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Kinetics of emulsion copolymerization of methylmethacrylate and ethylacrylate: effect of type and concentration of initiator in unseeded polymerization system

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Abstract

The free radical emulsion copolymerization of methylmethacrylate (MMA) and ethylacrylate (EA) initiated by a water-soluble initiator (potassium persulphate, KPS) at 50 °C in the presence of anionic emulsifier above critical micelle concentration under constant stirring speed in an inert atmosphere is investigated. The effect of blend of KPS and oil-soluble initiators [KPS $+ 2,2'$-azobisisobutyronitrile (AIBN)] is also examined. The order of the interval-II polymerization rate (R_p) is found to be 0.76 ± 0.03 in KPS initiation alone and 0.72 ± 0.04 in presence of fixed concentration of AIBN under similar experimental condition. On the other hand, interestingly, the rate of polymerization is found to be propotional to the 0.40th power of the AIBN concentration in presence of fixed concentration of KPS. The kinetic features of the present investigation indicate that probably the radical desorption is relatively facile and also the cage effect may be operative under high conversions (i.e. in polymer particles) in this MMA/EA emulsion copolymerization system. It is also found that the polydispersity index of polymer is being influenced by the type and concentration of initiators.

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Keywords: Emulsion polymerization; Cage effect; Polydispersity index

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1. Introduction

Emulsion polymerization has been an important and widely used process for the manufacture of polymer products. The kinetics and mechanism of the conventional polymerization has been studied extensively. The principal loci for the initiation using the water-soluble initiator were proposed to be the monomer swollen micelles [1] and aqueous phase [2]. The features of initiation in emulsion system are determined to a significant extent by chemical structure of initiator and its solubilities in aqueous phase or monomer. The different solubilities of the initiator influences its concentration distribution in the phases, the orientation of its molecules with respect to the adsorbed layers and consequently the activating influence of the emulsion medium. In fact, the structure of the radicals has recently been the subject of many investigations and still there is no consensus on the conformation of the free radicals. In 1989, Weerts et al. [3] have found that the concentration of three dissociative initiators differing in structure on water solubility hardly affects in reaction kinetics of the emulsion polymerization of butadiene. The effect of initiator concentration on particle size, particle size distribution (PSD) and polydispersity index (PDI) yield little information concerning the validity of published model [4]. However, the experimental trends generated from such experiments are most valuable in terms of

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latex design. Further, in a system where the principal ingredients are distilled water, monomers, emulsifier and initiator, it would seem appropriate and logical to begin the investigation of such a system with the initiator variable. Despite the industrial importance of the emulsion copolymerization of acrylates and methacrylate system, very little information has been reported about its kinetic and mechanistic features particularly using free radical forming mixed initiator system.

Therefore, attempt has been made to investigate the effect of type and concentration of initiators kinetically in methylmethacrylate (MMA)/ethyl acrylate (EA) emulsion copolymerization system using sodium laurylsulphate (NaLS) as micelle generator at 50 °C. This study has described the effect of potassium persulphate (KPS) alone and mixed initiator (i.e. blend of KPS and 2,2′-azobisisobutyronitrile (AIBN)) on the rate of polymerization (R_p) as well as molecular weight and molecular weight distribution (MWD) of polymers. Recipe and results from several polymerizations are reported here.

2. Experimental

2.1. Materials

Commercially available MMA and EA monomers are used for polymerization. KPS and AIBN both extrapure (from Fluka) are used as supplied. Sodium laurylsulphate (NaLS, from Fluka) reagent grade is used as emulsifier without further purification. Twice distilled demineralised (DM) water is used for polymerization medium.

2.2. Polymerization procedure

Polymerization is carried out at 50 °C constant temperature using a 1 l capacity glass buchi jacketed reactor provided with an excellent variable agitator facility. The reaction temperature has been maintained by circulating hot water through the jacket from a Haake Model NB22 water circulator. Polymerization experiments are conducted at a normal atmospheric pressure under strict exclusion of oxygen with a constant stirring of 250 rpm. All reagents, except the initiator and part of DM water used to dissolve the initiator are charged into the reactor after it is purged by nitrogen for complete deoxygenation. Polymerization is initiated by injection of an aqueous solution of the initiator pre-purged with nitrogen. The sudden appearance of haze or turbidity indicated the end of the induction period and the onset of polymerization. The polymerization is carried out for 2 h and stream of nitrogen gas is maintained throughout the entire span of reaction. Samples are withdrawn at regular interval and is discharged into a weighing beaker containing a few crystals of *p*-benzoquinone to inhibit further polymerization. After re-weighing, the polymer is precipitated with cold methanol. After that, it is filtered through a G-4 sintered glass crucible, washed successively with methanol, hot water and finally dried in vacuum at 50 °C to a constant weight. Time–conversion curves are obtained by testing the aliquots at fixed interval and from these the rate of polymerization is measured. This exercise ultimately help to study the kinetics of polymerization with respect to various process parameters.

3. Characterization of polymers

3.1. Intrinsic viscosity

The intrinsic viscosity (IV) of polymers are determined viscometrically in benzene solvent at 30 °C (0.2% polymer solution) using Ubbelohde suspension level viscometer attached with Schott Gerate AVS-400 recorder which record automatically the flow time of solvent and polymer solution.

3.2. Molecular weight and molecular weight distribution of polymers

Polymer samples are characterized for molecular weight and MWD by gel permeation chromatography (GPC) technique using Waters model 150C ALC/GPC liquid chromatograph (Water Division of Millipore, USA).

4. Results and discussion

The free radical emulsion copolymerization of MMA and EA initiated by KPS alone as well as separately by mixed initiator system (i.e. blend of KPS and AIBN) at 50 °C using NaLS as anionic emulsifier has been investigated kinetically by the conventional gravimetric method. In this study, Figs. 1–3 show the conversion versus time data of the radical emulsion copolymerization of MMA and EA.

In first set, the KPS concentration is changed from 0.84×10^{-3} to 8.41×10^{-3} m/l (Fig. 1 and Table 1) and in second set at fixed concentration of AIBN (i.e. 12.20×10^{-3} m/l), KPS concentration is further altered in the range (1.68–13.46) $\times 10^{-3}$ m/l (Fig. 2 and Table 2). Furthermore, in final set, AIBN concentration is changed from 6.09×10^{-3} to 48.78×10^{-3} m/l as shown in Fig. 3 and Table 3 using fixed concentration of KPS (1.68×10^{-3} m/l) in mixed catalyst. The other variables such as monomer and emulsifier concentration, and reaction temperature, etc., remain unchanged in all these sets of experiments. The polymerization rate in interval-II

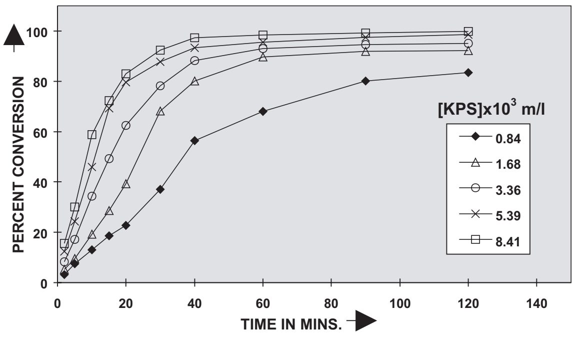


Fig. 1. Gravimetrtic yield–time curves at various KPS concentration.

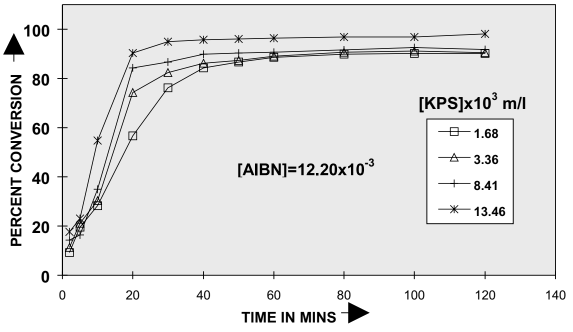


Fig. 2. Gravimetric yield–time curves at various KPS concentration in presence of fixed AIBN concentration.

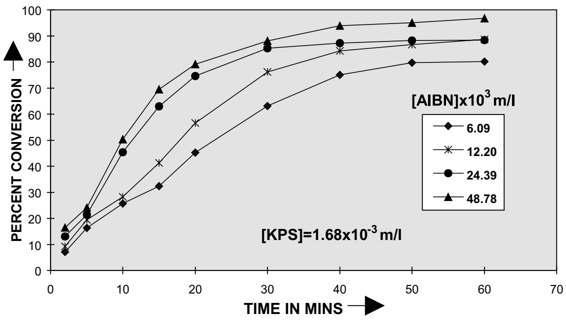


Fig. 3. Gravimetric yield–time curves at various AIBN concentration in presence of fixed concentration of KPS.

is found to be highly sensitive to changes in the initiator concentration irrespective of the different structure and water solubility of the dissociative initiator. The time–conversion curves obtained in these sets of experiments indicate that the rate of polymerization increases with increasing concentration of initiator. Particularly, in all KPS runs the final conversion is almost close to 100% as shown in Figs. 1 and 2.

Concerning the initiation process in the presence of oil-soluble initiator (i.e. AIBN), it has already been suggested that two main sources of initiation might interfere (i) diffusion of radicals formed in organic phase towards the aqueous monomer droplets and (ii) generation of radicals coming from the decomposition of AIBN dissolved in the aqueous phase droplets or located in the large interfacial layer. Inspection of the conversion versus time curves (Fig. 4) indicate that particle formation is a relatively slow process in AIBN initiation as compared to KPS intiation since the reaction period is usually long. The shape of conversion–time curves are also different for various type of initiator system as shown in Fig. 4. However, it is useful to note that the quantitative nature of an emulsion polymerization depend strongly on a number of factors viz. monomer solubility and polarity in water, polymer solubility in water, monomer solubility in polymer, initiator solubility in the aqueous phase or oil phase and emulsion characteristics. The extent of monomer water solubility varies considerably from monomer to monomer and largely determines both the principal reaction loci and the mechanism of particle formation. The solubility characteristic of the initiator determines the phase in which free radicals are formed.

Experimentally, the rate of polymerization (R_p) has been estimated from the conversion versus time curves during constant rate period (i.e. from 10% to 40% conversion) using conventional rate determination technique from gravimetric results obtained under different set of experiments in initiator variation system described in Tables 1–3 [5]. In KPS initiation system alone, when Log [R_p] was plotted against Log [I], a straight line of slope 0.76 ± 0.03 was obtained as shown in Fig. 5. This indicates that the R_p is proportional to the power of 0.76 which eventually yield the following rate equation i.e.

Table 1
Variation of percent conversion at different KPS concentrations

[KPS] × 10^3 m/l	Variation of percent conversion at different time interval (min)									
	2	5	10	15	20	30	40	60	90	120
0.84	3.21	7.51	13.01	18.59	22.71	37.08	56.43	67.98	80.10	83.44
1.68	5.23	9.48	19.26	28.63	39.21	68.23	80.12	89.62	91.91	92.23
3.36	8.29	17.19	34.36	49.35	62.41	78.25	88.29	92.98	94.56	95.11
5.39	12.32	24.39	45.87	69.23	79.69	87.79	93.38	95.61	97.52	98.49
8.41	15.57	30.09	58.82	72.29	82.99	92.32	97.28	98.32	99.18	99.87

Recipe: DM water—550 g, MMA—40 g, EA—10 g, NaLS—2.2 × 10^{-2} m/l, temperature—50 °C, time—120 min, RPM—250.

Table 2
Variation of percent conversion at different KPS concentrations in presence of fixed concentration of AIBN

[KPS] × 10^3 m/l	Variation of percent conversion at different time interval (min)										
	2	5	10	20	30	40	50	60	80	100	120
1.68	9.23	19.48	28.26	56.63	76.21	84.23	86.63	88.62	89.91	90.23	90.14
3.36	11.29	21.19	30.36	74.35	82.41	86.25	87.29	88.98	90.56	91.11	90.47
8.41	14.32	16.39	34.87	84.23	86.69	89.79	90.38	90.61	91.52	92.49	91.72
13.46	17.57	23.09	54.82	90.29	94.99	95.73	95.98	96.32	96.88	96.87	98.08

Recipe: DM water—550 g, MMA—40 g, EA—10 g, AIBN—12.2 × 10^{-3} m/l, NaLS—2.2 × 10^{-2} m/l, temperature—50 °C, time—120 min, RPM—250.

Table 3
Variation of percent conversion at different AIBN concentrations in presence of fixed concentration of KPS

[AIBN] × 10^3 m/l	Variation of percent conversions at different time intervals (min)								
	2	5	10	15	20	30	40	50	60
6.09	7.12	16.29	25.63	32.40	45.27	63.18	75.09	79.74	80.21
12.20	9.23	19.41	28.26	41.29	56.63	76.21	84.23	86.63	88.62
24.39	12.98	21.39	45.41	62.98	74.54	85.19	87.2	88.21	88.43
48.78	16.43	24.15	50.37	69.46	79.19	88.03	92.88	95.02	96.69

Recipe: DM water—550 g, MMA—40 g, EA—10 g, KPS—1.68 × 10^{-3} m/l, NaLS—2.2 × 10^{-2} m/l, temperature—50 °C, time—60 min, RPM—250.

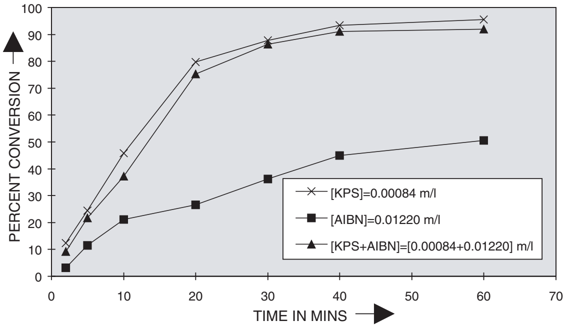


Fig. 4. Comparision of gravimetric yield–time curves obtained from different initiator system.

$$R_p \propto [\mathrm{KPS}]^{0.76\pm0.03} \tag{1}$$

On the other hand, further in KPS system in presence of fixed concentration of AIBN, the order of the interval-2 polymerization rate (R_p) was found to be 0.72 ± 0.04 as shown in Fig. 6. This can also be expressed in empirical form as follows:

$$R_p \propto [\mathrm{KPS}]^{0.72\pm0.04} \tag{2}$$

In both cases, the initiator order is almost the same but the order of reaction is higher from conventional order of 0.5. This deviation from the ideal value of 0.5 is an indication of termination of growing chain radicals predominantly due to the combination of polymer chain radicals [6,7] along with a little primary radical termi-

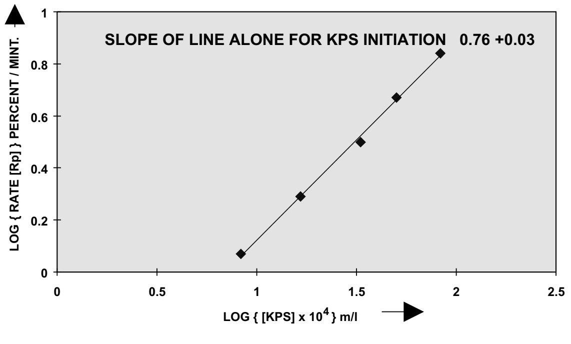


Fig. 5. Conventional order plot for persulphate variation.

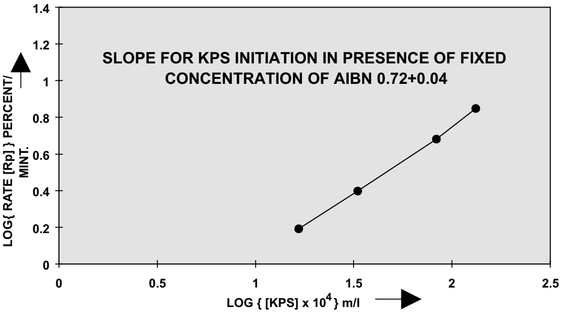


Fig. 6. Conventional order plot for persulphate variation in presence of AIBN.

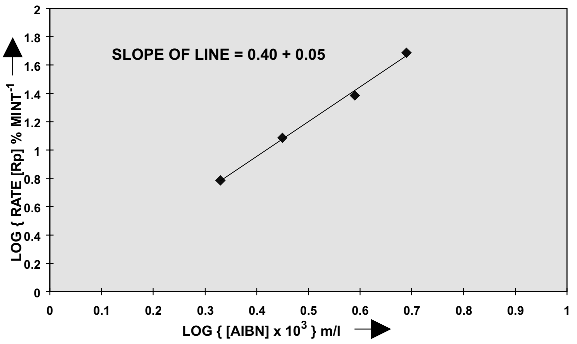


Fig. 7. Conventional order plot for AIBN variation in presence of KPS.

nation [8]. The influence of AIBN concentration in presence of fixed concentration of KPS without changing other variables of polymerization has also been examined kinetically as shown in Fig. 3 and Table 3. Interestingly, it is found that the R_p is proportional to the power of 0.40 ± 0.05 as shown in Fig. 7. The empirical form of the rate expression is also given below:

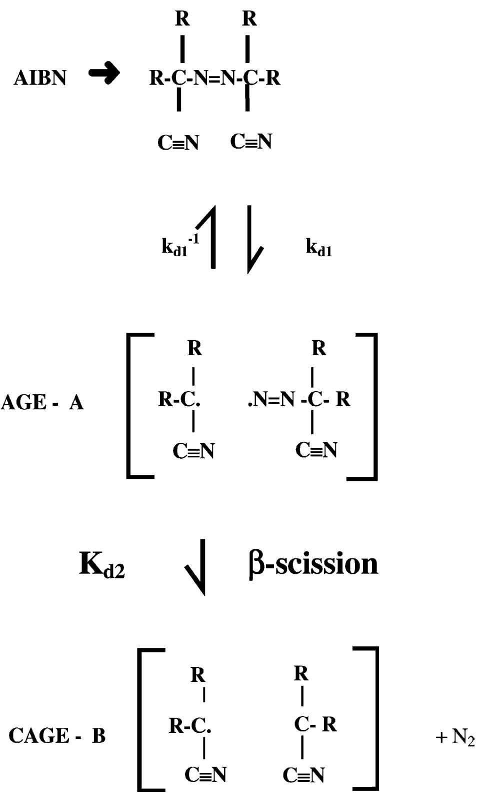
$$R_\mathrm{p}\alpha[\mathrm{AIBN}]^{0.40\pm0.05} \tag{3}$$

This order indeed is lower (i.e. just half) as compared to order (i.e. 0.76 or 0.72) estimated from KPS initiation system in presence or absence of AIBN.

According to micellar theory [7] and homogeneous nucleation model [8], the relation between the rate of polymerization in the interval-2 and the initiator concentration can be expressed by

$$R_\mathrm{p}\alpha[I]^{0.4} \tag{4}$$

Incidentally, in this present copolymerization system initiated by mixed catalyst where particularly AIBN concentration has been changed in presence of fixed concentration of KPS, the order of reaction is found to be 0.40 as already shown in Fig. 7. This indeed obeys Eq. 4 of Smith–Ewart interval-2 emulsion polymerization of vinyl monomers. The micellar mechanism is generally applied to sparingly water-soluble monomers viz. butyl acrylate, MMA, EA, ethyl methacrylate, etc. The reaction order 0.5 should be discussed in terms of bimolecular termination between growing radicals. The bimolecular termination between entangled radicals is however, improbable, and therefore these macroradicals are deactivated in reaction with mobile radicals (i.e. transferred monomeric and/or entered oligomeric) and/or by the residual termination by propagation [9]. The former process (primary radical termination) is characterised by a reaction order below 0.5. The latter process can be considered as a first order radical loss process with a reaction order above 0.5. Thus, the overall reaction order should be a function of both contributions and thereby the order of polymerization reaction will be higher as compared to conventional order 0.5 as shown in Figs. 5 and 6, respectively.



Scheme 1. Kinetic scheme for decomposition of AIBN.

The decomposition of AIBN can be described as a two step reaction, as shown in Scheme 1.

A cynopropyl radical and a diazenyl radical are produced from an AIBN molecule in the 1st step. Then a cyanopropyl radical and N_2 are produced from a diazenyl radical in the second step [β-scission [10]]. If initiation of polymerization takes place before the cage-B situation is produced, initiator efficiency must be unity because recombination between cyanopropyl radicals and diazenyl radicals do not give any by products as only AIBN molecules are regenerated. However, if initiation occurs after the establishment of the cage-B situation, by products will be produced along side initiation causing a decrease in initiator efficiency. In our present copolymer system where AIBN is used as initiator at fixed concentration of KPS, it is found that there is a significant reduction in initiator order (i.e. 0.40, Fig. 7) as compared to the persulphate initiation system alone and also in presence of fixed concentration of AIBN (i.e. 0.76 and 0.72). The kinetic behaviour is also in good agreement with Smith–Ewart case-2. This is probably due to the reduction of initiator efficiency with increase of conversion during polymerization and the deactivation of growing radicals is suggested to produce through the cage effect mechanism. The limiting conversion (≅80%) observed (Figs. 3 and 4) in this acrylate copolymerization system is also attributed to reactions of initiator molecules with growing radicals and is also due to strong cage effect. Similar observation is also reported by others [11a,b].

It is reported that two cynopropyl radicals produced from an AIBN molecules are likely to recombine inside the cage rather than outside [12,13]. At low concentration of monomer (10^{-2} to 1 m/l) and radical (10^{-9} m/l) in the MMA–EA copolymerization system, the likelihood of one primary radical meeting another in the presence of monomer is very low. Even when the monomer concentration is low at high conversion, the primary radical will be substantially outnumbered by monomer molecules. However, the various mechanisms in which the single radical are formed by desorption of radicals, from the particles [14–16] and those radicals which are considered to be formed in the aqueous phase from the fraction of oil-soluble initiator dissolved in the water are responsible for the kinetic similarities between oil soluble and water soluble initiators [17].

It is also found that the rate of polymerization (R_P) in KPS initiation system alone is faster as compared to AIBN initiation and also higher when polymerization was initiated by a blend of KPS and AIBN in MMA–EA copolymerization. The results are displayed in Table 4. The increasing order rate is as follows:

$$[R_P]_{KPS} > [R_P]_{KPS+AIBN} > [R_P]_{AIBN}$$

The lower rate in mixed free radical initiation system (i.e. KPS + AIBN) indicate that the presence of AIBN decrease the radical activity of the polymer particles. The contribution of the primary radical termination is considered to dominate over all termination mechanism. This indicates that interaction of KPS with AIBN molecules or their radical fragments is responsible for the decrease of the overall polymerization rate. Thus, recombination radicals, derived from KPS and AIBN lead to a decrease in rate of initiation (R_i) as well as rate of polymerization (R_p). The reaction is expected to proceed at the particle interface. This is a zone where the oil-soluble radical fragments and the polar oligomeric radicals can be encountered and react.

4.1. Effect of initiator on intrinsic viscosity, molecular weight and molecular weight distribution

The IV of polymers synthesized under different polymerization conditions is determined by viscometry method while molecular weight (M_w) and molecular weight distribution (MWD) of some selective samples have been determined by GPC technique. The results are summarised in Tables 5–7.

It is observed that the IV and molecular weight of polymers decrease with increase of KPS concentration in absence and presence of fixed concentration of AIBN as shown in Tables 5 and 6. The PDI is also influenced with the change of type (i.e. mixed system) and concentration of initiator (Tables 5 and 6). Similar observation is also reported by others in emulsion polymerization of vinyl monomers [18,19]. It is found that there is no regular trend in the PDI data (Table 6), whereas polymers produced by increasing concentration of KPS alone have a distinct decreasing trend of molecular weight and PDI (Table 5). It is also noticed that the PDI of polymers remains almost constant showing narrow molecu-

Table 4
Comparision of R_p under various initiation systems

Initiating system	Percent conversion at different time interval (min)							Overall rate of polymerization $[R_p] \times 10^4$ m/l s
	2	5	10	20	30	40	60	
[KPS]	12.12	24.25	45.09	74.50	87.21	93.09	95.49	10.69
[AIBN]	3.15	11.50	21.18	26.58	36.22	45.17	50.87	3.03
[KPS] + [AIBN]	9.48	22.14	37.34	75.62	86.27	88.39	90.01	7.20

Recipe: DM water—550 g, MMA—40 g, EA—10 g, NaLS—2.2×10^{-2} m/l, temperature—50 °C, time—60 min, RPM—250, $[KPS] = 0.84 \times 10^{-3}$ m/l, $[AIBN] = 12.2 \times 10^{-3}$ m/l and $[KPS + AIBN] = (0.84 + 12.20) \times 10^{-3}$ m/l.

Table 5
Effect of KPS concentration on MW and MWD at final conversion

$[KPS] \times 10^3$ m/l	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	$[\eta]$ dl/g
0.84	5.48	2.6	2.01	4.20
1.68	3.45	1.95	1.80	3.25
13.46	2.64	1.62	1.62	1.20

Recipe: DM water—550 g, MMA—40 g, EA—10 g, NaLS—2.2×10^{-2} m/l, temperture—50 °C, time—120 min, RPM—250.

Table 6
Effect of KPS concentration in presence of fixed concentration of AIBN on MW and MWD at final conversion

[KPS] × 10^3 m/l	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	[η] dl/g
0.84	11.68	4.34	2.69	6.3
1.68	9.01	5.07	1.77	6.1
13.46	1.59	0.798	2.01	2.8

Recipe: DM water—550 g, MMA—40 g, EA—10 g, AIBN—12.2 × 10^{-3} m/l, NaLS—2.2 × 10^{-2} m/l, temperature—50 °C, time—120 min, RPM—250.

Table 7
Effect of AIBN concentration in presence of fixed concentration of KPS on MW and MWD at final conversion

[AIBN] × 10^3 m/l	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	[η] dl/g
6.09	4.67	2.85	1.64	6.3
24.39	3.76	2.44	1.54	4.19
48.78	3.65	2.41	1.51	2.14

Recipe: DM water—550 g, MMA—40 g, EA—10 g, KPS—1.68 × 10^{-3} m/l, NaLS—2.2 × 10^{-2} m/l, temperature—50 °C, time—60 min, RPM—250.

lar distribution trend when AIBN concentration changes from 6.02 × 10^{-3} to 48.78 × 10^{-3} m/l in presence of fixed concentration of KPS as shown in Table 7. However, overall, MWD of polymers are influenced by the type and concentration of initiator in MMA/EA emulsion copolymerization system. Particularly, in a run, the IV of polymer increases initially and reaches a maximum and finally it decreases with conversion which pattern is very similar for KPS alone and even under two different KPS concentrations (i.e. keeping AIBN concentration fixed) in mixed catalyst systems as shown in Fig. 8 and Table 8. The rapid increase of IV in the beginning of polymerization may be due to the transfer of radical activity from the continuous phase and the hydrophilic primary particles to the hydrophobic premature polymer particle. However, interestingly, the IV of polymer produce by mixed catalyst system is relatively higher as compared to polymer synthesised by KPS initiator alone as shown in Fig. 8 and Table 8. Probably, the formation of high molecular weight polymer using AIBN initiation in presence of fixed concentration of KPS is due to the slower rate of termination of growing radicals with AIBN radical fragments or their radical pairs generated from AIBN during polymerization.

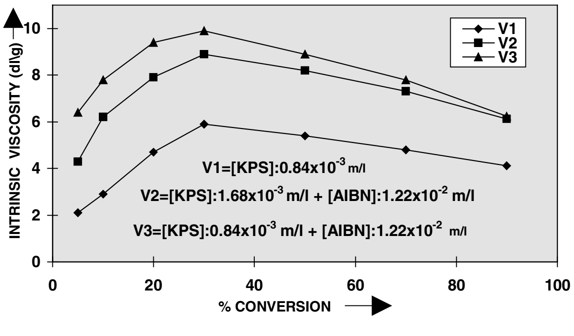


Fig. 8. Variation of IV at various percent conversion in a run under different initiator concentration.

Table 8
Variation of IV in a run at various conversion condudcted under different initiator systems

Conversion (%)	$(IV)_B$ dl/g	$(IV)_{A+B}$ dl/g	$(IV)_{A+C}$ dl/g
5	2.1	6.4	4.3
10	2.9	7.8	6.2
20	4.7	9.4	7.9
30	5.9	9.9	8.9
50	5.4	8.9	8.2
70	4.8	7.8	7.3
90	4.12	6.3	6.1

A: AIBN = 12.20 × 10^{-3} m/l, B: KPS = 8.4 × 10^{-4} m/l, C: KPS = 16.8 × 10^{-4} m/lIV: intrinsic viscosity.

It is established that the exit (or desorption) of free radical activity in an emulsion polymerization has kinetic significance even for relatively insoluble monomers such as styrene [20–23]. The radical concentration within polymer particles is reported to be affected by the radical desorption from the particles [24]. It is also suggested that the exit of radicals from latex particles may depend on initiator concentration, mass fraction of polymer within particles, the surface properties of polymer particles, and the water solubility of monomers [25]. Therefore, the understanding of the exit mechanism would also play an important role in designing and controlling of latex properties and polymer production for this MMA/ EA copolymerization system. Hence, the effect of the radical desorption from the polymer particles for the emulsion polymerization of methacrylate and acrylate system particularly using mixed free radical initiator is thus still open to both experimental and theoretical verifications. It appears that the radical desorption is relatively facile in such emulsion copolymerization system and so there is a scope for experimental verification.

5. Conclusion

It is finally concluded that the initiation of emulsion polymerization by water-soluble initiator is a two step process. It starts in the aqueous phase by the primary free radicals from the water-soluble initiator and the second step occurs by the entry of radicals into particles. Termination between propagating radicals in the particles is very restricted due to strong reduction of translation diffusion of growing chains. The main growth events, chain transfer and termination, however, proceed in the particles. The molecular weight and MWD are also influenced by the type and concentration of initiator. However, in spite of partial agreement of experimental data with Smith–Ewart theory, the mechanism and kinetics of the polymerizations are extremely complicated and will require much additional research.

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References

[1] Smith WV, Ewart RH. J Am Chem Soc 1948;70:3695.
[2] Fitch RM, Tsai CH. J Polym Sci, Polym Lett Ed 1970;8:703.
[3] Weerts Pierre A, Vander Loos Jos LM, German Anton L. Makromol Chem 1989;190:777.
[4] Shouldice Grant TD, Vandezande Gerald A, Rudin A. Eur Polym J 1994;30(2):179.
[5] Brandrup J, Immergut EH. Polymer handbook. 2nd ed. New York: Wiley; 1975.
[6] Misra US, Bajpai UDN. J Macromol Chem Sci Chem 1979;13(8):2235.
[7] Flory PJ, editor. Principles of polymer chemistry. Ithaca, New York: Cornel University Press; 1975.
[8] Deb PC, Meyerhoof G. Eur Polym J 1974;10:709.
[9] Schultz GVZ. Phys Chem 1956;8:290.
[10] Pryor WA, Smith K. J Am Chem Soc 1970;92:5403.
[11] (a) Capek I. Makromol Chem 1994;195:1137;
(b) Capek I, Riza M, Akashi M. Polym J 1992;24:959.
[12] Moad G, Rizzardo E, Soloman DH, Johns SR, Willing RI. Makromol Chem Rapid Commun 1984;5:793.
[13] Fink JK. J Polym Sci, Polym Chem Ed 1983;21:1445.
[14] Vanderhoff BME. Adv Chem Ser 1962;34:6.
[15] Edelhauser H, Breitenbach JW. J Polym Sci, Polym Chem Ed 1959;35:423.
[16] Breitenbach JW, Edelhauser H. Macromol Chem 1961;44–46:196.
[17] Barton J, Karpatyora A. Makromol Chem 1987;188:693.
[18] Satpathy US, Paul TK, Banerjee M, Konar RSJ. Macromol Sci Chem 1981;A-15:1495.
[19] Banerjee M. PhD thesis, Burdwan University, West Bengal, India, 1982.
[20] Hawket BS, Napper DH, Gilbert RG. J Chem Soc Faraday Trans 1 1980;76:1323.
[21] Adams M, Napper DH, Gilbert RG, Sangster DF. J Chem Soc Faraday Trans 1 1986;82:1979.
[22] Gilbert RG, Napper DH. J Macromol Sci Rev Macromol Chem Phys C 1983;23:127.
[23] Lansdowne SW, Gilbert RG, Napper DH, Sangets DF. J Chem Soc Faraday Trans 1 1980;76:1344.
[24] Litt M, Patsiga R, Stannett V. J Polym Sci 1970;8(Part A-1):3607.
[25] Ballard MJ, Napper DH, Gilbert RG. J Polym Sci, Polym Chem Ed 1984;19:3225.