Synthesis and kinetics of ‘crumpled’ PMMA latex by non-conventionally initiated emulsion polymerization

Roomky Mohapatra & Prafulla K Sahoo*
Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751 004, India

Received 29 July 2004; revised received 24 January 2005; accepted 21 February 2005

The aqueous emulsifier-free emulsion polymerization of methyl methacrylate (MMA) was studied under the catalytic effect of a prepared complex, [Cu(NH₃)₄]SO₄, with various initiators like potassium peroxodisulphate (KPS), potassium monopersulphate (KMPS) and ammonium persulphate (APS). The apparent activation energies $E_a$ were found to be 36.52 (KMPS), 40.47 (KPS) and 31.9 kJ/mol (APS). The activation energies of initiator decomposition $E_d$ were found to be, 31.04, 38.93 and 21.79 kJ/mol for KMPS, KPS and APS, respectively. The emulsion polymer (PMMA) latex was characterized through the determination of the size and morphology by scanning electron microscopy (SEM), FTIR spectroscopy, the average molecular weight by GPC and viscosity methods. The surface of the polymer latex was found to be somewhat ‘crumpled’. From the kinetic results, the rates of polymerization, $R_p$ at 50°C were determined.

Keywords: Non-conventional emulsion, complex catalyst, kinetics, SEM

IPC Code: C08F2/32

Conventional emulsion polymerizations begin with a mixture of water, monomer, initiator and emulsifier. The role of the emulsifier is crucial and multifaceted1 enabling the emulsification of the monomer into micron or even sub-micron sized droplets and stabilizing the resulting polymer particles during nucleation, growth and storage of the final latex. But the use of surfactants as in conventional methods has a disadvantage of not being removed completely2. So the use of non-conventional emulsifier-free process helps in eliminating the complicated, costly and time consuming process of removal of the surfactants. There have been reports on various mechanisms on particle formation and growth in polymer latex without emulsifiers3,4. Emulsifier-free emulsion polymerization of various vinyl and acrylic monomers has received much attention because of both practical and academic interests5-16 and also with a view to synthesizing commercial polymers for biomedical purposes, as coatings, magnetic materials or as adhesives. Again, the use of complex catalyzing system as an emulsifier free emulsion system in the synthesis of various polymeric latex particles has also been reported17-22. The complex systems used in these studies are all in situ developed systems i.e., the complexes are developed in the bulk media itself and also some of the papers report the development of polymer nanoparticles by this novel technique.

In the present study, attempts were made to study the catalytic effect of a complex on the oil in water ($o/w$) homopolymerization of MMA with three initiators namely ammonium persulphate (APS), potassium persulphate (KPS), and potassium monopersulphate (KMPS). The effect of the initiators on the polymerization was studied and compared. In addition to this, detailed kinetics and surface morphology of the polymeric latex were studied.

Experimental Procedure

Materials
Methyl methacrylate (MMA), (BDH, UK) was purified as reported earlier23. The initiators APS (SRL, India), KPS (E Merck, Germany) and KMPS (gift from Du Pont Co., USA) were used as received. All other reagents were of BDH (AR) grade and were used after purification by standard techniques.

Preparation of complex
A solution of 10 g of finely divided CuSO₄·5H₂O in 15 mL of concentrated NH₃ and 10 mL of water was filtered and precipitated by slow addition of 15 mL of alcohol. After standing for several hours in cold,
crystals were filtered on a Buchner funnel, washed with a mixture of alcohol and concentrated ammonia (1:1) and then with alcohol and ether, and dried by suction and stored in a desiccator for further use.

**Synthesis of PMMA**

The oil in water (o/w) emulsion polymerization was carried out in a round-bottom flask containing known concentrations of the complex and the monomer (MMA), in N₂ atmosphere. The solutions were stirred at 400-500 rpm, which helped in the formation of micelles in the complex medium. The speed in this range has no remarkable effect on the rate of polymerization. The requisite amounts of the initiator solutions were carefully injected to the reaction mixture. With the addition of the initiator the deep blue colour due to the complex, fades away and subsequently turns dusky due to the initiation of the polymer. The change in colour is characterized by taking the UV-visible spectra of the system. The pH of the medium is shown in Table 1. The reaction was stopped by keeping the flask in ice-cold water and by addition of a known excess of hydroquinone, which spontaneously consumed the unreacted free radicals. The precipitated polymers were filtered and purified by washing repeatedly with distilled water and absolute alcohol. Then they were dried at about 60°C till a constant weight. The percentage conversion and the rate of polymerization (\(R_p\)) were determined gravimetrically.

**Characterization**

The visible spectra of the complex as well as those of the monomer and the initiators were studied using a Perkin-Elmer UV-Visible spectrophotometer model Lambda-20. The morphology of the PMMA samples were measured by model number 5200 Scanning electron microscope (SEM), Jeol Ltd, Japan. The FTIR spectra of the samples were taken with a Perkin-Elmer Paragon 500 FT-IR spectrophotometer using KBr pellets. The average molecular weights of the purified samples were determined by using methods such as GPC (\(M_n\)) and intrinsic viscosity (\(\eta_sp\)) using the relationship of Mark-Houwink-Sakurada in pure benzene at 30°C:

\[
[\eta] = 5.20 \times 10^{-5} M^{0.7}.
\]

**Results and Discussion**

The results of the polymerization of MMA catalyzed by [Cu(NH₃)₄]SO₄ complex with various initiator systems are shown in Table 2. It was found that the conversion and the \(R_p\) were strongly affected by the monomer, initiator and complex concentrations, by the reaction time and temperature and also by the pH of the system. The possibility that the complex may itself act as an initiator was ruled out as the yield was negligible in the absence of the initiators.

**Effect of time**

Figure 1 shows the variation of percentage conversion of MMA with the reaction time at 50°C for all the initiator systems keeping the concentrations of MMA, initiator and complex constant at 0.94×10⁻³, 10.0×10⁻³ mol dm⁻³, respectively. It was found that for all the three initiator systems the conversion increases rapidly till 2-3.5h. However, after 4 h, the percentage conversion slows down asymptotically confirming the dead end polymerization tendency of PMMA. A dead end
polymerization refers to a polymerization in which the initiator concentration decreases to such a low value that the half-life of the propagating polymer chains approximates that of the initiator. Under such circumstances the polymerization stops short of completion and this results in a limiting conversion of monomer to polymer at infinite reaction time\textsuperscript{25}. 

**Effect of temperature and determination of activation energy**

The Arrhenius plot of log \( R_p \) versus \( 1/T \) was found to be linear (Fig. 2) with a negative slope and the activation energy was computed to be 36.52, 40.47 and 31.9 kJ/mol for KMPS, KPS and APS, respectively which is very low as compared to the standard value of 47 kJ/mol for peroxo compounds. In most of the conventional polymerization, the overall activation energy \( (E_a) \) of the polymerization is related to the activation energies of initiator decomposition \( (E_d) \), propagation \( (E_p) \) and termination \( (E_t) \) by the following equation:

\[
E_a = E_p + E_t/2 + E_d/2
\]

Taking \( E_a = 29 \) kJ/mol, \( E_t=16 \) kJ/mol reported for MMA\textsuperscript{26} and \( E_a = 36.52, 40.47 \) and 31.9 kJ/mol for KMPS, KPS and APS, respectively from Fig. 2, the respective activation energy for initiator decomposition, \( E_d \) was found to be, 31.04, 38.93 and 21.79 kJ/mol which is much lower than the standard value of 56.6 kJ/mol and 137 kJ/mol for \( t \)-butyl perbenzoate\textsuperscript{27}. 

### Variation of monomer concentration

The conversion and the rate of polymerization reaction increase with the increase in monomer concentration (0.470-1.882 mol dm\(^{-3}\)) at a fixed concentration of the other reagents at 50°C. The results are presented in Table 2. From the double logarithmic plot of \( R_p \) versus [MMA], the rate of polymerization was found to be 0.72 (KPS), 1.01 (KMPS) and 0.93 (APS) powers dependent on the monomer concentration. This may be attributed to the greater rate of participation of the monomer in the initiation step. Under KPS medium the \( R_p \) value was less than first order, which may be due to the presence of impurity in the polymerization system. These types of findings have already been reported by Chapiro\textsuperscript{28}. 

![Fig. 2—Arrhenius plot of log \( R_p \) versus \( 1/T \) at [Complex]=10.0×10\(^{-3}\), [MMA]=0.941, [KPS]=10.0×10\(^{-3}\), [KMPS]=10.0×10\(^{-5}\) & [APS]=10.0×10\(^{-5}\) mol dm\(^{-3}\) for 3 h.](image)

<table>
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<th>[MMA] mol dm(^{-3})</th>
<th>[Complex] ( \times 10^{-3} ) mol dm(^{-3})</th>
<th>[Initiator] ( \times 10^{-3} ) mol dm(^{-3})</th>
<th>% conversion</th>
<th>( R_p \times 10^5 ) mol dm(^{-3}) s(^{-1})</th>
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Table 2—Effect of the concentrations of MMA, complex, initiator on the % conversion, \( R_p \) and molecular weight at 50°C for 3h.
The molecular weights $M_n$ and $M_v$ of the PMMA samples determined by GPC and viscosity methods are found to increase $0.48 \times 10^5$ - $0.72 \times 10^5$ and $0.59 \times 10^5$ - $1.92 \times 10^5$ for KPS; $0.39 \times 10^5$ - $0.63 \times 10^5$ and $0.72 \times 10^5$ - $1.88 \times 10^5$ for KMPS; and $0.41 \times 10^5$ - $0.86 \times 10^5$ and $0.89 \times 10^5$ - $2.83 \times 10^5$ for APS with increase in MMA concentration (Table 2).

**Variation of initiator concentration**

The effects of the $R_p$ and the conversion have been studied by varying the concentrations of the initiators in the range $5.0 \times 10^{-3}$ to $25.0 \times 10^{-3}$ mol dm$^{-3}$ as given in Table 2. With the increase in the initiator concentrations in the given range the conversion and $R_p$ were found to increase due to an increase in concentration of the active species resulting in smaller oligomers with higher critical micelle concentration. Further, the micelle number is calculated to be $5.2 \times 10^{17}$ against the theoretical values of $10^{18}$. The double logarithmic plot gave a regular increasing trend with the order of 0.34, 0.14 and 0.40 for KPS, KMPS and APS, respectively. From the plots, APS has a distinct rise in the $R_p$ value suggesting that this initiator together with the complex forms a good couple for the free radical polymerization of MMA. The explanation is described later basing on the pH factor. The overall rate for all the three initiators were found to be slightly less as compared to the normal half order as in the conventional free radical polymerization of AN using Cu(II)/α-naphthol/KMPS/H$_2$O system.

**Variation of complex concentration**

The rate of polymerization and conversion for the increase in the complex concentration were found to increase uniformly (Table 2). From the double logarithmic plot, the order of the reaction, with respect to the [Complex], was found to be 0.22, 0.31 and 0.18 for the three initiator systems. As in the case of variation of initiators, in the complex variation, $R_p$ due to APS, at a particular concentration of the complex, is higher as compared to the other two systems. The slopes for all the three initiators are very small suggesting that the catalytic effect is comparatively less than the other systems like the in situ formed complexes as reported earlier on the catalytic effect of Cu(II)/histidine on the polymerization of MMA. These inferences may be due to the pH factor. As seen from results in Table 1, the pH of the complex is around 9.4 and on addition of KPS and KMPS separately, the pH drops down to 5.9 and 6.1, respectively whereas with the addition of APS, the pH shows a minute decrease to 9.3 only which may probably be explained on the basis of common ammonium ion in both the initiator and the complex. The stability of the complex decreases at lower pH and thus lowering the $R_p$ value as found in case of KPS and KMPS initiator systems.

**Proof of complex formation**

The UV-visible spectra of various mixtures like Cu(II)SO$_4$, [Cu(NH$_3$)$_4$]SO$_4$, [Cu(NH$_3$)$_4$]SO$_4$/MMA, [Cu(NH$_3$)$_4$]SO$_4$/MMA/KPS, [Cu(NH$_3$)$_4$]SO$_4$/MMA/KMPS, [Cu(NH$_3$)$_4$]SO$_4$/MMA/APS were measured in an aqueous solution to obtain a complete picture of the interaction between the reacting species and their relationship with the rate data (Fig. 3). Cu(II)SO$_4$ shows a maximum absorbance at 760 nm and a decrease in its value to 649 nm confirms the formation of the complex. Again, with addition of the monomer and the initiators the $\lambda_{max}$ value decreases below 600 nm suggesting the interaction of the complex with the monomer as well as the initiators.

**Characterization and properties of the polymer**

The characterization of PMMA emulsion latex was done by FTIR, SEM (size and morphology) and molecular weight measurements.

**FT-IR Spectra**

From the FTIR spectral data (Fig. 4), the sharp peak at 1734 cm$^{-1}$ indicates the presence of >C=O group. The peak at 2952 cm$^{-1}$ is due to the (C-H)$_{str}$ a
δ\text{asy} (C-H)\text{str} peak at around 1458 cm\(^{-1}\) and a O-C = C asymmetric stretching at 1242 cm\(^{-1}\) confirms the ester linkage. From all the above data the formation of the polymer is confirmed. Again, a peak between 1438 and 1388 cm\(^{-1}\) suggests the presence of a SO\(_4\) end group, (S=O)\text{str} which is also shown by the mechanism for the formation of SO\(_4^–\) radical. The presence of SO\(_4\) group as end group is indicated from end group analysis of the purified polymer according to the method of Palit\textsuperscript{31}, Saha and Choudhury\textsuperscript{32}.

**SEM analysis**

For the complex/MMA/APS/H\(_2\)O system, the SEM data reveal the particle size of the PMMA emulsion latex in the range of 50-500 nm (Fig. 5 a & b). Moreover, the surface of the latex was seen to be crumpled. Although, PMMA is amorphous in nature the surface tightens, on exposure to air immediately after the latex formation, giving it a crumpled look. The present findings show their difference from those of earlier studies\textsuperscript{19,30}. In those studies, especially in the preparation of PMMA latex using a complex initiating system, there was no change in the shape of the polymer latex. Only the particle size was found to decrease due to the effect of the complex. But in the present case, the shape gets deformed, i.e., it loses the usual spherical shape and the particle size decreases too.

**Mechanism**

The mode of initiator decomposition, the chain initiation and termination mechanism of polymerization involving [Cu(NH\(_3\))\(_4\)]SO\(_4\) can be interpreted as follows:

- **Chain initiation by [Cu(NH\(_3\))\(_4\)]SO\(_4\) complex**

\[
\begin{align*}
\text{Complex} + \text{HSO}_5^- & \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \\
\text{Complex} + \text{S}_2\text{O}_8^{2-} & \rightarrow 2\text{SO}_4^{2-} + \text{H}_2\text{O}
\end{align*}
\]

- **Propagation**

\[
\begin{align*}
\text{R}^+ + \text{MMA(M)} & \rightarrow \text{RM}_1^+ (\text{R}^+ = \text{SO}_4^{2-}) \\
\text{RM}_1^+ + \text{M} & \rightarrow \text{RM}_2^+ \\
\text{RM}_{n-1}^+ + \text{M} & \rightarrow \text{RM}_n^+ \\
\text{RM}_0^+ + \text{Cu(II)-Complex} & \rightarrow \text{Polymer + Cu(I)-Complex + H}^+
\end{align*}
\]
Applying steady state principles and assuming mutual termination, the rate expression is observed as follows,

\[
R_p \propto [\text{Complex}]^{0.22} [\text{KPS}]^{0.34} [\text{MMA}]^{0.72} \\
R_p \propto [\text{Complex}]^{0.18} [\text{KMPS}]^{0.14} [\text{MMA}]^{1.01} \\
R_p \propto [\text{Complex}]^{0.31} [\text{APS}]^{0.40} [\text{MMA}]^{0.93}
\]

Conclusion
The most significant outcome of this work is the development of a novel non-conventional complex initiating system leading to stabilizing the emulsion latex to a high conversion in absence of added surfactant. Complex catalyzed emulsion polymerization of MMA has been successfully carried out using a synthesized complex, \([\text{Cu(NH}_3)_4]\)SO\(_4\) and various peroxo initiators like KPS, KMPS and APS. Out of the various initiators, APS was found to form a better initiator system for the polymerization of MMA using this particular complex. Surfactant is not necessary for the system as the complex most likely plays the role of a surfactant/emulsifier in stabilizing the emulsion latex. The formation of the complex and its interaction with the initiators as well as the monomer interaction with the initiators as well as the monomer was confirmed by taking the UV-visible spectra of the mixtures. The SEM characterized the surface morphology of the polymer latex to be “crumpled” and the particle size were found to be in the range of 50-500 nm. From the rate data, the complex/APS system was found out to be a better catalyst for the polymerization of PMMA and the order of catalysis is complex/APS > complex/KPS > complex/KMPS. From the size of the PMMA particles obtained, it is proposed that choosing different complex catalytic systems, the particle size can be decreased to nano order resulting in preparing polymer nano particles.

Acknowledgement
The financial support of Council of Scientific and Industrial Research (project number: 01 (1713)/01/EMR-II), New Delhi, India is acknowledged.

References