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### TEMPLATE POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF SEVERAL HOMO- AND COPOLYMERS INCLUDING METHYL VINYL KETONE, METHYL METHACRYLATE, AND STYRENE

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## TEMPLATE POLYMERIZATION OF ACRYLAMIDE IN THE PRESENCE OF SEVERAL HOMO- AND COPOLYMERS INCLUDING METHYL VINYL KETONE, METHYL METHACRYLATE, AND STYRENE

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Key Words: Carbonyl-Amide Interaction, Acrylamide, Poly(methyl vinyl ketone), Syndiotactic Poly(methyl methacrylate), Isotactic Poly(methyl methacrylate), Template Polymerization

### ABSTRACT

Template polymerization of acrylamide (AAM) in the presence of several homo- and copolymers such as poly(methyl vinyl ketone) (poly-MVK), poly(methyl methacrylate) (poly-MMA), copoly(MVK-styrene) and copoly(MMA-styrene) was carried out in THF at 30 or 40°C. The rate of polymerization ( $R_p$ ) of AAM was greatly enhanced by the presence of a template polymer. However, a small amount of styrene (St) units in the template polymer markedly decreased the  $R_p$  of AAM. It was assumed that the contamination of the St units in the chain of the template polymer impeded the continuous absorption of AAM monomers onto the active sites of the template polymer. Also, the effect of stereo-regularity of poly-MMA on the  $R_p$  and the number-average molecular weight ( $M_n$ ) of the resulting poly-AAM was investigated. The syndiotactic poly-MMA had pronounced influence on the  $R_p$  of AAM and  $M_n$  of poly-AAM comparing with the isotactic poly-MMA. This effect can be explained in the terms of the different conformational features of the two tacticity forms of templates.

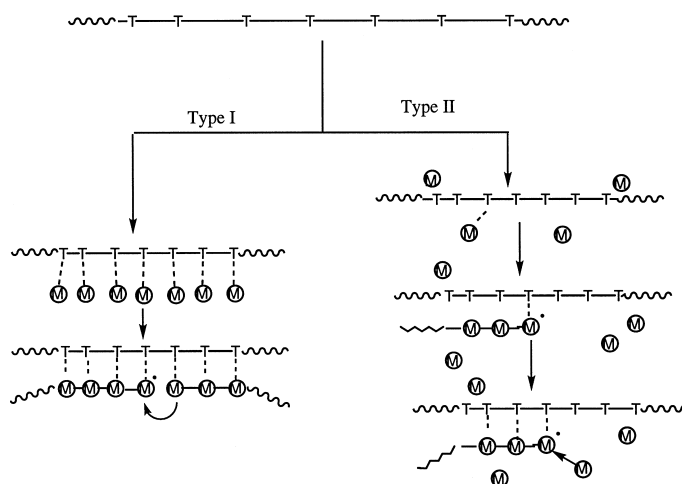
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## INTRODUCTION

In template polymerization, one seeks to achieve the polymerization of monomer units associated with a template in a predetermined manner, and thus to synthesize polymers having precise structures or microstructures. The outstanding characteristics [1] of this template polymerization are: (a) complex formation takes place between the monomer and template polymer, (b) the rate of polymerization ( $R_p$ ) increases as the concentration of template increases, and (c) the structural and conformational features of the daughter polymers are affected by the template.

This template effect was originally discovered by C. H. Bamford [2]. The mechanism of template polymerization as shown in Scheme 1 can be classified ideally into two types (type I and II), as was proposed and studied extensively by V. A. Kargin [3] and other authors [4, 5]. The fundamental difference in these two types is the mode of propagation [6], namely, in the type I system, template polymerization proceeds by subsequent addition of adjacently adsorbed monomer molecules, whereas in the type II system the template polymerization proceeds by addition of monomer molecules from the surrounding solution. The number-average degree of polymerization ( $P_n$ ) for the resulting daughter polymer is always close to that of the template in the ideal type I system, but there is no correlation to that of the template in the type II system.



Scheme 1. Diagrammatic presentation of mechanistic types of the template polymerization. -T-T-T- = template polymer, M = monomer, -M-M-M- = growing radical of daughter chain.



It has been reported that poly(acrylamide) (poly-AAm) showed a template effect in the polymerization of acrolein initiated by imidazole in a water-ethanol mixed solvent [7-9]. The observed enhancement of polymerizability of acrolein was explained in terms of interaction between the carbonyl group in acrolein and the amide group in poly-AAm. Also, the template polymerization of AAm [10, 11] could be induced by the presence of a template polymer having carbonyl groups on its side chain such as poly(methyl vinyl ketone) (poly-MVK), poly(*N*-vinylpyrrolidone) and poly(methyl methacrylate) (poly-MMA). The  $P_n$  of templates was reflected on the resulting poly-AAm (daughter polymer). However, no template polymerization [12] of *N,N*-dimethylacrylamide occurred, even in the presence of poly-MVK and copoly(MVK-styrene) in THF at 30°C. These phenomena indicated that the formation of the hydrogen bondings between the carbonyl groups in the template polymers and the amide groups in the monomers was the most important factor to drive the initiation and propagation in this template polymerization.

On the other hand, an additional interesting fact about the effects of template tacticity was investigated in detail in the polymerization of a vinyl monomer system [13-20]. Challa found that in the polymerization of MMA initiated by tacticity template of poly-MMA, the presence of an isotactic poly-MMA template promoted the formation of syndiotactic poly-MMA (daughter polymer) [13], and the enhancement of  $R_p$  for MMA due to the template effect was more remarkable with the isotactic poly-MMA template than with syndiotactic ones [14].

In the present paper, we report on the template polymerizability of AAm in the presence of homopolymers such as poly-MVK and poly-MMA, and copolymers such as copoly(MVK-St) and copoly(MMA-St) in tetrahydrofuran. Also, the effects of the stereoregular poly-MMA on the  $R_p$  of AAm are discussed.

## EXPERIMENTAL

### Materials

Acrylamide (AAm) was purified by recrystallization from benzene twice. Styrene (St), methyl vinyl ketone (MVK) and methyl methacrylate (MMA) were distilled twice in reduced pressure under a dry oxygen-free nitrogen stream in the presence of hydroquinone as a radical inhibitor, respectively. 2,2'-Azobisisobutyronitrile (AIBN) as a radical initiator was recrystallized from methanol. Tetra-



hydrofuran (THF) and other solvents were purified as described previously [9-11].

### Synthesis of Template Polymers

The template polymers such as poly(methyl vinyl ketone) (poly-MVK), poly(methyl methacrylate) (poly-MMA), copoly(MVK-St) and copoly(MMA-St) were prepared by a method of radical-initiated polymerization. Homo- and copolymerizations of MVK with St were carried out in benzene at 60°C using AIBN as a radical initiator. The yield and the number-average molecular weights (Mn) of the resulting poly-MVK and copoly(MVK-St) are summarized in Table 1.

The poly-MMA and copoly(MMA-St) were also synthesized in benzene at 60°C by use of AIBN as an initiator. The yield and the characteristics of the resulting poly-MMA and copoly(MMA-St) are shown in Table 2.

The isotactic poly-MMA was prepared by the anionic polymerization, which was carried out in toluene at -78°C using n-BuLi as a catalyst. 2.7 mmol of n-BuLi and 50 mL of toluene were placed in a flask, and 47 mmol of MMA was added successively. After the polymerization at -78°C for 2 hours, a small amount of methanol was added to terminate the polymerization. The resulting polymers were reprecipitated from the acetone-methanol system. The obtained polymers were characterized by <sup>1</sup>H NMR, IR spectra and GPC (Yield 72%, Mn = 1.03 x 10<sup>4</sup>, Mw/Mn = 2.8).

### Method of Template Polymerization

Template polymerization of AAm in the presence of poly-MVK, copoly(MVK-St), poly-MMA, and copoly(MMA-St) was carried out in THF at 30

TABLE 1. Copolymerization<sup>a</sup> of the MVK with the St

Run	Charged the Monomer, (mol %)		Yield, %	Incorporated MVK <sup>b</sup> in the Copolymer, (mol%)	Mn X 10 <sup>-4</sup>
	MVK	St			
1	100	0	78	100	0.99
2	80	20	82	78	1.65
3	49	51	71	51	2.04
4	34	66	69	39	2.14

<sup>a</sup>Polymerization conditions: [AIBN], 0.03 mol/L; benzene; total monomer, 2.5mol/L ; polymn. time, 20 h; temperature, 60 °C; no irradiation.

<sup>b</sup>Determined by <sup>1</sup>H NMR.



TABLE 2. Copolymerization<sup>a</sup> of MMA with St

Run	Charged the Monomer, (mol%)		Yield, %	Incorporated MMA <sup>b</sup> in the Copolymer, (mol%)	MnX10 <sup>-4</sup>
	MMA	St			
1	100	0	88	100	1.78
2	84	16	85	85	2.48
3	58	42	62	58	1.98
4	38	62	54	38	1.62
5	15	85	51	15	1.76

<sup>a</sup>Polymerization conditions : [AIBN], 0.03 mol/L; benzene; total monomer, 3.0mol/L; polymn. time, 20 h; temperature, 60°C; no irradiation.

<sup>b</sup>Determined by <sup>1</sup>H NMR.

or 40°C. The calculated amount of the above homo- or copolymers was placed in a glass ampoule and dissolved completely in a small amount of THF. Then, the weighted amount of AAm was added into the ampoule. The ampoule was filled with THF until the total volume reached 20 mL and was degassed by four cycles of freeze-evacuated-thaw under reduced pressure, and sealed under vacuum. The polymerization was carried out heterogeneously in a water bath, keeping a constant temperature (30 or 40°C). The precipitated poly-AAm was filtered to dry and reprecipitated from the water-acetone system.

### Analyses

The IR spectra were recorded with a Perkin-Elmer 1760-X FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined 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 GL-W-550 column.

## RESULTS AND DISCUSSION

### Template Polymerization of AAm in the Presence of Poly-MVK, Copoly(MVK-St), Poly-MMA, and Copoly(MMA-St)

Template polymerization of AAm in the presence of poly-MVK, copoly(MVK-St), poly-MMA, copoly(MMA-St) was carried out in THF at 30 and



TABLE 3. Template Polymerization<sup>a</sup> of AAm in the Presence of the Copoly(MVK-St)

Run	Charged the Template Polymer			Yield, (%)	Mn X 10 <sup>-4</sup>	Pn
	MVK Content, (mol%)	Pn	g <sup>b</sup>			
1	100	141	0.11	92	1.00	141
2	78	213	0.15	21	1.15	163
3	51	235	0.25	11	1.33	185
4	39	236	0.35	42	1.20	169

<sup>a</sup>Polymerization conditions: THF; [AAm] = 1.2mol/L; polymn. time, 68 h; temperature, 30 °C; no irradiation.

<sup>b</sup>The amounts of MVK unit are fixed at 0.075 mol/L.

40°C. The polymerization of AAm proceeded readily in all cases (Tables 3 and 4); however, no polymerization of AAm occurred in the absence of the templates. Interestingly, the rate of polymerization (Rp) of AAm decreased markedly with decreasing content of MVK or MMA in the copolymers until it reached ca. 50-60% molar ratio, even if the net amount of the MVK or MMA units in all cases was fixed at the same value (0.075 mol/L). It is reasonable to assume that the contamination of the St units in the template greatly impedes the continuous adsorption of monomers on the active sites of the template polymers.

 TABLE 4. Template Polymerization<sup>a</sup> of AAm in the Presence of the Copoly(MMA-St)

Run	Charged the Template Polymer			Yield, (%)	Mn X 10 <sup>-4</sup>	Pn
	MMA Content, (mol%)	Pn	g <sup>b</sup>			
1	100	178	0.15	53	1.40	180
2	84	246	0.18	21	1.61	204
3	58	194	0.26	14	1.47	206
4	38	158	0.41	33	1.42	200
5	15	170	1.04	62	1.37	193

<sup>a</sup>Polymerization conditions: THF; [AAm] = 1.2mol/L; polymn. time, 64 h; temperature, 40 °C; no irradiation.

<sup>b</sup>The amounts of MMA unit are fixed at 0.075 mol/L.



The number-average degree of polymerization ( $P_n$ ) of poly-AAm (daughter polymer), is nearly equal to that of the template homopolymer, or the parts of  $P_n$  for MVK and MMA in the copolymers, in which the content of the MVK or MMA units is higher than 75% (molar ratio). However, no correlation was observed between the  $P_n$  of the daughter polymer and the template, when the content of MVK or MMA units in the copolymer is lower than 75% (molar ratio). It can be suggested that the monomer is absorbed along the chain of the template by hydrogen bonding between the  $-NH_2$  group in AAm and the  $-C=O$  group in the side chain of the template, and the polymerization of AAm proceeds along the chain of the template, in which the content of MVK or MMA units is higher than 75% (molar ratio). It is presumed that the formation of complexes between the monomers and templates drives the initiation and propagation reaction in this system. The mechanism can be described as a type I mechanism [6].

In the case of a low content of MVK or MMA units in the template polymers, the  $P_n$  of the resulting poly-AAm shows a varied value corresponding to the efficient parts of  $P_n$  of MVK or MMA in the template. This may be explained on the basis of the fact that the contamination of St in the template chain markedly impedes the continuous adsorption of AAm monomers onto the template, and the association of the segment of the growing chain radicals with one another takes place in the solution, which results in the different  $P_n$  of poly-AAm. In this case, some monomers are initially adsorbed by the active sites on the template through the hydrogen bonding between the carbonyl group in the template and the amide group in AAm, which results in the formation of a growing radical chain. In the course of the polymerization, the growing chain is exchanged for the monomers, and some propagation of the radical proceeds in the solution (deviating from the template chain). Such a template was suggested to behave just as the usual initiator [4]. The mechanism may be classified as the type II system [6].

On the other hand, higher concentration of St units in the copolymer also raised the  $R_p$  of AAm. This result can be attributed to the gel effect [21].

### Template Polymerization of AAm in the Presence of Mixtures of Poly-MMA and Poly-St

In order to investigate the influence of the contamination of St on the  $R_p$  of AAm more precisely, the template polymerization of AAm was performed in the presence of mixtures of poly-MMA and poly-St under the same conditions comparing to that of St units contained in the template copolymer. The results





TABLE 5. Template Polymerization<sup>a</sup> of AAm in the Presence of Mixtures of the Poly-MMA and Poly-St

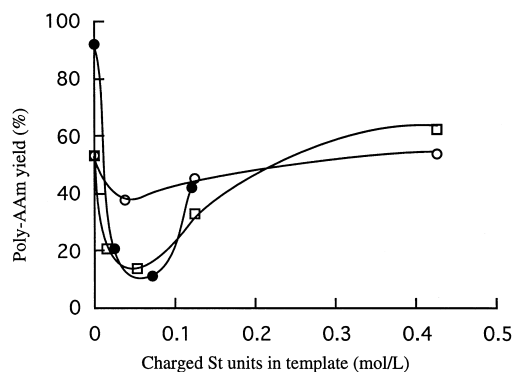
Run	Charged the Template Polymer, (mol/L)		Yield, %	Mn X 10 <sup>-4</sup>	Pn
	Poly-MMA <sup>b</sup>	Poly-St			
1	0.075	0	53	1.40	198
2	0.075	0.04	38	1.58	200
3	0.075	0.13	45	1.34	188
4	0.075	0.43	54	1.35	189

<sup>a</sup>Polymerization conditions: THF; [AAm] = 1.2 mol/L; polymn. time, 64 h; temperature, 40 °C; no irradiation.

<sup>b</sup>Pn = 178.

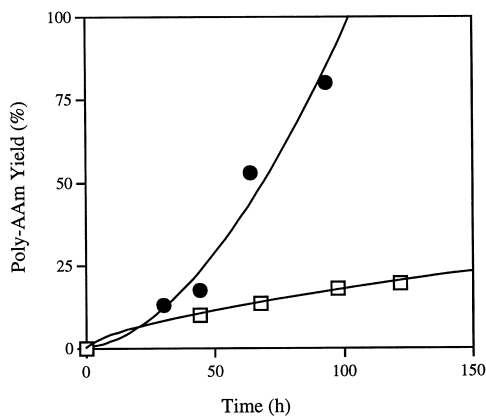
are summarized in Table 5. It is noted that the contamination of poly-St in the template mixtures only influences the R<sub>p</sub> of AAm but not the P<sub>n</sub> of poly-AAm. The P<sub>n</sub> of poly-AAm is nearly equal to that of template poly-MMA, which is considered as an efficient part of the template to control the P<sub>n</sub> of the daughter polymer. This mechanism also can be regarded as the type I mechanism [6].

As shown in Figure 1, a small amount of poly-St decreased the R<sub>p</sub> of AAm; however, the influence of the St sequence is not so great as in the case in which St units are included in a chain of copoly(MVK-St) or copoly(MMA-St).



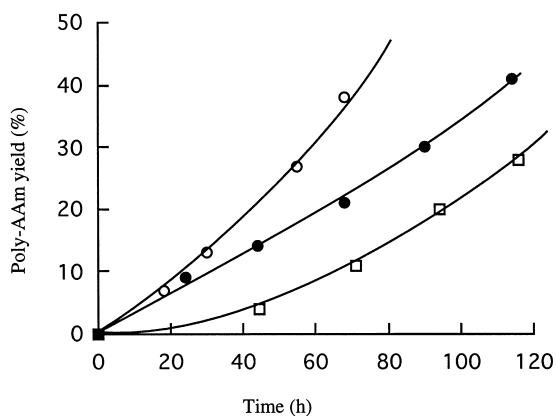
**Figure 1.** Effect of the St units on the yield of the template polymerization of AAm in the presence of the copoly(MMA-St) (□), mixtures of poly-MMA and poly-St (○), copoly(MVK-St) (●). Charged the MMA or MVK units content in the template of copolymer or mixtures are 0.075 mol/L.



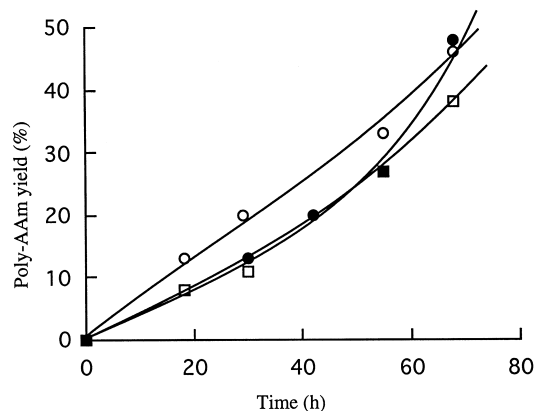


**Figure 2.** Time-conversion curves of the template polymerization of AAm in the presence of the poly-MMA (●) or copoly(MMA-St) (□) (the MMA molar content in copolymer is 58%). [AAm] = 0.3 mol/L, [MMA units ] = 0.075 mol/L, 40°C.

Higher concentration of poly-St in the template mixtures also raises the  $R_p$  of AAm. Similarly, this result can be explained in terms of the gel effect [21], because the higher concentration of template increased the viscosity of the solution, which leads to retard the segmental diffusion of the growing chain



**Figure 3.** Time-conversion curves of the template polymerization of AAm in the presence of the poly-MVK (○) and copoly(MVK-St) [the MVK molar content in the copolymer is 78% (●), 51% (□)] at 30°C.



**Figure 4.** Time-conversion curves of the template polymerization of AAm in the presence of the poly-MVK varying the Pn in THF at 30°C. Pn = 73 (○), Pn = 124 (□), Pn = 247 (●), [AAm] = 0.3 mol/L, [MVK unit] = 0.3 mol/L.

radicals or the monomer radicals, and results in the higher  $R_p$  of AAm in this template polymerization system. This fact has also been proven clearly by G. Challa [5].

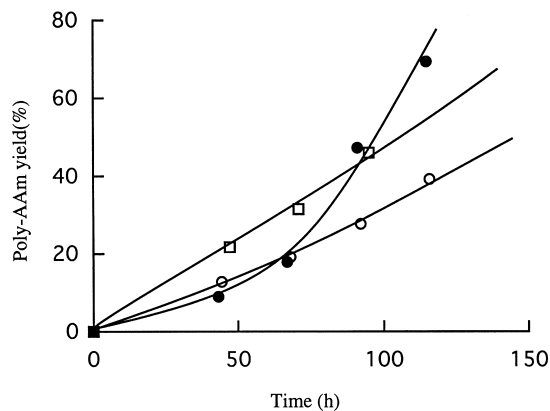
#### Relationship Between Time and Conversion for the Polymerization of AAm in the Presence of Template Homo- and Copolymers

The time vs conversion curves for the template polymerization of AAm in the presence of poly-MMA and copoly(MMA-St) are shown in Figure 2, and those in the presence of poly-MVK and copoly(MVK-St) are shown in Figure 3. The acceleration of poly-MMA and poly-MVK on the initial  $R_p$  of AAm is markedly greater than that of copoly(MMA-St) and copoly(MVK-St). This fact is in good agreement with the views as mentioned above, namely, a small amount of St units included the template chain severely decreased the initial  $R_p$  of AAm. It can be presumed that the St units spreading out in the template chain impedes the successive absorption of AAm monomers onto the active sites of the template, which results in lower initial  $R_p$  of AAm.

#### Effect of Pn for the Template Polymer on the Yield of Poly-AAm

The effect of the Pn for the template homopolymer, poly-MVK and poly-MMA, on the yield of poly-AAm is represented in Figures 4 and 5. Higher Pn of template poly-MVK results in lower  $R_p$  of AAm, because the mobility of longer templates is lower than that of shorter ones, which retards the termination of the bimolecular or segmental chain of the radical. In the case of a long segmental





**Figure 5.** Time-conversion curves of the template polymerization of AAm in the presence of the poly-MMA varying the Pn in THF at 40°C. Pn = 139 (○), Pn = 1166 (□), Pn = 3733 (●), [AAm] = 0.3 mol/L, [MMA unit] 0.3 mol/L.

sequence of template poly-MVK, however, the  $R_p$  of AAm gradually increased as the polymerization proceeded. The rate of propagation probably becomes faster when the AAm monomers are adsorpted onto most of the empty active sites in the template chain (Figure 4). The same result is also observed in the case of poly-MMA (Figure 5).

### Template Polymerization of AAm in the Presence of Stereoregular Poly-MMA

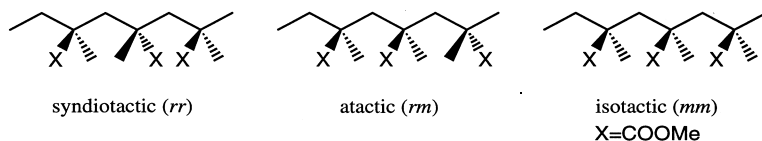
It has been reported [13, 15, 22] that the radical polymerization of MMA in the presence of stereoregular poly-MMA as a template polymer could proceed

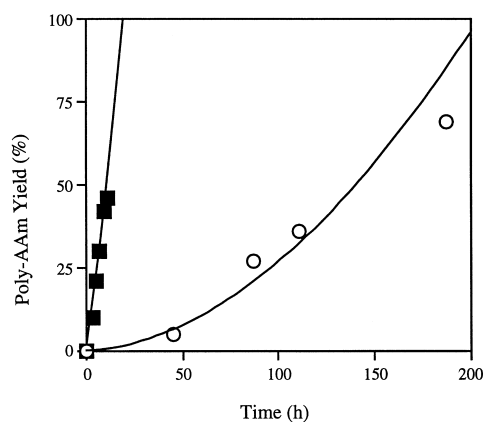
TABLE 6. Determination of Triad Tacticities of the Template Poly-MMA

Run	Initiator/Solvent	$M_n^a \times 10^{-4}$	Propotion <sup>b</sup> $\times 10^2$		
			<i>rr</i>	<i>rm</i>	<i>mm</i>
1	AIBN/Benzene	1.78	59.6	34.6	5.8
2	<i>n</i> -BuLi/Toluene	1.03	16.6	19.4	64.0

<sup>a</sup>Estimated by GPC (based on the polystyrene standard).

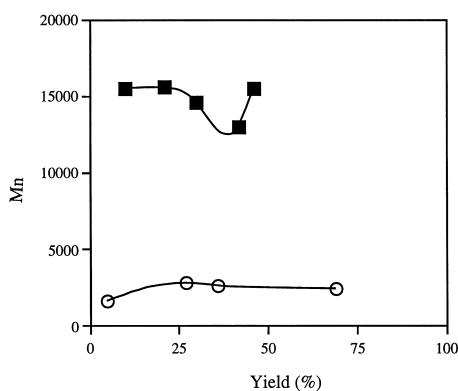
<sup>b</sup>Determined by <sup>1</sup>H NMR .





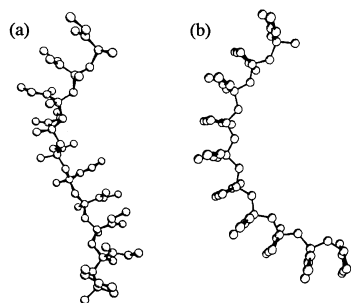
**Figure 6.** Time-conversion curves of the template polymerization of AAm in the presence of the *i*-poly-MMA (○) or *s*-poly-MMA (■) at 40°C, [AAm] = 0.3 mol/L, [poly-MMA] = 0.3 mol/L.

according to a stereospecific template-type mechanism. The tendency of isotactic (*i*) and syndiotactic (*s*) poly-MMA to form stereocomplexes was assumed to be the main factor to control the stereoselectivity of the template polymerization of MMA. This template polymerization mechanism was originally suggested by V. A. Kargin [23]. Similarly, the influence of stereoregular poly-MMA on the  $R_p$  of AAm is observed in THF at 40°C. The triad tacticities of the used template poly-MMA are presented in Table 6. As shown in Figure 6, it is clear that syndiotactic rich poly-MMA (*s*-poly-MMA) as a template has greater effect on the  $R_p$  of AAm than isotactic rich poly-MMA (*i*-poly-MMA) in THF.



**Figure 7.** Relationships between the  $M_n$  and the yield of poly-AAm using *i*-poly-MMA (○) and *s*-poly-MMA (■) as a template.





Scheme 2. Projections of conformation for the lowest energy of segment of tacticity poly-MMA. (A) *i*-poly-MMA, (b) *s*-poly-MMA (see Reference 24).

The tacticity for the template poly-MMA also influenced the number-average molecular weight ( $M_n$ ) of poly-AAm (Figure 7). The use of *s*-poly-MMA as a template gave 5 to 6 times higher  $M_n$  of poly-AAm than that of *i*-poly-MMA. The  $P_n$  of the resulting poly-AAm is nearly equal to the  $P_n$  of the template *s*-poly-MMA, but is far lower than that of *i*-poly-MMA. This fact is quite different from the results by G. Challa [15]. In their work, *i*-poly-MMA template showed the most pronounced influence on the initial  $R_p$  of MMA than that of *s*-poly-MMA template. It was suggested that the observed difference in template effect of the stereoregular of poly-MMA was due to the stereoselection of the growing chain radicals or the monomer radicals in the propagation step and the hindrance of segmental diffusion in the termination step of the complexed growing chain radicals. In the case of AA<sub>m</sub>, the observed greatly different effect of *s*-poly-MMA and *i*-poly-MMA on the  $R_p$  and the  $M_n$  of daughter polymer can be attributed to the difference in the conformation features of the *i*- and *s*-poly-MMA chain.

According to the theory of P. J. Flory [24], the conformation of lowest energy for stereoregular poly-MMA chains is greatly different. The most stable conformations of *i*- and *s*-poly-MMA chains are shown in Scheme 2. In the

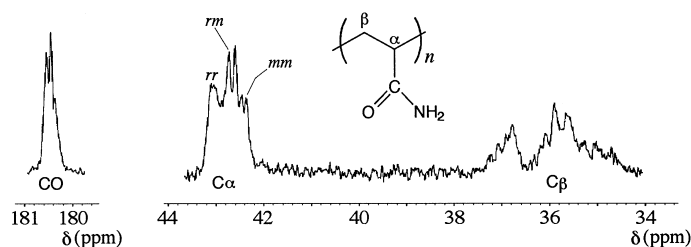


Figure 8.  $^{13}\text{C}$  NMR spectra of the resulting poly-AA<sub>m</sub> (27°C,  $\text{D}_2\text{O}$ ).



conformation of *s*-poly-MMA, the carbonyl groups are aligned in nearly the same direction, so AAm monomers can be absorbed onto the *s*-poly-MMA template along the same way by the hydrogen bonding between the amide group and the carbonyl group and, as a result, the Pn of the daughter polymer is nearly equal to the template of *s*-poly-MMA.

On the other hand, in the conformation of *i*-poly-MMA, the bone chain is twisted and the carbonyl groups are diffused in different orientation around the main chain. Thus, the continuous absorption and propagation of the segment or monomer radicals are impeded by the steric hindrance of the twisting bone chain of the *i*-poly-MMA template. Thus, the *i*-poly-AAm results in shorter sequence of poly-AAm.

### Tacticity of the Resulting Poly-AAm

The microstructures of the resulting poly-AAm were measured by  $^{13}\text{C}$  NMR in  $\text{D}_2\text{O}$ , and the obtained spectrum is shown in Figure 8. The tacticities of the resulting poly-AAm were estimated according to the method by J. Cabestany [25]. The three peaks at 42.6, 42.9, and 43.2 ppm are assigned to *mm*, *rm* (or *mr*) and *rr* sequences of the  $\alpha$ -carbon atom, respectively.

As shown in Table 7, a slight tendency of a decrease in the syndiotactic (*rr*) parts and enhancement of the isotactic (*mm*) parts of poly-AAm in the total amounts of the resulting poly-AAm is observed as the polymerization proceeded in both systems. This fact is quite different from the report by R. Buter [22], namely, in the template polymerization of MMA using *i*-poly-MMA as a template

TABLE 7. Determination of Triad Tacticities of the Resulting Poly-AAm

Run	Template Polymer	Poly-AAm Yield, %	Proportion <sup>a</sup> × 10 <sup>2</sup>		
			<i>rr</i>	<i>rm</i>	<i>mm</i>
1	iso rich poly-MMA <sup>b</sup>	27	33.5	41.2	25.3
2	iso rich poly-MMA <sup>b</sup>	69	31.2	41.5	27.3
3	syndio rich poly-MMA <sup>c</sup>	21	35.4	38.1	26.5
4	syndio rich poly-MMA <sup>c</sup>	46	32.5	40.3	27.2

<sup>a</sup>Determined by  $^1\text{H}$  NMR in  $\text{D}_2\text{O}$ .

<sup>b</sup> $P_n = 103$ , *rr* = 16.6 %, *rm* = 19.4 %, *mm* = 64.0 %.

<sup>c</sup> $P_n = 164$ , *rr* = 58.7 %, *rm* = 33.7 %, *mm* = 7.6 %.



polymer, the polymerization could proceed according to a stereospecific template or replica-type mechanism, and produce a far higher ratio of the syndiotactic daughter polymer in the initial step. The ratio of *s*-poly-MMA was decreased rapidly with the proceeding of polymerization. However, in the present study, it was observed that the tacticity of the resulting poly-AAm was not significantly changed as the template polymerization proceeded in the presence of *i*- and *s*-poly-AAM. We are continuing further investigation on this point.

## CONCLUSION

The  $R_p$  of AAm was remarkably enhanced by the template of poly-MVK, copoly(MVK-St), poly-MMA, copoly(MMA-St) and the mixtures of poly-MMA with poly-St in THF at 30 or 40°C; however, a small amount of contamination by St in the chain of template copoly(MVK-St) or copoly(MMA-St) greatly decreased the  $R_p$  of AAm comparing with the template poly-MVK and poly-MMA. It is reasonable that a small amount of contamination by St units impedes the continuous adsorption of monomers onto the active site of the template polymer. On the other hand, longer sequence of template poly-MMA and poly-MVK results in lower  $R_p$  of AAm in the THF, and the  $R_p$  of AAm gradually increased as the polymerization proceeded.

The template effects of stereoregular poly-MMA on the  $R_p$  of AAm and the  $M_n$  of daughter polymer were also different depending on their tacticity. The initial  $R_p$  of AAm and the  $M_n$  of the resulting poly-AAm in the presence of *s*-poly-MMA template is far higher than that of *i*-poly-MMA template. A slight tendency of decrease of the syndiotactic ratio of the resulting poly-AAm is observed as the template polymerization proceeded. It can be concluded that the various structural factors of the template polymer, such as tacticity, composition of copolymer, and distribution of polymer sequences, greatly affected the  $R_p$  and the microstructure of the daughter polymer.

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