

# Mechanistic study on polymerization of acrylamide induced by methyl ethyl ketone and its derivatives based on the interaction between carbonyl and amide groups

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Polymerizations of acrylamide (AAM) were carried out in the presence of methyl ethyl ketone (MEK), methyl isopropyl ketone (MIK) and *t*-butyl methyl ketone (tBMK) in tetrahydrofuran at 30 °C. It was found that the rate of polymerization ( $R_p$ ) increased according to this order: MEK < MIK < tBMK in the case of AAM, but in the methyl methacrylate (MMA) system the order was as followed: MEK > MIK > tBMK. The maximum value of  $R_p$  for AAM reached the point of equimolar ratio of AAM to ketone in any of the three systems. The polymerization was confirmed to proceed through radical mechanism. Effects of temperature on the  $R_p$  were discussed in a temperature range of 30–60 °C. The overall activation energy ( $E_a$ ) was estimated to be 52.6, 35.7, and 22.7 KJ/mol for MEK, MIK, and tBMK, respectively. No acceleration of the polymerization of *N,N*-dimethylacrylamide system was observed even in the presence of these ketones. The participation of  $-NH_2$  in the complexation of monomer with the ketones is proposed in the initiation of this radical polymerization. © 1999 Kluwer Academic Publishers

## 1. Introduction

Radical polymerization of several polar vinyl monomers in the presence of some active acidic hydrogen atom containing compounds (e.g., aldehydes, ketones, etc.) has been the subject of many publications [1–8]. As shown in Scheme 1, the mechanism of the reaction involving transfer of the hydrogen radical abstracted from these compounds to the monomer, originally proposed by Imoto *et al.* [3–5]. They found the poly(acrolein-co-styrene) [9] and poly(methyl vinyl ketone-co-styrene) [10] could initiated the radical polymerization of methyl methacrylate (MMA). When the  $-CHO$  group of poly(acrolein-co-styrene) was hydrogenated with  $NaBH_4$  to  $CH_2OH$  group, the initiation ability of poly(acrolein-co-styrene) was lost. It was concluded that the active center of poly(acrolein-co-styrene) was the  $-CHO$  group.

Also, as shown in Scheme 2, a similar type of interaction between MMA and cyclohexanone (CHn) molecules has been reported by Kaim [6, 7, 11], which results in the formation of radicals in a polymerization system. Also it was considered of interest to find that some additional compounds containing active methylene group (such as cyclopentanone, cycloheptanone, diethyl malonate, and ethyl cyanoacetate) would initiate the radical polymerization of MMA [12].

On the other hand, it has been reported [13–16] by our laboratory that the polymerization of acrolein and

methyl ketone (MVK) can be initiated with poly(AAM), and the copolymerization of AAM with MVK proceeded smoothly in tetrahydrofuran. In this case, interaction between carbonyl group and amide group was proved to induce this radical polymerization.

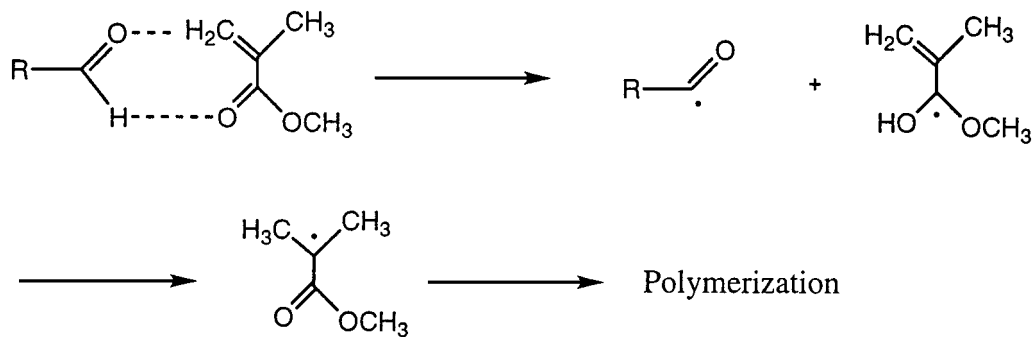
Recently, we reported [17] that the acceleration effect of 2,6-dimethyl cyclohexanone on the polymerization of AAM was higher than that of CHn, and no effect of CHn was found in the polymerization of *N,N*-dimethylacrylamide under the same conditions. It was suggested that the amide group in AAM and the carbonyl oxygen of CHn (having relatively higher electronic density) is the main factor in the initiation of AAM in this system.

In the present paper, the polymerizations of AAM in the presence of methyl ethyl ketone, methyl isopropyl ketone, and *t*-butyl methyl ketone were investigated in detail.

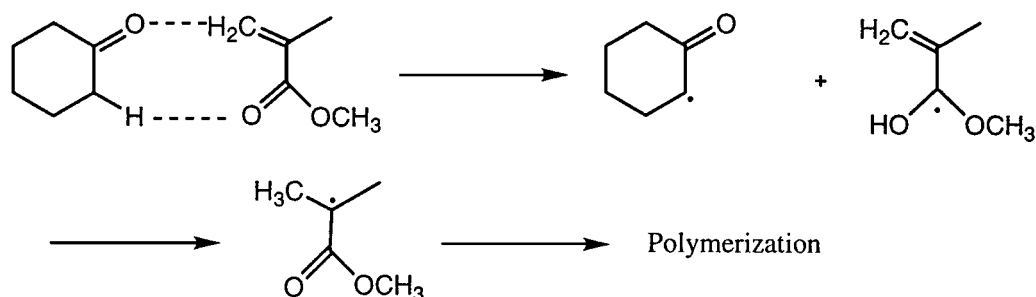
## 2. Experimental procedure

### 2.1. Materials

Acrylamide (AAM) and methacrylamide (MAAM) were recrystallized twice from benzene. *N,N*-Dimethylacrylamide (DMAAM) and methyl methacrylate (MMA) were distilled in reduced pressure in the presence of hydroquinone as a radical inhibitor under a dry oxygen-free nitrogen stream before use. Methyl



Scheme 1



Scheme 2

ethyl ketone (MEK), methyl isopropyl ketone (MIK) and *t*-butyl methyl ketone (tBMK) were distilled twice in reduced pressure under a dry oxygen-free nitrogen stream. Tetrahydrofuran (THF), and the others solvent were purified as the previous papers [15, 18, 19].

## 2.2. Polymerization procedure

All of polymerizations were carried out with no irradiation (light shielded condition). The measured amount of monomers and THF were placed in a glass ampoule under argon atmosphere. The ampoule was degassed by repeating freeze-evacuate-thaw cycles five times, and sealed under vacuum. The reaction was carried out in a water bath which was maintained at constant temperature (30 °C). After the specified polymerization time, the reaction was stopped by placing the ampoule into an ice-water bath. The polymerization mixture was poured into a large amount of acetone, and the resulting precipitate was filtered and dried to constant weight in a vacuum oven at room temperature. The crude polymer was purified by reprecipitation from water into THF. The structure of resulting poly(AAm) was confirmed by the IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra.

## 2.3. Analysis

IR spectra were recorded with a Perkin-Elmer 1760-X FT-IR. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded by a Nippon-Denshi JNM-FX200 (270) and a JNM-GX500 instrument, respectively. Gel permeation chromatography (GPC) analyses were carried out on a Hitachi L-6000 high performance liquid chromatography, L-3350 RI detector in KF-804L column and GLW-550 column.

## 3. Results and discussion

### 3.1. Effect of ketone concentration on the polymerization of AAm

Polymerizations of AAm in the presence of MEK, MIK, and tBMK were carried out in THF under vacuum. The time-conversion curves for polymerization of AAm initiated by MEK, MIK, and tBMK were presented in Fig. 1. AAm was smoothly polymerized in the presence of these ketones, however, no homopolymerization of AAm (no thermal polymerization) occurred in the absence of the above ketones under the same conditions. The fact that the thermal polymerization of AAm was not observed could be explained by the great tendency of AAm to make the hydrogen bonding with another molecule of AAm [20]. No radical species to initiate the polymerization seems to generate in this self association of AAm, when there is no additional hydrogen bonding to affect the self association. In all cases,

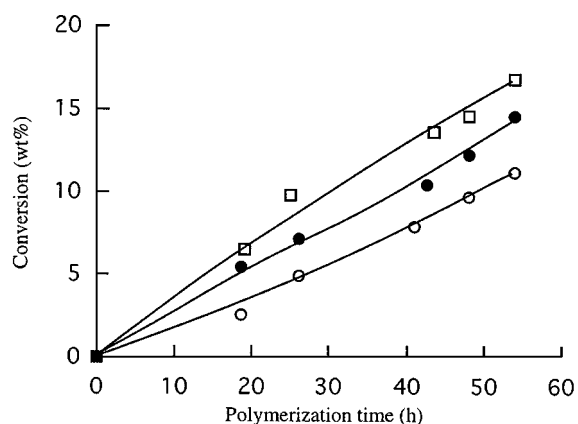


Figure 1 Conversion vs. time curves for the polymerization of AAm initiated with MEK, MIK, and tBMK in THF at 40 °C. (○), polymerization of AAm initiated with MEK; (●), polymerization of AAm initiated with MIK; (□), polymerization of AAm initiated with tBMK.

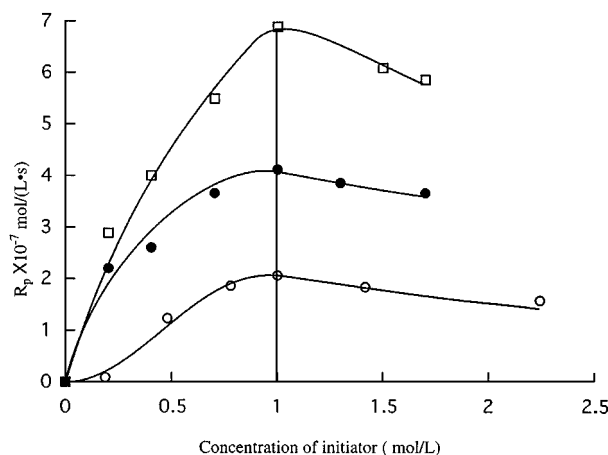


Figure 2 Relationship between  $R_p$  and concentration of initiator in THF at 30 °C. (O), polymerization of AAm initiated with MEK; (●), polymerization of AAm initiated with MIK; (□), polymerization of AAm initiated with tBMK.

the polymerizations of AAm were inhibited by adding a small amount of 1,1-diphenyl-2-picrylhydrazil, which is known as an inhibitor of radical polymerization.

The concentration effects of these ketones on the rate of polymerization ( $R_p$ ) were shown in Fig. 2. The  $R_p$  of AAm increased with the increase of ketone concentration at the range of 0.2–1.0 mol/l in THF at 30 °C, and reached the local maximum value at the equimolar ratio of monomer to ketones ( $[AAm]/[Ketones] = 1$ ). The  $R_p$  tended to decrease when the concentration of ketones was increased over than that of monomer (1.0 mol/l). Two overlapped effects can be responsible for this curve of  $R_p$ : the formation of a reactive complex between AAm and ketones which results in the radical polymerization of AAm, and the retardation of radical polymerization by the chain transfer reaction.

As shown in Scheme 3, in the case of methylene compounds, not only an activated methylene but also a terminal alkyl group can be a point of radical attack [21, 22]. Thus the decreased of  $R_p$  of AAm in the case of higher concentration of ketones can be attributed to the terms of the chain transfer reaction from the monomer to ketones, which retards the radical polymerization of AAm.

The substitution pattern on  $\alpha$ -position of MEK remarkably affected the  $R_p$  of AAm (Fig. 2). The  $R_p$  increased according to the order MEK < MIK < tBMK, which is the same as the order of the electronic density of carbonyl oxygen of ketones. It is good agreement with the result of our previous report [17] that higher electronic density of carbonyl oxygen of ketone results in stronger interaction between monomer and ketone, which induces the generation of the radical initiators.

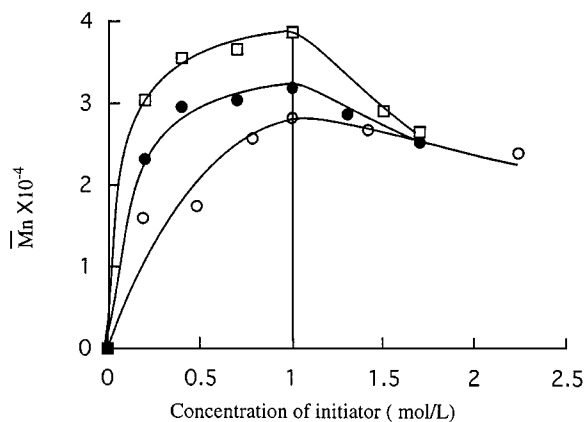


Figure 3 Relationship between  $\bar{M}_n$  and concentration of initiator in THF at 30 °C. (O), polymerization of AAm initiated with MEK; (●), polymerization of AAm initiated with MIK; (□), polymerization of AAm initiated with tBMK.

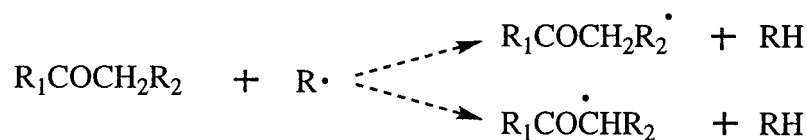
### 3.2. Effect of ketone concentration on the number-average molecular weight of resulting poly(AAm)

Number-average molecular weight ( $M_n$ ) of poly(AAm) was calculated by the GPC using Pullulan as a standard sample (Fig. 3). It is interesting to find that the  $M_n$  of poly(AAm) increased with the increase of the concentration of ketones at a range of 0.2–1.0 mol/l, and tended to decrease with the increase of the concentration of the ketones being over than 1.0 mol/l. Similarly, the maximum value of  $M_n$  is attained at the 1.0 mol/l (the point of equimolar ratio of monomer to ketones). Also, the substitution of hydrogen atom at  $\alpha$ -position by methyl group in MEK greatly affected the  $M_n$  of resulting poly(AAm). The  $M_n$  increased with the increase of the electronic density of carbonyl oxygen of ketone (MEK < MIK < tBMK). It is in good agreement with the opinion just suggested above.

### 3.3. Effect of ketones on the polymerizations of AAm and its derivatives

As shown in Fig. 4, the polymerizations of DMAAm were carried out in the presence of MEK, MIK, and tBMK in the THF at 40 °C. As expected, no acceleration of any ketones (MEK, MIK, and tBMK) on the  $R_p$  of DMAAm was observed in this condition. This result can be explained by the reason that DMAAm monomer, in which two hydrogen atoms on amide group was replaced with methyl groups, does not form adequate complex with CHn, so the reactivity of DMAAm monomer or the corresponding radical are unchanged (original thermal polymerizability).

To confirm the interaction between  $N$ -hydrogen atom of amide group and carbonyl group more



Scheme 3

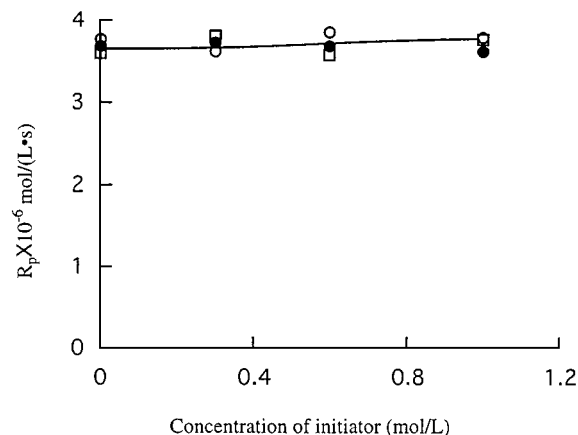


Figure 4 Relationship between  $R_p$  of DMAAm and concentration of initiator in THF at 40 °C. (O), polymerization of DMAAm initiated with MEK; (●), polymerization of DMAAm initiated with MIK; (□), polymerization of DMAAm initiated with tBMK.

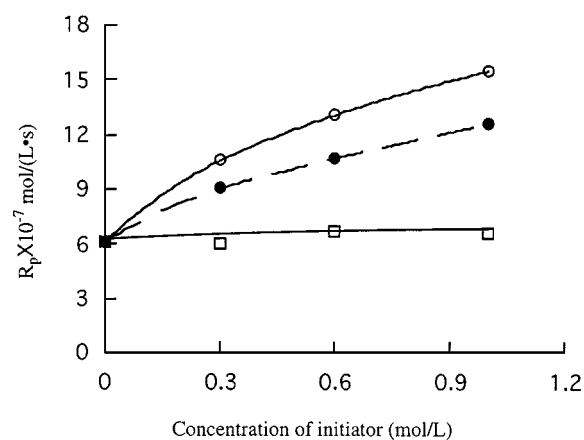


Figure 5 Relationship between  $R_p$  of MMA and concentration of initiator in THF at 40 °C. (O), polymerization of MMA initiated with MEK; (●), polymerization of MMA initiated with MIK; (□), polymerization of MMA initiated with tBMK.

TABLE I Solvent effect on the polymerization<sup>a</sup> of acrylamide in the presence of MEK

Run	Solvent	Yield (%)
1	Water	9.6
2	Methanol	10.0
3	1,4-Dioxane	13.7
4	THF	24.6

<sup>a</sup>Polymerization conditions: [AAM] = [MEK] = 1.0 mol/l; Polymerization time, 330 h; Temperature, 30 °C.

precisely, the polymerizations of MAAm, and *N*-methyl acrylamide (NMAAm) were also investigated in the presence of MEK. The results are summarized in Table I. MAAm and NMAAm presented some polymerizabilities only in the presence of MEK, and no polymerization of MAAm and NMAAm occurred in the absence of MEK. The lower reactivity of MAAm and NMAAm in the presence of MEK can be explained by the steric hindrance of the substituted methyl group in  $\alpha$ -position or amide group, which interrupts effective interaction of carbonyl oxygen of ketone with *N*-hydrogen atom in amide group.

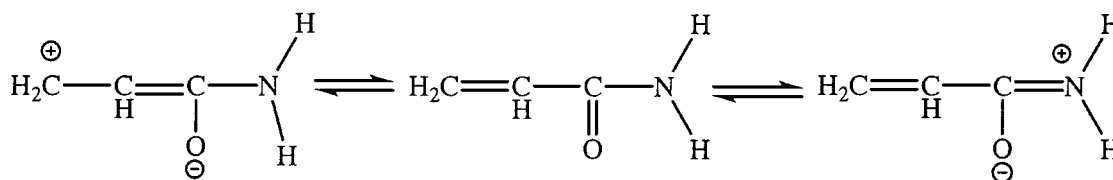
### 3.4. Effect of MEK, MIK, and tBMK on the polymerizations of MMA

Kaim have reported [6, 12] that in the polymerizations of MMA initiated with CHn or the other active methylene containing compounds, the hydrogen atoms in  $\alpha$ -position of CHn molecule or in active methylene group are proved to play an important role in the generation of radicals which initiate the polymerization of MMA. In order to confirm this point suggested by Kaim, the polymerizations of MMA were investigated in the presence of the MIK, and tBMK comparing to

the case of MEK. The results are presented in Fig. 5. the  $R_p$  of MMA decreased according to this order: MEK > MIK > tBMK, and the acceleration polymerization of MMA was hardly observed in the presence of tBMK. This result may be explained in terms of following: as seen in Scheme 2, the hydrogen atom on  $\alpha$ -position of methylene group is an important factor in the formation of a complex with carbonyl oxygen of MMA by the hydrogen bonding, which is suggested to promote the radical polymerization of MMA [6, 11]. Due to the lack of any opportunity for a hydrogen bridge for MMA with tBMK, the reactivity of MMA monomer and its radicals remain comparatively unchanged (original thermal polymerizability) in the presence of tBMK. Also, due to the steric hindrance of the replacement of a hydrogen atom by methyl substituent in the methylene group of MEK, the MMA and its radicals present relatively lower reactivity in the presence of MIK in comparison with the case of MEK.

However, there are not these additional steric hindrance effect in the AAm system, and the  $R_p$  of AAm initiated with tBMK was highest. It seems to indicate that the mechanism of polymerization of AAm initiated with ketones is quite different from that of MMA.

As shown in Scheme 4, AAm can be described by several resonant structures in polar solvent [20, 23]. In the presence of ketone having relatively higher electronic density on the carbonyl oxygen, the interaction of AAm monomer with the ketone occurs by the hydrogen bonding between amide group and carbonyl oxygen of the ketone. This hydrogen bridge is assumed to affect the AAm monomer association [24] and consequently disturbs the keto/enol equilibrium of AAm [20], which raises vinyl bond activity in this system. Thus, it can be suggested that the radical to induce the initiation of AAm is preferentially generated from the AAm



Scheme 4

TABLE II Polymerization<sup>a</sup> of AAm derivatives in the presence of MEK

Run	Momomer	MEK	Yield (%)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
1	AAm	Presence	24.6	2.46	2.0
2	AAm	Absence	0	—	—
3	NMAAm	Presence	Trace	—	—
4	NMAAm	Absence	0	—	—
5	MAAm	Presence	4.9	1.32	2.3
6	MAAm	Absence	0	—	—

<sup>a</sup>Polymerization conditions: [Monomer] = [MEK] = 1.0 mol/l; Solvent, THF; Polymerization time, 330 h; Temperature, 30 °C.

monomer itself which activated by the interaction of the amide group with the carbonyl group of ketones by the hydrogen bonding.

### 3.5. Effect of solvent on the polymerization of AAm initiated with MEK

The polymerization of AAm in the presence of MEK proceeded smoothly not only in THF but also in other polar solvents such as 1,4-dioxane, methanol, and water. As shown in Table II, the polymerizability of AAm decreased as the solvent polarity increase. It is reasonable that low polarity is preferable in the formation a complex of AAm with MEK by the hydrogen bridge.

### 3.6. Effect of temperature on the $R_p$ of AAm initiated with MEK, MIK, and tBMK

Influences of temperature on the  $R_p$  of AAm in the presence of MEK, MIK, and tBMK were studied in a temperature range of 30–60 °C in THF. The calculated  $R_p$  values were correlated with the reciprocals of the polymerization temperature. Fig. 6 is an Arrhenius plot which shows that the relationship between  $\ln R_p$  and  $1/T$  in a temperature range of 30–60 °C forms curved lines for the polymerizations of AAm initiated with MEK, MIK, and tBMK. From the slope of the line (30–60 °C), the overall activation energy ( $E_a$ ) was calculated as 52.6, 35.7, and 22.7 kJ/mol for MEK, MIK, and tBMK, respectively. A comparison of the results obtained with the values of  $E_a$  for the polymerizations of MMA initiated with aldehyde ( $E_a = 36$ –37 kJ/mol) or Poly(vinyl alcohol) ( $E_a = 85$ –89 kJ/mol) [5, 25] and

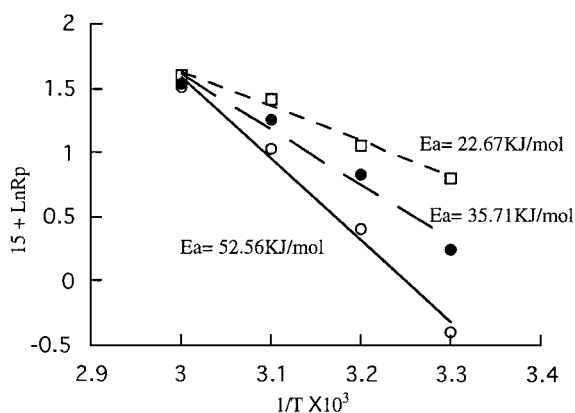


Figure 6 Relationship between  $\ln R_p$  and polymerization temperature ( $1/T$ ) in THF. (O), polymerization of AAm initiated with MEK; (●), polymerization of AAm initiated with MIK; (□), polymerization of AAm initiated with tBMK.

cyclohexanone ( $E_a = 137$  kJ/mol) [7] shows that the  $E_a$  of the polymerization depends strongly on the initiator.

## 4. Conclusion

The  $R_p$  of AAm in the presence of ketones increased with the increase of the electronic density of the carbonyl of ketones as this order: MEK < MIK < tBMK, but in the polymerization of MMA system, the  $R_p$  decreased according to this order: MEK > MIK > tBMK. The maximum value of  $R_p$  for AAm reached the point of equimolar ratio of AAm to ketone in all systems. No effect of steric hindrance of the substitution of hydrogen atom in the  $\alpha$ -position by the methyl group in MEK was observed in the polymerization of AAm. However, it is predominantly in the MMA system. Effects of temperature on the  $R_p$  were discussed in a temperature range of 30–60 °C. The overall activation energy ( $E_a$ ) was estimated to be 52.6, 35.7, and 22.7 kJ/mol for MEK, MIK, and tBMK, respectively. It can be assumed that the radical to initiate the polymerization of AAm is preferentially generated from the AAm monomer itself which activated by the hydrogen bonding interaction between the amide group and the carbonyl group of ketone.

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