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STUDY ON COPOLYMERIZATION OF ACRYLAMIDE WITH STYRENE INITIATED BY METHYL ETHYL KETONE AND ITS DERIVATIVES IN COMPARISON WITH CONVENTIONAL RADICAL INITIATOR

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Key Words: Acrylamide, Methyl Ethyl Ketone, Methyl Isopropyl Ketone, *t*-Butyl Methyl Ketone, Carbonyl-Amide Interaction, Copolymerization

ABSTRACT

Copolymerization of acrylamide (AAm) with styrene (St) was carried out in the presence of methyl ethyl ketone (MEK), methyl isopropyl ketone (MIK) and *t*-butyl methyl ketone (tBMK) without any conventional initiator in tetrahydrofuran (THF) at 60°C. The copolymerization of AAm with St proceeded readily in the presence of the MEK, MIK, and tBMK, while no copolymerization of AAm with St proceeded in the absence of these ketones under the same conditions and no homo-polymerization of St proceeded even in the presence of the ketones. The reactivity ratio of monomer AAm (r_1) is smaller than that of St (r_2) in all of the copolymerization systems, and increases as the order: MEK < MIK < tBMK. The conversion of the copolymerizations increases as the same order described above. The interaction

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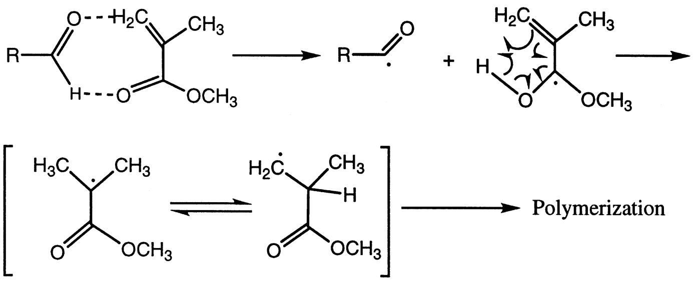
between AAm and the ketones with hydrogen bonding was estimated by the shifts of the absorption bands of the amide carbonyl and N-H groups in the infrared spectra. From the results of the copolymerization between AAm and St, the greater the shift in the N-H absorption, the higher the amount of AAm found in the copolymer.

INTRODUCTION

Radical polymerization of several polar vinyl monomers initiated by compounds having active acidic hydrogens (e.g., aldehydes, ketones, etc.) has been the subject of many publications [1-8]. As shown in Scheme 1, the reaction mechanism involving the transfer of hydrogen radical from these compounds to the monomers, was originally proposed by M. Imoto [3-5]. A similar type of interaction between methyl methacrylate (MMA) and ketones such as cyclohexanone (CHn) [6, 7], cyclopentanone, cycloheptanone, and acetylacetone [9], was also proposed by A. Kaim *et al.* They have reported the initiating activity of these compounds in the copolymerization systems of MMA with styrene (St) [10-12] and AAm with St [13]. However, in all of the literature, the major investigation point was the effect of the polarity of solvents, not the structure of the initiators (ketones).

We have recently been studying the interaction between the amide group of AAm and the carbonyl group of the template polymer [14] or ketones [15-17] in the homopolymerization system of AAm in the presence of poly(methyl methacrylate), CHn, methyl ethyl ketone (MEK), methyl isopropyl ketone (MIK), and *t*-butyl methyl ketone (tBMK). We have found that the higher is the



Scheme 1.

electronic density on the carbonyl oxygen of the ketone, the stronger is the interaction between the carbonyl group in the ketone and the amide group of AAm. The interaction was suggested to induce the initiation of polymerization of AAm. In this paper, we have carried out the copolymerizations of AAm with styrene in the presence of MEK, MIK and tBMK, comparing with the conventional initiator, 2,2'-azobisisobutylonitrile, in order to verify the initiation mechanism of this polymerization system more clearly.

EXPERIMENTAL

Materials

Acrylamide (AAm) was recrystallized twice from benzene. 2,2'-Azobisisobutylonitrile (AIBN) was recrystallized twice from methanol. Styrene (St) was distilled under reduced pressure in the presence of hydroquinone as a radical inhibitor before use. Methyl 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) was purified by the conventional method [18].

Polymerization Method

All copolymerizations were carried out with no irradiation (light-shielded condition). The measured amounts of monomers, ketones, and THF were placed in a glass ampoule under argon. The ampoule was degassed by repeating freeze-evacuate-thaw cycles five times, and sealed under argon. The copolymerization was carried out in a water bath, which was maintained at constant temperature (60°C). After the specified polymerization time, the reaction stopped by placing the ampoule in an ice-water bath. The copolymerization mixture was poured into a large amount of diethyl ether or methanol, and the resulting precipitate was filtered and dried to constant weight in a vacuum oven at room temperature. The crude copolymer was purified by reprecipitation from dimethylforamide into diethyl ether, or acetone into methanol. The structure of the resulting copoly(AAm-St) was estimated by use of IR, ^{1}H NMR, and ^{13}C NMR spectra.

Analyses

IR spectra were recorded with a Perkin-Elmer 1760-X FT-IR. ^{1}H NMR and ^{13}C NMR spectra were recorded by a Nippon-Denshi JNM-FX200 (270) and a JNM-GX500 instrument, respectively.

RESULTS AND DISCUSSION

Effect of Temperature on the Copolymerization of AAm with St

Copolymerization of AAm and St in the presence of MEK was carried out in THF at 40 and 60°C. The results for the copolymerization of AAm and St in the presence and absence of MEK were presented in Table 1. The AAm monomer smoothly copolymerized with St in the presence of MEK either at 40°C or 60°C; however, no copolymerization of AAm with St occurred in the absence of MEK under the same conditions. The temperature markedly affects the conversion of these copolymerizations. All copolymerization systems of AAm and St initiated with MEK were inhibited by adding a small amount of a radical inhibitor (hydroquinone). This fact indicated that these copolymerizations proceeded by a radical-initiated mechanism.

In order to confirm the resulting polymer is the copolymer of the AAm with St, not the mixture of the homopolymers (poly(AAm) and poly(St)), the resulting polymer was dealt with various kinds of solvents according to the steps as shown in Scheme 2. The resulting polymer proved to be the copolymer of AAm with St since no fractions indicating the same solubility to the homopolymer of AAm or St were obtained.

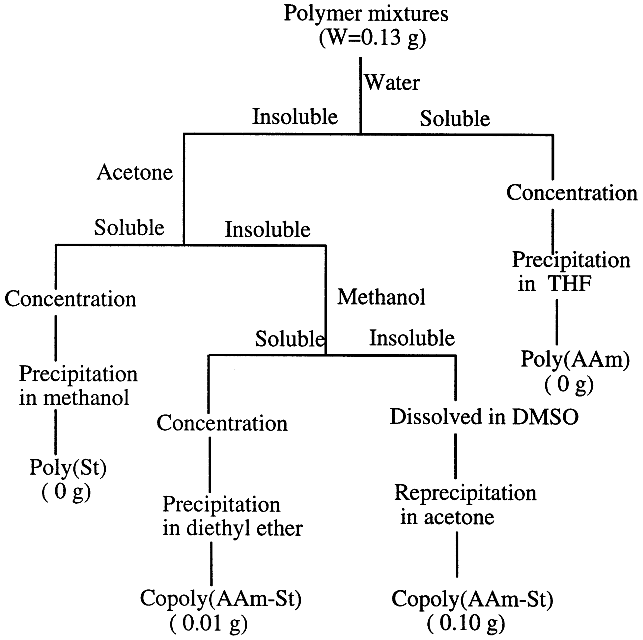
Result of Copolymerization of AAm with St in the Presence of Ketones or AIBN

The copolymerizations of AAm with St in the presence of the MEK, MIK, tBMK and AIBN were carried out in THF at 60°C. The copolymer composition data for AAm-St in the presence of the MEK, MIK, tBMK and the con-

TABLE 1. Copolymerization[a] of Aam with St in the Presence of MEK at the Different Temperature

Run	AAm (M_1), mol/L	St (M_2), mol/L	Initiator (MEK), mol/L	Temperature, °C	Time, h	Yield, mol%
1	1.0	1.0	–	40	235	0
2	1.0	1.0	1.0	40	235	1.7
3	1.0	1.0	–	60	42	0
4	1.0	1.0	1.0	60	42	5.1

a) Copolymerization conditions: Solvent, THF; total volume, 15 ml; no irradiation.



Scheme 2.

ventional initiator, AIBN, are summarized in Tables 2-5 together with mol% conversion. All of the copolymerizations proceeded smoothly in the presence of these ketones, however, no homopolymerization of St occurs in the presence of these ketones under the same conditions.

The AAm-St copolymerization curves as a function of monomer feed versus copolymer composition are shown in Figure 1 and refer to the copolymerization initiated by a conventional radical initiator, AIBN, as well as copolymerization of monomers initiated by MEK, MIK and tBMK in THF at 60°C.

The analytical data (estimated by ^{1}H NMR spectra) of the obtained copolymers have been used to determine the *r*-parameters. The reactivity ratio of AAm (r_1) and St (r_2) are calculated by the Kelen and Tüdös (KT) method [19] and the Finemann and Ross (FR) method [20]. The reactivity coefficient data are represented in Table 6. As expected [12, 13], different calculation methods reduced different *r*-parameter values from the same set of experimental data. The thermal copolymerization of AAm with St in the absence of the MEK, MIK and tBMK and the thermal homopolymerization of St in the presence of these

TABLE 2. Copolymerizations of AAm with St in the Presence of MEK[a]

Run	Mole fraction in feed		MEK, mol/L	Incorportated M_1 (AAm) in copolymer, mol%	Conversion, mol%
	M_1 (AAm)	M_2 (St)			
1	0.8	0.2	1.0	78.9[b]	7.0
2	0.7	0.3	1.0	63.8[b]	6.5
3	0.6	0.4	1.0	38.1[c]	4.8
4	0.5	0.5	1.0	25.4[c]	3.7
5	0.4	0.6	1.0	19.3[c]	2.1
6	0.2	0.8	1.0	13.2[d]	1.7
7	—	1.0	1.0	—	0

a) Copolymerization conditions: Solvent, THF; temperature, 60°C; total monomer, 2 mol/L; reaction time, 44.0 hours; no irradiation.

b) Determined by ^{1}H NMR in D_2O+ DMSO-d_6. c) Determined by ^{1}H NMR in DMSO-d_6.

d) Determined by ^{1}H NMR in $CDCl_3$.

TABLE 3. Copolymerizations of AAm with St in the Presence of MIK[a]

Run	Mole fraction in feed		MIK, mol/L	Incorportated M_1 (AAm) in copolymer, mol%	Conversion, mol%
	M_1 (AAm)	M_2 (St)			
1	0.8	0.2	1.0	80.7[b]	19.8
2	0.7	0.3	1.0	67.4[b]	15.6
3	0.6	0.4	1.0	40.4[c]	10.7
4	0.5	0.5	1.0	29.5[c]	5.7
5	0.4	0.6	1.0	21.2[c]	3.7
6	0.2	0.8	1.0	16.5[d]	3.3
7	—	1.0	1.0	—	0
8	0.5	0.5	—	—	0

a) Copolymerization conditions: Solvent, THF; temperature, 60°C; total monomer, 2 mol/L; reaction time, 44.0 hours; no irradiation.

b) Determined by ^{1}H NMR in D_2O+ DMSO-d_6. c) Determined by ^{1}H NMR in DMSO-d_6.

d) Determined by ^{1}H NMR in $CDCl_3$.

TABLE 4. Copolymerizations of AAm with St in the Presence of tBMK[a]

Run	Mole fraction in feed M_1 (AAm)	Mole fraction in feed M_2 (St)	tBMK, mol/L	Incorportated M_1 (AAm) in copolymer, mol%	Conversion, mol%
1	0.8	0.2	1.0	81.2[b]	26.5
2	0.7	0.3	1.0	69.2[b]	20.1
3	0.6	0.4	1.0	42.5[c]	15.2
4	0.5	0.5	1.0	32.8[c]	11.9
5	0.4	0.6	1.0	25.3[c]	6.1
6	0.2	0.8	1.0	18.5[d]	3.7
7	–	1.0	1.0	–	0
8	0.5	0.5	–	–	0

a) Copolymerization conditions: Solvent, THF; temperature, 60°C; total monomer, 2 mol/L; reaction time, 44.0 hours; no irradiation.

b) Determined by ^1H NMR in D_2O+ DMSO-d_6. c) Determined by ^1H NMR in DMSO-d_6.

d) Determined by ^1H NMR in $CDCl_3$.

TABLE 5. Copolymerizations of AAm with St in the Presence of AIBN[a]

Run	Mole fraction in feed M_1 (AAm)	Mole fraction in feed M_2 (St)	Reaction time, hours	Incorportated M_1 (AAm) in copolymer, mol%	Conversion, mol%
1	0.8	0.2	3.0	42.0[b]	11.4
2	0.7	0.3	3.0	34.8[c]	10.7
3	0.6	0.4	3.0	24.1[c]	10.0
4	0.5	0.5	4.0	15.6[c]	12,1
5	0.4	0.6	4.0	13.1[c]	9.3
6	0.2	0.8	4.0	10.3[d]	7.3

a) Copolymerization conditions: Solvent, THF; temperature, 60°C; total monomer, 2 mol/L; no irradiation.

b) Determined by ^1H NMR in D_2O+ DMSO-d_6. c) Determined by ^1H NMR in DMSO-d_6.

d) Determined by ^1H NMR in $CDCl_3$.

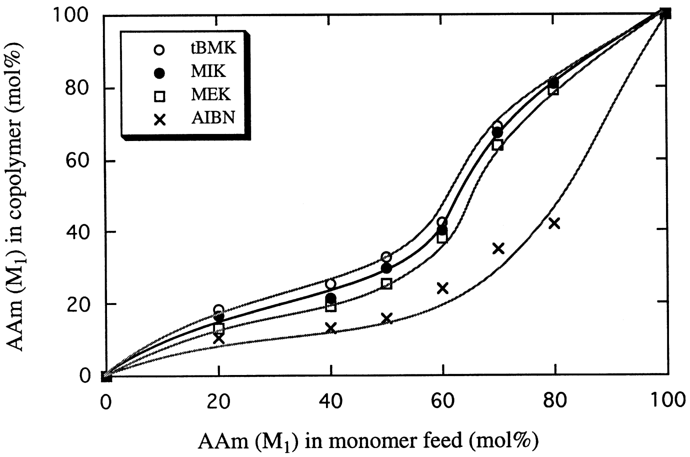


Figure 1. Monomer-copolymer composition curves for the copolymerization of Aam with St in the presence of MEK, MIK, tBMK in THF at 60°C. [MEK] = [MIK] = [tBMK] = 1.0 mol/L, [AIBN] = 0.02 mol/L.

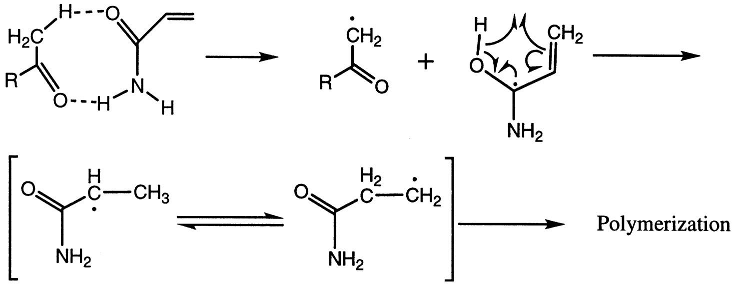
TABLE 6. The Reactivity Ratio of the r_1 (Aam) and r_2 (St) Calculated by FR and KT Method in the Presence of MEK, MIK, tBMK and AIBN

Reaction initiator	*r*-Values	FR method	KT method
AIBN	r_1	0.04 ± 0.05	0.12 ± 0.08
	r_2	3.45 ± 0.05	4.41 ± 0.09
MEK	r_1	0.31 ± 0.05	0.44 ± 0.09
	r_2	1.58 ± 0.08	1.85 ± 0.12
MIK	r_1	0.34 ± 0.08	0.48 ± 0.13
	r_2	1.28 ± 0.08	1.39 ± 0.17
tBMK	r_1	0.47 ± 0.10	0.56 ± 0.28
	r_2	1.20 ± 0.12	1.23 ± 0.29

Polymerization conditions: Solvent, THF; temperature, 60°C.

ketones did not proceed under the same conditions. In all the copolymerization systems, the r_1 (AAm) value is greatly smaller than that of the r_2 (St) value, and the r_1 value in the copolymerization systems initiated by the ketones is higher than by the conventional radical initiator, AIBN. The r_1 values increased as the order: MEK < MIK < tBMK, that is the same order as the electronic density of carbonyl oxygen atom for ketones [16, 17]. This fact may be explained on the basis of the strong hydrogen bonding ability of ketones to the amide group, which is assumed to affect the AAm monomer association [21], and consequently disturbs the keto/enol equilibrium of AAm [22]. Due to the lack of an additional opportunity for a hydrogen bridge, the AAm monomer and its radical remain comparatively unchanged in the AIBN environment. The initiating radicals in these copolymerization systems in the presence of the ketones probably generated from the AAm monomer which formed a complex with the ketone (Scheme 3), as we reported in the homopolymerization systems of AAm in previous papers [16, 17]. The radicals from ketones seemed to have no ability to initiate the polymerization since the resulting polymers were found to include no ketone units and ketones were almost completely recovered unchanged.

L. M. Minsk [23] and G. Saini [22] have also reported that the higher amount of the St units were included in the copolymer in the free radical copolymerization systems. In their publications, the free radical copolymerization of AAm and St was carried out in a variety of solvents, and the observed *r*-parameter data r_1 (AAm), r_2 (St) is listed in Table 7. The r_1 is smaller than r_2 in ethanol, 2-(2-methoxy-ethoxy)ethanol, water-t*ert*-butylalcohol and dimethylsulfoxide solvent, but is higher in the benzene, α-dichlorobenzene, benzene-benzonitrile and benzonitrile [23]. The effect of the solvents (i.e., by hydrogen



Scheme 3.

TABLE 7. The *r*-Parameter Data and the Shift Values in Infrared Spectra of AAm[a]

Solvent	r_1 (AAm)	r_2 (St)	Δ Absorption, cm^{-1}			
			CO	NH^I	NH^{II}	ΔNH (avg.)
Benzene	12.5	0.25	1.0	15.0	10.0	12.5
α-Dichlorobenzene	12.5	0.25	3.0	5.0	5.0	5.0
Benzene-benzonitrile	4.4	1.50	8.0	46.0	45.0	45.5
Benzonitrile	2.4	1.35	12.0	70.0	55.0	62.5
Ethanol	0.30	1.44	13.0	205.0	230.0	217.5
2-(2-Methoxy-ethoxy)ethanol	0.27	1.66	22.0	205.0	230.0	217.5
Water-*tert*-butyl alcohol	0.78	2.93	28.0	205.0	230.0	217.5
Dimethyl sulfoxide	0.16	2.01	17.0	245.0	235.0	242.5
Methyl alcohol	0.2	1.05	13.0	205.0	230.0	217.5

a) Data from Ref. 23.

bonding, by dipole-dipole interaction only, or by a combination of both) upon the AAm was measured by the shift in the infrared spectra of the amide carbonyl and N-H groups (Table 7). The greater the shift in the N-H absorption, the smaller the amount of AAm monomer that is found in the copolymer. This fact does not match our results (Table 8). Table 8 shows a summation of the infrared shifts of the carbonyl (ΔCO) and NH bonds in the MEK, MIK and tBMK media. The higher the electronic density of the carbonyl oxygen atom in ketones, the greater is the shift in the C=O and N-H absorption for the monomeric AAm that is observed in this study. A slight shift of the C=O and N-H absorption of AAm is also found in the THF media, however, it is smaller than that in the ketone media. Thus, it can be suggested that the interaction between AAm and THF is too weak to induce the generation of the radical from AAm in the absence of ketones. This result shows a reasonable agreement with the fact that the homopolymerization of AAm and the copolymerization of AAm with St do not occur in the absence of ketones in these systems.

TABLE 8. Infrared Absorption of Monomeric AAm in a Variety of Medium[a]

Media	Infrared absorption, cm^{-1}			Δ Infrared absorption, cm^{-1}		
	C=O	NH ^{I}	NH ^{II}	C=O	NH ^{I}	NH ^{II}
Neat (KBr pressing)	1674.5	3353.5	3181.1			
Tetrahydrofuran	1679.8	3357.1	3212.8	5.3	3.6	31.7
Methyl ethyl ketone	1689.5	3418.9	3353.2	15.0	65.4	172.1
Methyl isopropyl ketone	1692.7	3455.6	3359.5	18.2	102.1	178.4
t-Butyl methyl ketone	1713.5	3461.5	3361.7	39.0	108.0	180.6

a) 10 mol% concentration in these medium.

In the case of ketones, the interaction between the carbonyl group in ketone and the amide group in AAm results in the generation of the radicals of AAm, then the resulting radicals transfer to the St monomer. The source of the radical in these systems can be assumed to be preferentially generated from the AAm monomer, in which the vinyl bond is activated by the hydrogen bridge between the carbonyl group in the ketones and the amide group in the AAm monomer. Similarly, as this reason, the radical of AAm is easier to combine with the radical itself, especially, in the case of the higher concentration of AAm. Also, the reason that the r_1 values in the presence of MEK, MIK and tBMK increase as the order: MEK < MIK < tBMK, can be explained in terms of the interaction strength between the AAm monomer and the ketone molecules which increases as the same order: MEK < MIK < tBMK.

On the other hand, only the solvent effect induced by the dipole-dipole interaction exists in the AIBN-initiated system. The activity of the AAm monomer or the radical of AAm does not change. Thus, the amount of AAm that is observed in the copolymer of AIBN-initiated system is lower than in the ketone-initiated system. However, these data are not sufficient enough to explain this mechanism of the copolymerization of AAm with St induced by the ketone, the further investigation is being performed in our laboratory.

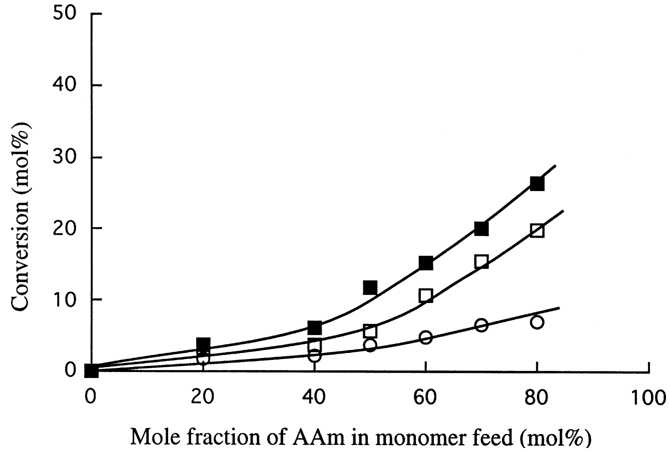


Figure 2. Conversion of copolymerization for Aam and St vs. mole fraction of AAm in monomer feed in THF at 60°C. (O), initiated by the MEK, polymerization time, 44 hours. (□), initiated by the MIK, polymerization time, 44 hours. (■), initiated by the tBMK, polymerization time, 42 hours.

Relationship between the Conversion of Copolymerization of AAm with St *vs.* the Mole Fraction of AAm in Monomer Feed

The relationship between the conversion of the copolymerization of AAm and St *vs.* the mole fraction of AAm in the monomer feed is shown in Figure 2. The conversion increases with the increase of the mole fraction of AAm in the monomer feed, and increases as the same order as the electronic density of the carbonyl oxygen atom in the ketones (MEK < MIK < tBMK). This fact is in excellent agreement with our concept described in the previous papers [15-17].

Effect of the Ketone Concentration on the Conversion of Copolymerization of AAm with St

In order to estimate further the interaction effect on the conversion of the copolymerization of AAm with St, the copolymerization of AAm with St was run in a varied amount of ketones at the range of 0-1.5 mol/L. As shown in Figure 3, the conversion of these systems increases with the increase of the ketone concentration in the range of 0.0-1.0 mol/L and reaches the local maximum value at the point of equimolar ratio of the AAm monomer to ketones ([AAm]/[Ketones]

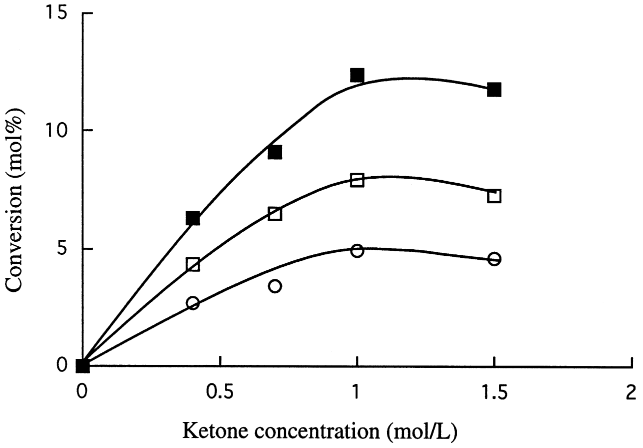


Figure 3. Effects of the ketone concentration on the conversion of the copolymerizations of Aam with St in THF at 60°C. (O), initiated with the MEK. (□), initiated with the MIK. (■), initiated with the tBMK.

= 1). The conversion tends to decrease when the concentration of ketones is over than that of the monomer (1.0 mol/L). The following two overlapped effects can be responsible for this fact: the formation of a reactive complex between AAm and ketones which results in the generation for the radical of AAm, and the retardation of the radical copolymerization by the chain transfer reaction [24].

As well as the homopolymerization of AAm in the presence of MEK, MIK, and tBMK in THF, the substitution pattern on α-position of MEK remarkably affected the conversion of the copolymerization of AAm with St. The conversions increased as the order: MEK<MIK<tBMK, which is the same order as the electronic density of carbonyl oxygen atom of the ketones. It is also in good agreement with the result of our previous reports [16, 17] that the higher electronic density of the carbonyl oxygen atom in ketone results in the stronger interaction of the monomer with the ketone.

CONCLUSION

The copolymerization for AAm and St proceeds readily in the presence of MEK, MIK and tBMK in THF at 60°C. No copolymerization of AAm with

St occurred in the absence of these ketones under the same conditions and no homopolymerization of St proceeded even in the presence of the ketones. The copolymerization for AAm and St is suggested to proceed by a radical-initiated mechanism. The r_1 values for AAm is smaller than r_2 (St) in any of the copolymerization systems, and increases as the order: MEK < MIK < tBMK. Similarly, the conversion of the copolymerization systems increases as the same order. The interaction between the AAm monomer and the ketone molecule with hydrogen bonding was estimated by the shifts of the absorption bands of the amide carbonyl and N-H groups in the infrared spectra. From the result of the AAm-St copolymerization, the greater the shift in the N-H absorption, the higher is the amount of the AAm that is found in the copolymer.

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