N$_2$ atmosphere (Table I). From the double-logarithm plot of rate versus [AN], the rate has been found to depend on the 0.56 power of monomer concentration. The deviation from first-order dependence may be ascribed to more active participation of monomer in the initiation step. Further, a value of order less than 1 has also been cited in the literature, as Chapiro[25] found the monomer exponent varying from 1 to < 1, and the findings were attributed to the presence of impurity in the polymerization system. In addition, deviation from unity is normally observed as the polymerization system is heterogeneous in nature.[26]

The average molecular weight $\bar{M}_V$ of PAN determined by viscosity was found to increase from 3.24 × 10^4 to 5.14 × 10^4 with [AN] increasing from 1.517 to 3.034 mol dm^{-3}.

Effect of initiator concentration

The effect of [APS] on the conversion was studied by varying concentration in the range (10.0 × 10^{-3})–(30.0 × 10^{-3}) mol dm^{m3}. It was found that the rate of polymerization and conversion increase with [APS].

Figure 2 TEM micrographs of PAN particles at different magnifications obtained by the complex-catalyzed microemulsion polymerization at [Co^{III}(en)$_2$Cl$_2$]Cl = 10 × 10^{-3} mol dm^{-3}, [AN] = 1.51 mol dm^{-3}, [APS] = 10 × 10^{-3} mol dm^{-3} at 50°C for 4 h.

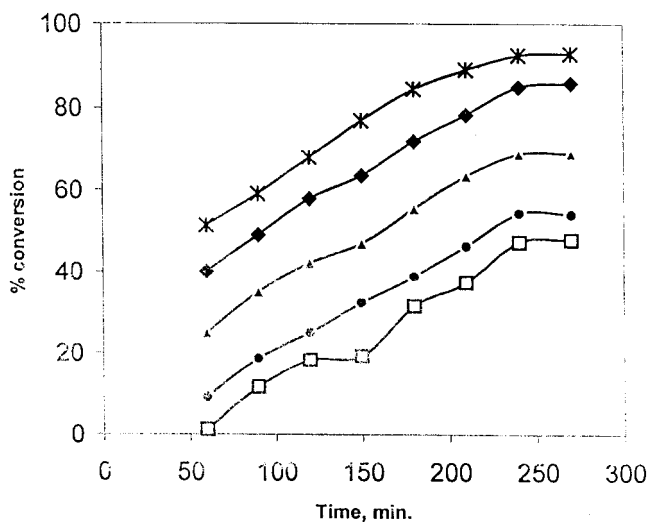**Figure 3** Variation of percent conversion with reaction time for $[Co^{III}(en)_2Cl_2]Cl$ complex-catalyzed polymerization of AN with $[Co^{III}(en)_2Cl_2]Cl = 10 \times 10^{-3}$ mol dm^{-3}, [AN] = 1.51 mol dm^{-3}, [APS] = 10×10^{-3} mol dm^{-3} at various temperatures: (□) 50°C, (●) 55°C, (✿) 60°C, (▲) 65°C, (■) 70°C.

the conversion is negligible in the case of benzene. The retardation of the reaction in presence of these solvents may be due to reduction of Co(III) to Co(II) and simultaneous oxidation of additives by APS, thus reducing the optimum concentration of the initiating radicals in the immediate vicinity of the monomer (the oxidation of acetic acid to ethyl acetate has been established[24]) and also due to premature termination of growing polymer chains resulting from activity transfer to those solvents.

Effect of complex concentration

R_P and percent conversion increase with increase in trans-$[Co^{III}(en)_2Cl_2]Cl$ concentration from 10.0×10^{-3} to 20.0×10^{-3} mol dm^{-3} and then decrease (Table I), which is due to the high concentration of complex of the AN/APS/trans-$[Co^{III}(en)_2Cl_2]Cl$ system. The rate is found to be 0.75-power dependent on trans-$[Co^{III}(en)_2Cl_2]Cl$ concentration. From the experimental evidence, it is observed that particle size increases with increase in concentration of complex at decreasing temperature (Table II). Hence it may be suggested that the polymerization was stabilized by the presence of the complex with reduction of the particle size into the nano range.[27]

Effect of time variation

The polymerization of AN was carried out over a time range of 60 min up to 270 min (Fig. 3). It was found that conversion increased steadily with time up to 240

min and then decreased, perhaps due to a high population of free radicals with increase in duration of polymerization.

Effect of temperature and arrhenius plot

The R_P and percent conversion were investigated by varying the temperature in the range of 50–70°C. The results showed a steady increase in both R_P and percent conversion up to a temperature of 70°C.

From the Arrhenius plot of log R_P versus $1/T$ (Fig. 4), the overall activation energy, E_a, was found to be 39.26 kJ/mol and, taking $E_P = 16.2$ kJ/mol, $E_t = 15.5$ kJ/mol reported for AN,[28] the activation energy for initiator decomposition was found to be 61.62 kJ/mol by using the formula

$$E_a = E_p - E_t/2 + E_d/2,$$

and the number of micelles, 0.122×10^{18} against the theoretical values[27] of 10^{18}, characteristics of emulsifier-free emulsion polymerization. Figure 5 shows the relationship between R_p with the reciprocal of DP of PAN at different initiator concentrations at 50°C. The linear relationship observed excludes any significant chain transfer to the initiator in the present system. As the conversion depends upon the rate of production of primary free radicals from the initiator decomposition, the number of primary free radicals generated from the initiator decomposition increases with increasing temperature.

Mechanism

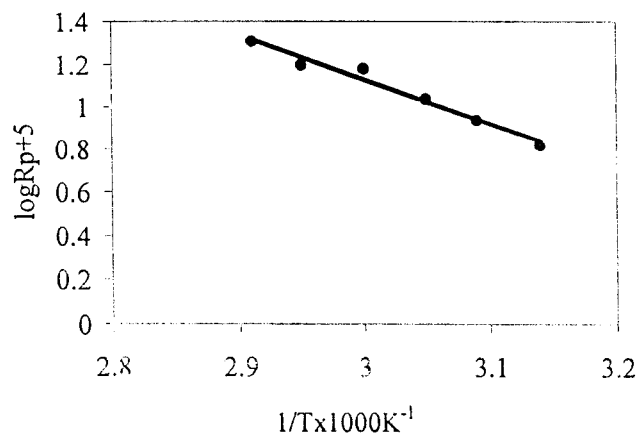The microemulsion mechanism involves the following steps:

Figure 4 Arrhenius plot of log R_P versus $1/T$ at $[Co^{III}(en)_2Cl_2]Cl = 10 \times 10^{-3}$ mol dm^{-3}, [AN] = 1.51 mol dm^{-3}, [APS] = 10×10^{-3} mol dm^{-3} .
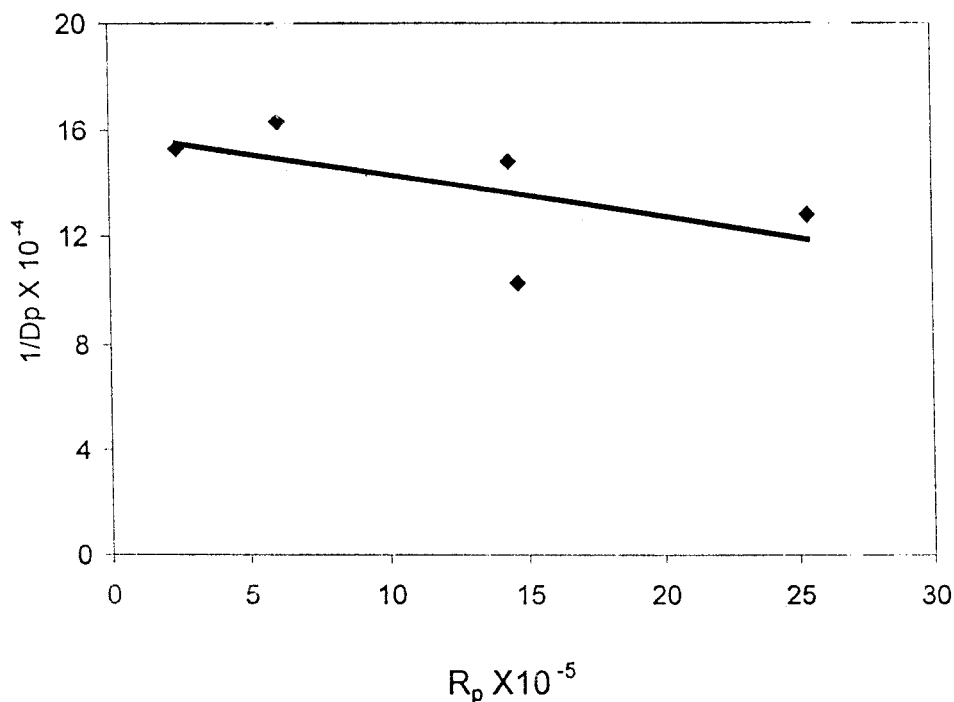
Figure 5 Dependence of the reciprocal of degree of polymerization (1/DP) of AN on R_P on varying [APS] from 10.0×10^{-3} to 30.0×10^{-3} mol dm^{-3} at [AN] $= 1.51$ mol dm^{-3}, [Co^{III}(en)$_2$Cl$_2$]Cl $= 10 \times 10^{-3}$ mol dm^{-3} at 50°C.

I. Production of free radicals (SO$_4^-$ ·) from initiator decomposition catalyzed by Co(III) complex, as shown in Scheme I.
II. Production of free radicals in an aqueous phase to form oligomeric free radicals or to precipitate homogeneously from the aqueous phase and to form colloidal particles.
III. Capture of free radicals by monomer swollen micelles or monomer droplets.
IV. Termination of free radicals in the aqueous phase, leading to a capture efficiency less than 100%.

The rate of complex catalysis has been found to be dependent on the proportions obtained as below, and the rate expression is derived applying the steady-state principle and assuming mutual termination:

$$R_P \propto [AN]^{0.57} [APS]^{0.84} [complex]^{0.75}$$

CONCLUSION

The most significant outcome of this research described herein is the development of a novel nonconventional initiating system leading to stabilizing the emulsion latex to a high conversion in absence of added emulsifier. The *trans*-[Co(en)$_2$Cl$_2$]Cl complex most likely plays the role of surfactant in decreasing the latex particles to the nano-order scale. The poly-mer latex was characterized by TEM (size and morphology) and molecular weight measurements. Nano-scale latex particles could be obtained without emulsifier more easily than in a conventional emulsion polymerization. Hence it is a promising technique for the preparation of polymer nanoparticles and nanocomposites that are under study in our laboratory.

References

1. Chem, S. A.; Tai, S. L. Macromolecules 1991, 24, 3340.
2. Shouldice, G. T. D.; Vanderzande, G. A.; Rudin, A. Eur Polym J 1994, 30(2), 129.
3. Song, Z.; Poehlein, G. W. J Polym Sci Part A: Polym Chem 1990, 28, 2359.
4. Harkins, W. D. J Am Chem Soc 1997, 69, 1428.
5. Smith, W. V.; Ewart, R. W. J Chem Phys 1948, 16, 192.
6. Fitch, R. M.; Tsai, C.H. In Polymer Colloids; Plenum: New York, 1971.
7. Fitch, R. M. Br Polym J 1973, 5, 467.
8. Moustafa, A. B.; EL-Latif, Z. R.; Amer, L. I.; Sayah, S. M. Acta Polym 1986, 38, 137.
9. Feeney, I. J.; Napper, D. H.; Gilbert, R. G. Macromolecules 1987, 20, 2912.
10. Arabina, L. L.; Barandiaram, M. J.; Gugliotta, L. M.; Asva, J. M. Polymer 1997, 38, 143.
11. Roy, S.; Devi, S. J Appl Polym Sci 1996, 62, 1509.

12. Zang, I.; Zeng, Z.; Chen, Y.; Wu, C.; Gao, J. J Appl Polym Sc 1997,66, 2543.
13. Xiangling, X.; Xuewur, G.; Zicheng, Z.; Manwei, Z. Polymer 1998, 39, 5321.
14. Sahoo, P. K.; Dey, M.; Swain, S. K. J Appl Polym Sci 1999,74 (12), 2785.
15. Swain, S. K.; Sahoo, P. K. Indian J Chem Technol 2000, 7, 259.
16. Swain, S. K.; Sahoo, P. K. Arab J Sci Eng 2002, 27(IA), 55.
17. Sahoo, P. K.; Sahoo, G. C.; Swain, S. K. Eur Polym J 2002, 38, 345.
18. Huang, X.; Brittain, W. J. Macromolecules 2001, 34, 3255.
19. David, G.; Ozer, F.; Simionescu, B. C.; Zareie, H.; Piskin, E. Eur Polym J 2002, 38(1), 73.
20. Eliseeva, V. I. Emulsion Polymerization and Application in Industry; Consultants Bureau: New York, 1981.
21. Krisnamurthy, M. J Inorg Nucl Chem 1972, 34, 3915.

22. Sahoo, P. K.; Send, S.; Samantaray, H. S.; Samal, R. K. J Ind Chem Soc 1986, 53, 210.
23. Shibukawa, T.; Sumo, M.; Vehida, A.; Sawahori, K. J Polym Sci Polym Chem Ed 1986, 61, 147.
24. Sangri, P. G.; Pokhrial, N. K.; Devi, S. Polym Int 2002, 51(8), 721.
25. Chapiro, A. J Chem Phys 1995, 52, 568.
26. Odian, G.; Principles of Polymerization; John Wiley and Sons: New York, 1981, p 205.
27. Capek, I.; Jeranicova, V. Polym J 2002, 32(2), 91–96..
28. McKenna, T. F.; Santos, A. M. In Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1999; Vol II, p 415.
29. Carraher, C. E. Polymer Chemistry, 5th ed.; Marcel Dekker, Inc.: New York, 2000.