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Polymerization of Methacrylic Acid in the Presence of Isotactic Poly(methyl Methacrylate) as Possible Template

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ABSTRACT

Based on the stereoassociation ability between *it*-PMMA and *st*-polymethacrylic acid (PM acid) in DMF, methacrylic acid (*M*-acid) was polymerized in the presence of *it*-PMMA templates between 45 and -10°C . At temperatures between 0 and 45°C the polymerization rate and the radical lifetimes were identical with those of the corresponding blank polymerization, although gel formation took place. This could be explained by termination of growing PM acid radicals in the "free" solution before their association with *it*-PMMA could take place, in other words the association rate of the formed PMAA radicals with *it*-PMMA is too low. Only below ca. 0°C was a kinetic template effect observed; at -10°C the rate relative to that of the blank reaction (without *it*-PMMA) is $v_{\text{R}} = 1.5 \pm 0.1$. The decrease in ΔE^{\ddagger} by the template is ascribed to mainly an increased hindrance of termination of associated PM acid radicals. The decrease in ΔS^{\ddagger} may be caused by a sterically more stringent transition state of the propagation steps in which the template chain is involved. For the solvents, 2-methoxyethanol (2-ME) and EtOH/H₂O (volume ratio 83/17) in which complexation is moderate to strong, no template effect was observed, probably due to the bad

solubility of *it*-PMMA. However, $v_R = 2.2$ was found when a polymerization was performed at -10°C in a mixture of 30 vol % dioxane and 2-ME.

INTRODUCTION

Template polymerization of methyl methacrylate (MMA) in the presence of tactic poly(methyl methacrylates) (PMMA) has been investigated extensively by using radical [1, 2] as well as anionic [3] initiators. The PMMA template affects the polymerization rate of MMA [2], as well as the microstructure [1, 3] and \overline{M}_v [1, 2] of the PMMA formed, because the growing polymer chain is associated with the template macromolecule most of the time. This behavior is related to the strong association tendency between isotactic (*it*) and syndiotactic (*st*) PMMA [4]. Recently we have found that, of the four possible cross combinations between tactic PMMA and poly(methacrylic acid) (M acid), only the one between *it*-PMMA and *st*-M acid is able to associate [5, 6]. This stereoselectively formed stereocomplex resembles the mentioned *it*/*st*-PMMA complex in many respects though its association tendency is weaker. Despite this disadvantage, we have examined the possibility of template polymerizing methacrylic acid (M acid) in the presence of *it*-PMMA.

RESULTS AND DISCUSSION

Polymerizations in DMF

Most of the experiments have been done in DMF which is one of the few common solvents for PMMA and M acid. Radical initiation is as yet the only means to realize polymerization of the acid monomer.

Polymerization of M acid in the absence (blank polymerizations) and presence of *it*-PMMA were investigated dilatometrically in a temperature range between 45 and -10°C . Very low bis(*p*-tert-butylcyclohexyl)peroxydicarbonate (TBCP) initiator concentrations of 0.04 mole % with respect to monomer were employed in order to increase the lifetime of the growing polymer radical, which is initiated in the "free" or bulk solution, thereby enhancing its chance to associate with an *it*-PMMA template macromolecule.

In all instances of polymerizations in the presence of *it*-PMMA, gels were formed even at low conversions, indicating association between the produced polyacid and *it*-PMMA. Nevertheless, over a broad temperature range, no change of rate relative to that of the

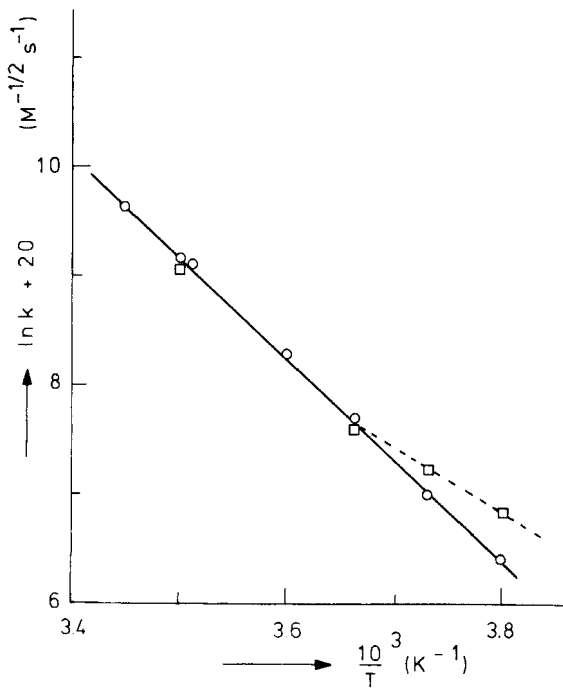


FIG. 1. Arrhenius plot of overall rate constants k for (○) blank and (□) template polymerizations of M acid in DMF. $[M \text{ acid}] = 2.34 \text{ M}$; $[TBCP] = 0.001 \text{ M}$; $[it\text{-PMMA}] = 0.39 \text{ base mole/liter}$.

blank polymerization could be detected, in other words $v_{p,T}/v_{p,B} \equiv v_R \approx 1.0$, where the subscripts T and B stand for template and blank, respectively. Only below about 0°C was a small but distinct kinetic template effect found: at -10°C , $v_R = 1.5 \pm 0.1$ (9 experiments).

Arrhenius plots of the overall rate constants k , of blank and template polymerizations are given in Fig. 1 from which activation energies ΔE^\ddagger were derived. Activation entropies ΔS^\ddagger were calculated from the expression

$$\ln k = -(\Delta E^\ddagger/RT) + (\Delta S^\ddagger/R) + \ln(k_B T e/h)$$

in which R , k_B , and h are the gas constant, the Boltzmann constant, and the Planck constant, respectively. ΔS^\ddagger appeared to be independent of temperature.

TABLE 1. Overall Activation Parameters for Blank and Template Polymerization of M Acid in DMF

	ΔE^\ddagger (kJ/mole)	ΔS^\ddagger (J/mole-°K)
Blank	74	-84
Template (T \geq 273°K)	74	-84
Template (T < 273°K)	51	-168

The activation parameters are collected in Table 1. For both polymerizations

$$\Delta E^\ddagger = \Delta E_p^\ddagger - \frac{1}{2}\Delta E_t^\ddagger + \frac{1}{2}\Delta E_d^\ddagger$$

and

$$\Delta S^\ddagger = \Delta S_p^\ddagger - \frac{1}{2}\Delta S_t^\ddagger + \frac{1}{2}\Delta S_d^\ddagger$$

where the subscripts p, t, and d, pertain to the propagation and termination steps of the polymerization and decomposition of the initiator, respectively.

From Table 1 it is seen that the decrease of ΔE^\ddagger and ΔS^\ddagger due to the template effect amounts to -23 kJ/mole ($\Delta E_{T^\ddagger} - \Delta E_{B^\ddagger} \equiv \Delta\Delta E^\ddagger$) and -84 J/mole-°K ($\Delta S_{T^\ddagger} - \Delta S_{B^\ddagger} \equiv \Delta\Delta S^\ddagger$), respectively. This is less than that found for the template polymerization of MMA in the presence of it-PMMA [2]. The reason of the decrease may nevertheless be the same in both cases. Assuming that initiator decomposition is unaffected by it-PMMA ($\Delta E_{d,T^\ddagger} - \Delta E_{d,B^\ddagger} \equiv \Delta\Delta E_d^\ddagger = 0$) the finding of $\Delta\Delta E^\ddagger (= \Delta\Delta E_p^\ddagger - \frac{1}{2}\Delta\Delta E_t^\ddagger) < 0$ may be mainly due to a lower mobility of associated polyacid radicals, which retards the termination step ($\Delta\Delta E_t^\ddagger > 0$). The propagation step may remain unaffected ($\Delta\Delta E_p^\ddagger = 0$) or increase slightly ($\Delta\Delta E_p^\ddagger > 0$) because of steric imposition of adding monomer by the template, as has been noticed for the template polymerization of MMA [2]. The case $\Delta\Delta E_p^\ddagger < 0$ can occur only when monomer is adsorbed by the template macromolecule prior to propagation, creating a high local monomer concentration. There is, however, no evidence of preadsorption of M acid by it-PMMA.

A sterically more ordered transition state in which the template chain is involved should lead to $\Delta\Delta S_p^\ddagger < 0$ which may be the primary

TABLE 2. Characterizations of Blank and Template-Formed PM Acid^a

Temperature (°C)	$M_v \times 10^{-5}$		(mm):(mr):(rr)	
	Blank	Template	Blank	Template
45	1.32		0.07:0.22:0.71	
34	2.46		0.06:0.22:0.72	
25	4.60	5.2	0.05:0.22:0.73	0.03:0.25:0.72
17	6.73	5.7	0.05:0.22:0.73	0.04:0.24:0.72
5	13.0		0.04:0.21:0.75	
-10	30.0	23.0	0.03:0.20:0.77	0.04:0.22:0.74

^aPolymerization conditions: [M acid] = 2.34 M, [TBCP] = 0.001 M; [it-PMMA] = 0.39 base mole/liter; solvent, DMF.

cause of $\Delta\Delta S^\ddagger (= \Delta\Delta S_p^\ddagger - \frac{1}{2}\Delta\Delta S_t^\ddagger) < 0$, assuming $\Delta\Delta S_d^\ddagger$ to be zero.

Retarded termination under template conditions either does not affect ΔS_t^\ddagger or could only lead to a slightly lower ΔS_t^\ddagger -value ($\Delta\Delta S_t^\ddagger \leq 0$).

The temperature dependence of the relative rate can be expressed by

$$\begin{aligned} v_R &= \exp \left\{ -\frac{\Delta\Delta E^\ddagger}{RT} \right\} \exp \left\{ \frac{\Delta\Delta S^\ddagger}{R} \right\} \\ &= \exp \left(-\frac{\Delta\Delta H^\ddagger}{RT} \right) \exp \left(\frac{\Delta\Delta S^\ddagger}{R} \right) \\ &= \exp \left(-\frac{\Delta\Delta G^\ddagger}{RT} \right) \end{aligned}$$

Calculation for $T = 263^\circ\text{K}$ gives $\Delta\Delta G^\ddagger = -0.9$ kJ/mole, which is small as compared to $\Delta\Delta G^\ddagger = -3.2$ kJ/mole for the MMA/it-PMMA system and $\Delta\Delta G^\ddagger = -1.9$ kJ/mole for the MMA/st-PMMA system, calculated from data of Gons et al. [2].

The conclusion that $\Delta\Delta E_t^\ddagger > 0$ implies that the \bar{M}_v of the polyacid formed in the presence of it-PMMA should be higher than that of the blank polymer. For one sample, a \bar{M}_v of 2.3×10^6 (Table 2) was found which was lower than the blank \bar{M}_v . This lower value may be due to incomplete separation of PM acid formed from it-PMMA. This suggestion is supported by its somewhat lower syndiotacticity (Table 2), instead of a higher one as might be expected from

$\Delta\Delta S_p^\ddagger < 0$. This anticipation is based on results concerning the template polymerization of MMA in the presence of it- or st-PMMA templates [1, 2].

From Table 2, column 4, it can be seen that blank PM acid polymers have persistence ratios, $\rho = 2(m)(r)/(mr)$, greater than unity which means that (m)- and (r)- dyads are distributed in a non-Bernoullian fashion, although there is a tendency towards randomness at lower polymerization temperatures (ρ at $45^\circ\text{C} = 1.34$; ρ at $-10^\circ\text{C} = 1.13$). Assuming that isotactic (meso) and syndiotactic (racemic) additions proceed according to first-order Markov statistics, the (m)/(r)- temperature dependence is expressed by:

$$\begin{aligned} \ln \{ (m)/(r) \} &= - \frac{\Delta G_{r/m}^\ddagger - \Delta G_{m/r}^\ddagger}{RT} \\ &= \frac{\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger}{R} - \frac{\Delta H_{r/m}^\ddagger - \Delta H_{m/r}^\ddagger}{RT} \end{aligned}$$

where r/m pertains to the formation of an (m) dyad at a racemic chain end and m/r to that of an (r) dyad at a meso end.

From data in Table 2 on the temperature dependence of (m) - and (r)-dyads for blank polymerizations we obtain

$$\begin{aligned} (\Delta H_{r/m}^\ddagger - \Delta H_{m/r}^\ddagger)_B &= (\Delta E_{r/m}^\ddagger - \Delta E_{m/r}^\ddagger)_B \\ &= 5 \text{ kJ/mole} \end{aligned}$$

and

$$(\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger)_B = 2.5 \text{ J/mole-}^\circ\text{K}$$

which agree with literature values [7, 8]. In accordance with most radical vinyl polymerizations, $(\Delta H_{r/m}^\ddagger - \Delta H_{m/r}^\ddagger) \gg [T(\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger)]$ i. e., the predominance of syndiotacticity is mainly determined by the enthalpic (energy) difference between m and r addition in the transition state. If the presence of the it-PMMA template leaves $(\Delta H_{r/m}^\ddagger - \Delta H_{m/r}^\ddagger)$ unaltered, then an increase of syndiotacticity may be expected if $(\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger)_T < (\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger)_B$. This was found for the template polymerizations of MMA [1] and related to the finding that $\Delta\Delta S_p^\ddagger < 0$ [2]. If this relation is equally valid for the present system, then, taking account of the lesser

decrease in ΔS_p^\ddagger , increase in syndiotacticity of the template formed PM acid would be less than in the case of PMMA. The thermal behavior as well as the x-ray diffraction pattern (which showed a slight crystallinity) of a template-formed PM acid/it-PMMA complex did not differ significantly from those of a complex composed of blank PM acid and it-PMMA. However, these characterization methods are not very sensitive to small tacticity variations.

Polymerizations of Related Systems

It should be noted that polymerizations of M acid in the presence of st-PMMA does not lead to gelling of the reaction mixture nor to acceleration of the polymerization rate at -10°C . This is in agreement with the fact that it-PM acid as well as st-PM acid do not associate with st-PMMA [6]. Furthermore, identical results have been obtained when MMA was polymerized in the presence of either it-PM acid or st-PM acid. This is so because initially formed PMMA which contains about 70% syndiotactic (rr) triads, does not complex with it- or st-PM acid.

Reaction products recovered from these nontemplate polymerizations could be separated into their components by iterative selective extraction with acetone and methanol (see Experimental section). On the other hand, products obtained from M acid/it-PMMA template polymerization systems could be separated only partially, even when polymerizations were performed under nontemplate conditions ($> 0^\circ\text{C}$). This is not due to grafting, as a complex prepared by mixing it-PMMA and st- or low st(blank) PM acid, could neither be separated completely in this manner. Complete separation has only been achieved by treatment of the complex with Na methoxide in order to convert PM acid into its polysalt, which does not associate with it-PMMA. However, this method may have its limits, especially if the molecular weights of the polymers are very high.

Rotating-Sector Experiments

The findings that for the M acid/it-PMMA systems above 0°C v_R was always unity, notwithstanding gel formation, can be interpreted in two ways. One explanation is that PM acid chains are terminated in the "free" solution before association with it-PMMA takes place. The other is that a possible difference of k_p and k_t in absence and presence of template might not be revealed in the composite constant $k_p/k_t^{1/2}$ due to cancelling out. If this is the case, then the difference should be manifested in k_p/k_t , which can be determined by the rotating-sector method (intermittent illumination)

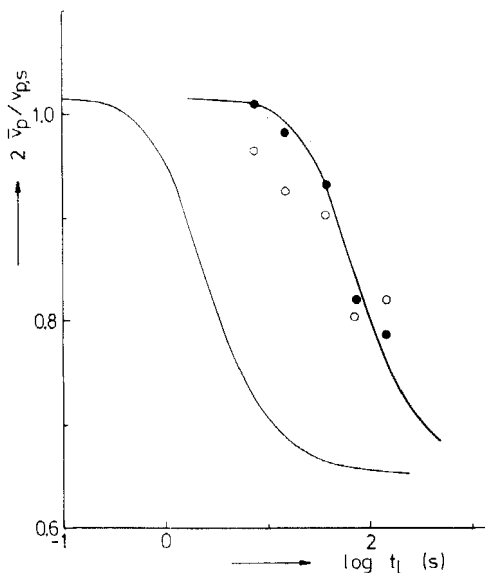


FIG. 2. Rotating-sector curve for (○) blank and (●) template polymerization of M acid in DMF at 5°C. $[M \text{ acid}] = 2.25 \text{ M}$; $[AIBN] = 0.004 \text{ M}$; $[it\text{-PMMA}] = 0.38 \text{ base mole/liter}$. The curve is drawn through points for template polymerization only. The theoretical curve at the left is for $\tau_s = 1 \text{ sec}$.

through the average lifetime τ_s of growing chain radicals [9]. The composite constant k_p/k_t is related to τ_s according to

$$k_p/k_t = 2 v_{p,s} \tau_s / [M]$$

where s refers to the stationary state.

A typical sector result is presented in Fig. 2. As may be seen from Table 3, at 5°C, τ_s in the presence of *it*-PMMA does not differ significantly from τ_s in the blank polymerization in spite of rather long lifetimes, hence $(k_p/k_t)_T = (k_p/k_t)_B$, which means that the explanation in terms of cancelling out does not apply. Therefore, we have to conclude that above 0°C association of growing PM acid radicals with *it*-PMMA occurs only after their termination.

TABLE 3. Results of Rotating-Sector Measurements^a

[AIBN] × 10 ² (M)	τ_s (sec)		v_R	$(k_p/k_t)_T$
	Blank	Template		$(k_p/k_t)_B$
0.93	13.5	13.5	1.05	1.00
0.40	23.0	23.5	1.03	1.01

^a Polymerization conditions: [M acid] = 2.25 M; [it-PMMA] = 0.375 base mole/liter.

Polymerization in Other Solvents

Association of it-PMMA and st-PM acid was found to be dependent on the medium. Based on the viscometrically determined association behavior of highly it-PMMA and highly st-PM acid in dilute solution at room temperature solvents have been classified into A, B, and C type solvents [6]. In C solvents no complexation occurs; in B-2 solvents, like DMF, association is rather weak; in B-1 solvents, it is moderate; and in A solvents it is strong. As a B-1 solvent we used 2-methoxyethanol (2-ME). A mixture of 83 vol % ethanol and 17 vol % H₂O, (EtOH/H₂O) was used as A solvent. Unfortunately, 2-ME and EtOH/H₂O in it-PMMA is only poorly soluble, especially at those concentrations employed for polymerizations. It-PMMA dissolved in 2-ME slowly precipitates on standing at room temperature, while it-PMMA dissolves in EtOH/H₂O only above 42°C. Fortunately the added M acid monomer postpones precipitation of it-PMMA, so that "template" polymerization could be carried out down to 0°C in 2-ME and to 10°C in EtOH/H₂O. In the latter solvent, 2,2'-azobis(2,4-dimethylvaleronitrile) had to be used instead of TBCP for solubility reasons.

In spite of the improved association-promoting media no enhanced polymerization rates were obtained, although again gels were formed which were opaque in EtOH/H₂O [10]. Presumably, conditions were still insufficient to realize proper dissolution of it-PMMA. If this was improved by adding DMF to 2-ME to a volume ratio of 2-ME/DMF = 1:2, $v_R \approx 1.5$ was found, identical with that in pure DMF.

Also, if dioxane was mixed with 2-ME in the volume ratio 2-ME/dioxane = 1:2, v_R of ca 2.2 was obtained [10]. This is unexpected,

because association of it-PMMA and st-PM acid turned out to be worse than in pure 2-ME and even worse than in pure DMF and DMF/2-ME mixtures, despite the fact that dioxane is a nonsolvent for PM acid. The situation is not completely comparable, however. In association experiments, PM acid is present as such, and its reluctance

to complex with *it*-PMMA in 2-ME/dioxane may be attributed to its densely coiled state which is stabilized by intramolecular hydrogen bonds between carboxyl groups. On the other hand, in polymerization experiments the PM acid is being formed from its monomer, and provided that initially formed short PM acid radicals which do not possess the coil configuration, associate rapidly with *it*-PMMA, growth can continue along the *it*-PMMA, thus leading to a template effect.

EXPERIMENTAL

Materials

it-PMMA was prepared by polymerizing MMA in toluene with phenylmagnesium bromide as initiator [10]. Its purification has been described in another paper [6]. The *it*-PMMA employed had \bar{M}_v values of 620,000 and 650,000 and contained 93 and 95% isotactic (mm) triads, respectively.

Methacrylic acid (M acid) was distilled under reduced N_2 pressure (bp/3 Torr = 40°C) prior to polymerization. Various solvents, of purest grade obtainable, were used without further purification. Bis(*p*-tert-butylcyclohexyl) peroxydicarbonate (TBCP), AIBN, and 2,2'-azobis(2,4-dimethylvaleronitrile) were obtained from AKZO-Chemie Deventer (Netherlands).

Polymerization

Reaction mixtures were usually composed of 24% by weight of M acid and *it*-PMMA with a base mole ratio of M acid/*it*-PMMA of 6, and 0.04% TBCP based on monomer. In blank mixtures the *it*-PMMA was replaced by solvent.

The reaction mixture was thoroughly freed from air by a N_2 /vacuum, freeze-thaw cycle procedure. About a 5 g aliquot was injected into a dilatometer (capillary diameter = 0.45 mm) filled with degassed mercury. After wrapping the dilatometer bulb with Al foil to protect the reaction mixture from light, it was placed into a thermostat bath (constancy $\pm 0.01^\circ C$). The Hg level was read by means of a kathetometer to within 0.01 mm accuracy. After a conversion of not more than 10% the reaction mixture was recovered and subjected to examination.

Conversions were determined by bromometric titration [11]. An aliquot, containing about 1.5 mmole M acid, was treated with 50 ml 0.1 N pyridinium sulfate dibromide and 50 ml 2.5% Hg(II) acetate, both dissolved in acetic acid, for 2 hr in the dark. Excess bromide was back-titrated iodometrically. Alternatively, conversions were calculated from partial specific volumes of monomer (\bar{v}_m) and

TABLE 4. Partial Specific Volumes of it-PMMA and Blank PM Acid^a

Polymer	Solvent	\bar{v}_p (ml/g)		
		5° C	20° C	50° C
it-PMMA	DMF	-	0.810	0.835
PM acid	DMF	0.707	0.714	-
PM acid	2-ME	-	0.711	0.713
PM acid	EtOH/H ₂ O	-	0.718	0.715
PM acid	2-ME/dioxane	-	0.721	0.729
it-PMMA/PM acid (1:1)	DMF	-	0.768 ^b	-

^a(mm):(mr):(rr) = 0.02:0.25:0.73.

^bBy calculation on assuming additivity of \bar{v}_p , a value of 0.769 is found.

formed polymer (\bar{v}_p) (see Table 4) assuming additivity of volumes of solvent and polymer [2]. The conversions obtained by the two methods differ less than 0.5%.

Rotating-Sector Measurements

Measurements were carried out at 5° C with AIBN as photoinitiator. The apparatus has been described elsewhere [2].

The polymerization rates at $[AIBN] = 4 \times 10^{-3}$ M as photoinitiator and $v_{p,B}$ with $[TBCP] = 10^{-3}$ M as thermal initiator, are comparable; viz., 1.20×10^{-6} mole/liter-sec and 0.53×10^{-6} mole/liter-sec, respectively.

Separation Techniques

Separation of PM acid from PMMA by means of selective extraction was performed by alternatively treating a finely powdered sample with boiling acetone to extract PMMA and boiling methanol to extract PM acid. The acetone-methanol cycle was repeated until no material dissolved. The acetone-solutions, as well as the methanolic solutions were combined, the solvent evaporated, and the polymers collected for characterization. This simple method led to complete separations of all combinations between PMMA and PM acid, except between it-PMMA and st- or blank PM acid. In these instances, complete separation was achieved by dissolving the polymer mixture (complex) in

DMF above 60°C and adding a solution of NaOCH₃ in methanol under vigorous stirring. After pouring into ether, the precipitate was dried and alternatively extracted with water and acetone. The aqueous part was acidified with HCl and dialyzed against demineralized water. By evaporation of the water PM acid was recovered, whereas the acetone solution yielded PMMA.

Characterization

Average molecular weights were obtained from viscometric determinations and tacticities from proton nmr measurements [6].

CONCLUSIONS

In spite of the capability of low [70% (rr)] and high [> 90% (rr)] *st*-PM acid to associate with *it*-PMMA, only at a temperature of -10°C was a small but distinct kinetic template effect detected in polymerizations of M acid in the presence of *it*-PMMA in DMF. Polymerizations in media where association is faster, such as in 2-ME and in EtOH/H₂O, did not result in any template effect, probably due to the poor solubility of *it*-PMMA at low temperatures. On the other hand, polymerization in a 2-ME/dioxane mixture which does not promote association very well gave a somewhat larger template effect than in DMF at -10°C. Hence, the occurrence of a template effect in this polymerization system does not run parallel with the rapidity of association between *st*-PM acid and *it*-PMMA as derived from association experiments.

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