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Template Polymerization of *N*-Vinylimidazole along Poly(methacrylic acid) in Water. 5. Influence of Template Tacticity

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ABSTRACT: The template polymerization of *N*-vinylimidazole in water along isotactic and syndiotactic poly(methacrylic acid) (PMAA) of various molecular weights was studied. The polymerization could be described with the same mechanism as developed for conventional PMAA. The maximum enhancement in the rate of polymerization followed the order isotactic < syndiotactic < conventional PMAA. This was explained by a lower template–radical interaction for isotactic PMAA and by a lower rate of radical propagation along syndiotactic PMAA with respect to conventional PMAA. Both effects were corroborated by different dependencies of the rate of polymerization and molecular weights of the formed poly(*N*-vinylimidazole) (PVIm) on the template molecular weight. The tacticity of the formed PVIm was different from PVIm synthesized in the absence of the template. The isotactic triad content was somewhat enhanced irrespective of template tacticity when high template molecular weights were used. Although radicals grow in close proximity to the template, Bernouillian statistics were obeyed except when comparatively short template chains were employed, in which case the most stereoregular PVIm was obtained. Independent of template tacticity, a partial suppression of anhydride formation at elevated temperatures was found in the case of template-formed complexes. This was ascribed to an enhanced interaction in the complex as compared to synthetic complexes.

1. Introduction

The influence of template tacticity on the template polymerization has been studied for a number of template systems.[1–6] Bartels et al.[2] studied the polymerization of *N*-vinylpyrrolidone along syndiotactic (st), atactic (at), and isotactic (it) poly(methacrylic acid)s, in which rate enhancements followed the order st-PMAA > at-PMAA > it-PMAA. Smid et al.[3] examined the polymerization of methacrylic acid along isotactic and atactic poly(2-vinylpyridine) in DMF. Higher rate enhancements were found for the isotactic template owing to a lower rate of termination caused by a better complexation between the isotactic template and formed polymer. Gons et al.[4] studied the polymerization of methyl methacrylate (MMA) along it- and st-PMMA using various solvents and found a higher rate enhancement for the isotactic template. Akashi et al.[5] investigated the adenine derivative of *N*-[β-(methacryloyloxy)ethyl] (MAO) in the presence of the uracil derivative of PMAO of different tacticities. The rate enhancements followed the order of at < st < it at 20 °C, which completely reversed at 40 °C. Klein[6] examined the system 2-vinylpyridine along it-, st-, and cv-PMAA and found only minor differences between the various tactic templates.

Essentially, two processes appeared to be sensitive to the tacticity of the template, the first one being complexation of the radical with the template[2–5] and the second one being the rate of template propagation. The strength of the former interaction is important since it determines the amount of complexed radicals and thus influences the magnitude of template effects. The influence of template tacticity on the rate of propagation may also depend on the template mechanism.[2,3] In the case of systems involving radical propagation with preadsorbed monomers (type I mechanism[1]), propagation by the template-associated radical is very much dependent on the spatial orientation of the radical end with respect to the neighboring monomer molecule. In the case of systems without monomer preadsorption involving the addition of monomer from solution (type II mechanism),[1] mismatching between the template and growing radical leads to non-template growth.

For the system *N*-vinylimidazole (VIm) along conventional poly(methacrylic acid) (cv-PMAA) in water, it has been established that radical complexation is feasible only under certain conditions as deduced from the existence of a critical chain length.[7] Furthermore, radical propagation was identified to take place with adsorbed monomers. Both these processes are anticipated to be sensitive to the tacticity of the template in view of that aforementioned.

The kinetic effect and the stereochemical effect are generally caused by different factors, though both are called template effects. The stereochemical effect is determined by the degree that the template segment near the radical end is able to participate in the transition state of monomer addition. This may affect the rate of propagation as was nicely demonstrated by Gons et al.,[4] but in addition the kinetic effect may result from a retardation of the termination step.[1] Consequently, if templates of different tacticity give rise to different kinetic effects, this does not necessarily have to be accompanied by a stereochemical effect. Moreover, it does not imply that strong interactions between the template and radical or monomer are required to obtain a stereochemical effect. The importance of a perfect matching of the two polymers is best illustrated by the polymerization of methyl methacrylate (MMA) along it-PMMA or st-PMMA leading to the formation of a stereocomplex between it- and st-PMMA.[8] The interactions leading to the formation of this stereocomplex are the weak van der Waals forces, indicating that the strength of the interactions between the template and growing radical is not as important as the stereochemical fitting.

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Table I
Characteristics of PMAA Templates

	$\bar{M}_v$, $\times 10^3$	$D = \bar{M}_w/\bar{M}_n$[e]	(mm):(mr):(rr), %	OCH_3, %
it-PMAA-1	12[a]	1.41	96:2:2	3
it-PMAA-2	22[b]	3.80	92:7:1	3
it-PMAA-3	42[c]	1.18	97:3:0	2.5
it-PMAA-4	96[d]	1.20	95:5:0	3
it-PMAA-5	48 and 1.4×10^3[f]		96:4:0	3
st-PMAA-1	5		0:4:96	
st-PMAA-2	58		0:8:92	
st-PMAA-3	101		0:5:95	
st-PMAA-4	220		0:5:95	
cv-PMAA-4	30		5:35:60	
cv-PMAA-8	95		5:35:60	

[a] $\bar{M}_n = 8.7 \times 10^3$. [b] $\bar{M}_n = 7 \times 10^3$. [c] $\bar{M}_n = 36 \times 10^3$. [d] $\bar{M}_n = 80 \times 10^3$. [e] Determined as it-PMAA. [f] Bimodal molecular weight distribution, $\bar{M}_n = 40 \times 10^3$ (50%) and 750×10^3 (50%).

With respect to the system (P)VIm–PMAA, we have established that the propagation step is influenced by the template as has been deduced from suppression of electrostatic interactions between the growing radical and an equally charged monomer.[7] In addition, we may expect that the radical end is firmly attached to the template in view of the strong template–monomer and template–radical interactions as well as the fact that polymerization proceeds with adsorbed monomers. The use of tactic PMAA's could affect these interactions and consequently also template effects. For st- and it-PMAA in aqueous solution, different conformations have been suggested: a (locally) planar zigzag conformation for st-PMAA[9] and a 3_1[9] or 7_2[10] helix for it-PMAA. Moreover, it should be noted that PMAA's are stiffer polymers than, e.g., poly(acrylic acid),[9] whereas atactic PVIm is a rather flexible polymer.[11] It is, therefore, difficult to predict whether or not the template or the PVIm radical is able to adapt its conformation to facilitate propagation along the template chain. If the radical becomes unfavorably orientated with respect to the neighboring monomer due to conformational constraints, it is also possible that the radical skips parts of the template chain during its growth.

This paper describes the use of syndiotactic PMAA (st-PMAA) and isotactic PMAA (it-PMAA) to assess the influence of template tacticity on the polymerization rate as well as a possible stereoregular control which would lead to tactic VIm polymers.

The following features of the template effect will be discussed in relation to the tacticity of the template: relative rate of polymerization, molecular weight and tacticity of the formed PVIm, influence of the template molecular weight, and finally analysis of the resulting polymer complexes. Most aspects have already been discussed with regard to the conventional PMAA template in previous papers.[12-14]

2. Experimental Section

2.1. Materials. All relevant data concerning the used templates are listed in Table I. The synthesis of the cv-PMAA samples has been reported as well as the purification of VIm.[7] The initiator 2,2′-azobis(2-amidinopropane)·2HCl (AAP; Polysciences) was used without purification.

Isotactic PMAA was obtained by acid hydrolysis of isotactic poly(methyl methacrylate) according to a known procedure.[15] This method is known to give the smallest losses compared to other available methods.[16,17] The tacticity of the polymer as determined by ^1H NMR was identical to that of the starting it-PMMA. The degree of hydrolysis was determined from the remaining OCH_3 groups and was found to be 97% in all cases (see Table I). It was further assumed that the viscosity-average degrees of polymerization were the same as the original it-PMMA. it-PMMA was synthesized in toluene at −78 °C using *tert*-butylmagnesium bromide as catalyst.[18] This method should result in it-PMMA with a narrow molecular weight distribution. However, all our samples (it-PMMA-1, it-PMMA-3, and it-PMMA-4) had a bimodal molecular weight distribution containing a small high molecular weight peak (<10%). These samples could easily be fractionated using acetone/petroleum ether 40/60 as solvent/precipitant. it-PMMA-5 appeared to have a 50%-50% molecular weight distribution with $\bar{M}_n = 40 \times 10^3$ and 800×10^3, respectively, and was not fractionated. it-PMMA-2 was synthesized in toluene at 20 °C using phenylmagnesium bromide as catalyst.[19]

Syndiotactic PMAA was obtained by ^{60}Co radiation polymerization of methacrylic acid in 2-propanol at −78 °C.[17,20] All samples were made by Koetsier[20] except st-PMAA-1. Molecular weights were determined in MeOH at 26 °C, using $K = 2.42 \times 10^{-4}$ and $a = 0.51$.[21] Synthetic complexes were obtained as described in a previous paper.[13]

2.2. Polymerization Procedure. The polymerization procedure using cv-PMAA as template was reported in a previous paper.[7] Polymerizations with st-PMAA as the template were performed in a similar way. In the case of it-PMAA as the template a different procedure had to be used because of the insolubility of it-PMAA at low degrees of neutralization.[21-23] A suspension of it-PMAA and water was stirred for 12 h. *N*-Vinylimidazole was added, and after 5 min of stirring the clear solution was degassed by conventional freeze–thaw cycles. The degassed VIm/it-PMAA solution was added to a thermostated reaction vessel at 50 °C, and after temperature stabilization (<2 min) the initiator solution was added. Sample preparation and sample analyses were identical to the procedure described for cv-PMAA.[7]

2.3. Techniques. Potentiometric titrations, WAXS, calorimetry, FTIR, and DSC procedures have been described.[14] The pH values were all determined at 50 °C.

Gel Permeation Chromatography. The molecular weights of the it-PMMA samples were determined by GPC using a Waters ALC/GPC 150 C equipped with two TSK GMH 6 columns using $CHCl_3$ as eluent, relative to polystyrene standards.

Complex Composition. Complex composition was determined using elemental analysis and ^1H NMR (Varian 300 MHz).

Molecular Weight Determination. Molecular weights of template-formed PVIm could not be measured directly because of its incomplete separation and isolation of the template complex.[13] Therefore, the molecular weights of PVIm formed in the presence of st-PMAA were determined in an indirect way by viscometry in water at pH 1 following the same procedure as described for cv-PMAA.[13]

In the case of it-PMAA as the template, molecular weights of PVIm were determined from $[\eta]_{\mathrm{mixture}}$ of the template complex dissolved in water with pH 12.5 because of the insolubility of it-PMAA at low degrees of neutralization.[21-23] The validity of the additivity relationship was verified using synthetic complexes. Straight Huggins and Kraemer viscosity plots support the absence of interactions between it-PMAA and PVIm under these conditions. A calibration line for converting $[\eta]^{\mathrm{pH}12.5}_{\mathrm{PVIm}}$ to $[\eta]^{\mathrm{EtOH}}_{\mathrm{PVIm}}$, for which K and a values are available,[21] was made using synthetic samples, similar to the procedure outlined in ref 9. Ubbelohde-type viscometers were used, and the inaccuracy in $[\eta]$ was ±3%.

NMR. NMR spectra were recorded at ambient temperature at 300 MHz (^1H) or 75 MHz (^{13}C) using a Varian 300. Decoupled ^{13}C NMR spectra were obtained from 8 wt % solutions using a pulse delay of 5 s and the Waltz-16 modulated decoupling technique.

Tacticity of PVIm. The tacticity of PVIm was determined by dissolving the template complex in D_2O at pD 12.5. A small amount of NaCl was added to reduce the high viscosity. In the case of it-PMAA, the β-CH_2 resonance of it-PMAA overlapped the peaks corresponding with the isotactic triad fraction of PVIm. The peak could be resolved by using the ratio of nuclear Overhauser enhancement factors between β-CH_2 and the α-C of PMAA. The ratio was determined to be 0.9 by measuring a mixture of it-PMAA and a PVIm sample of known tacticity, exactly corresponding with the ratio obtained by Schaeffer.[19]

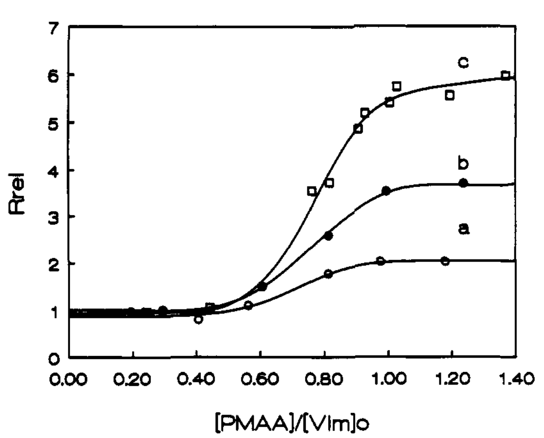

Figure 1. Relative rate of polymerization R_{rel} versus [PMAA]/$[VIm]_0$: it-PMAA-2 (curve a, ○); st-PMAA-3 (curve b, ●); cv-PMAA-8 (curve c, □). $[VIm]_0$ = 0.41 M; $[AAP]_0$ = 0.047 M.

Relative areas of the NMR signals were assessed by integration and the "cut and weigh" method. Both procedures gave identical results.

3. Results and Discussion

3.1. Influence of [PMAA]. In Table I the characteristics of the templates used in this study are listed. Both isotactic and syndiotactic PMAA are highly tactic materials of comparable molecular weight. Conventional PMAA has a strong syndiotactic bias. Molecular weight distributions are not available for st- and cv-PMAA, the latter of which will be broad. Some mention should be made of the 3% OCH_3 in it-PMAA remaining after the hydrolysis procedure. The hydrolysis reactions have been studied by a number of authors,[16,17] who concluded that residual OCH_3 groups reside in clusters. We assume that the presence of the $COOCH_3$ clusters does not affect the propagation of radicals along the template chain though a small part of the template chain may be less accessible for radical complexation. Radical complexation does not have to be influenced in view of the small critical chain length.[7]

In Figure 1, relative rates of polymerization R_{rel}, defined as the ratio of $R_p([PMAA]/[VIm]_0 = 1)$ to $R_p([PMAA]/[VIm]_0 = 0.2)$, are plotted versus $[PMAA]/[VIm]_0$ for it-, st-, and cv-PMAA as the template. Maximum rate enhancements follow the order it-PMAA < st-PMAA < cv-PMAA with the exact relation slightly obscured by the differences in molecular weight (see Table I). This will be discussed in section 3.4.

Similar to the distinction previously made for cv-PMAA,[7] three regions may be discerned independent of template tacticity, i.e., region A with R_{rel} = 1, region B with R_{rel} increasing, and region C with a nearly constant but elevated R_{rel}. The similarity between the profiles indicates that the template polymerization of VIm in the presence of st- and it-PMAA follows the same mechanism as previously described for cv-PMAA.[7] This mechanism involves propagation of template-associated radicals with adsorbed monomers. Rate enhancements are caused mainly by retardation of the termination reaction, suppression of degradative addition,[7,24] and reduction of electrostatic repulsions between a charged radical and a protonated monomer.[7] The AB transition, which coincided with complex formation, was explained by radicals achieving the critical chain length necessary for complexation with the template,[7] while the BC transition was ascribed to the maximal amount of radicals propagating along the template chains.

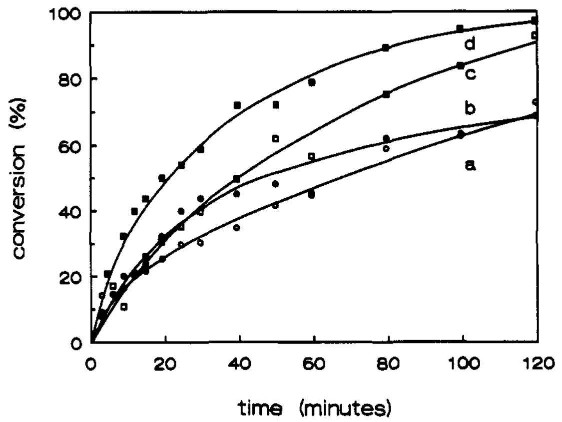

Figure 2. Conversion versus time curves for $[PMAA]/[VIm]_0$ = 1 and $[VIm]_0$ = 0.41 M using it-PMAA-1 (curve a, ○), it-PMAA-5 (curve b, ●), st-PMAA-3 (curve c, □), and cv-PMAA-8 (curve d, ■).

Identical to the template polymerization with cv-PMAA, conversion versus time plots were linear in region A due to the presence of degradative addition, whereas they were curved in regions B and C, indicating suppression of degradative addition.[7,12] The conversion curves of it-PMAA at $[PMAA]/[VIm]_0$ = 1 and $[VIm]_0$ = 0.41 M (Figure 2, curves a and b) are different since they show a deflection at 45% monomer conversion coinciding with the completion of the aggregation process of template complexes in solution.[14] At this point the rate changed to that of the blank rate[7] (i.e., in the absence of the template). Consequently, one has to assume that polymerization is no longer feasible for the aggregated complex which is in contrast with results for st- and cv-PMAA. Since a growing radical uses only half of the template chain statistically, the remaining half of the template is possibly less available for complexation by other radicals due to the presence of the OCH_3 groups.

On the other hand, it is known that it-PMAA binds divalent cations betterthan st- and cv-PMAA due to the spatial orientation of the COOH groups.[25] AAP^{2+} is a similar cation and will thus interact to a greater extent with it-PMAA than with st- or cv-PMAA. Aggregation of the complexes[14] might lead to inclusion of AAP and, consequently, to reduction of the overall radical concentration.

The AB transition is located at $[PMAA]/[VIm]_0$ = 0.45 for cv-PMAA, its position being determined by both the pH[7] and concentration of template chains.[14] In view of the weaker acidity of it-PMAA as compared to cv- and st-PMAA,[9,26] one would expect the AB transition to shift to the higher $[PMAA]/[VIm]_0$ of 0.6 (see Figure 3). Though this may not be readily observed in Figure 1 due to low rate enhancements and inherent inaccuracy in R_{rel}, it becomes clearer if the rate enhancements at $[PMAA]/[VIm]_0$ = 0.6 are expressed as a precentage of the maximum rate enhancement at $[PMAA]/[VIm]_0$ = 1. We obtain 10 ± 4% for it-PMAA-3 and it-PMAA-5, 18 ± 3% for st-PMAA-3, and 22 ± 3% for cv-PMAA-4 and cv-PMAA-8.

If we now turn to the lower rate enhancements for it-PMAA and st-PMAA, this may be attributed to either a lower concentration of template-associated radicals at the template, a higher rate coefficient for termination k_t, a lower rate coefficient for propagation k_p, or a combination of these factors along the template chain. In Table II, the heats of complexation are given for the complexation of PMAA and PVIm at pH 5.95. The order $\Delta H_{com,it} < \Delta H_{com,cv} \simeq \Delta H_{com,st}$ may be explained by the weaker acidity of the isotactic template, corresponding to a lower charge

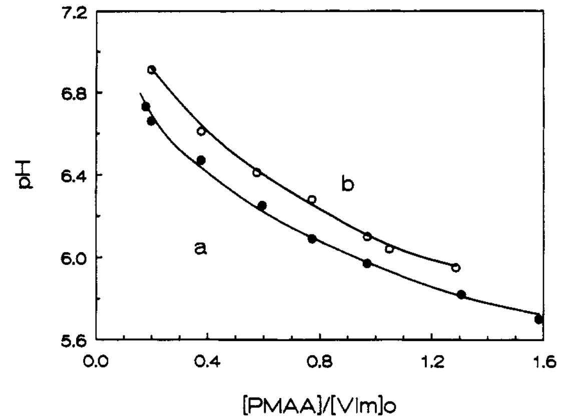

Figure 3. pH at 50 °C of reaction mixtures in the absence of initiator as a function of $[PMAA]/[VIm]_0$ for cv-PMAA-8 (curve a) and it-PMAA-3 (curve b).

Table II
Influence of Template Tacticity on Various Variables

	ΔH_{com},^{a} kJ/basemol	R_{rel}^{b}	$\bar{M}_{v,PVIm}$,^{c} $\times 10^3$	H_n^{d}	b_1 for R_p^{e}	b_2 for $\bar{M}_v$^{e}
it-PMAA-3	2.3 ± 0.2^f	2	200	2.7	0.19	
cv-PMAA-8	4.8 ± 0.4	5.3	510	6.3	0.31	0.59
st-PMAA-3	4.7 ± 0.4^g	3.5	400	4.2	0.09	0.19

^{a} Heat of complexation of PVIm ($\bar{M}_v = 13.6 \times 10^3$) and PMAA in a 1:1 basemolar ratio at pH 5.95 and 50 °C. ^{b} R_{rel} is the ratio of $R_p([PMAA]/[VIm]_0 = 1)$ to $R_p([PMAA]/[VIm]_0 = 0.2)$. ^{c} Polymerization conditions: $[PMAA]/[VIm]_0 = 1$, $[VIm_0] = 0.41$ M, $[AAP]_0 = 0.047$ M. ^{d} Hop number H_n is defined as the number of template chains along which a radical grows.[9] ^{e} Dependencies of R_p and $\bar{M}_{v,PVIm}$ on $\bar{M}_{v,PMAA}$ as calculated from the slopes in Figures 6 and 7. ^{f} it-PMAA-5. ^{g} st-PMAA-2.

density as compared to cv- and st-PMAA. This leads to a reduction of the number of template-associated radicals growing alongside the isotactic template being one cause for the lower rate enhancement. Previously, the small reduction of the degree of neutralization α_N of PMAA from 0.68 to 0.60 in region A was neglected in the elucidation of the AB transition.[7] In the present case, however, larger differences in α_N are probably present and α_N is close to the value of 0.35 where hydrophobic interactions start to influence the conformation of it-PMAA.[26] Furthermore, as propagation proceeds with adsorbed mobile monomers, their mobility being mainly caused by the dynamic adsorption–desorption processes, it is possible that the lower degree of ionization of it-PMAA affects the mobility of the monomer along the template. The amount of adsorbed monomer of 10 ± 2% at $[it\text{-}PMAA\text{-}5]/[VIm]_0 = 1$ and $[VIm]_0 = 0.41$ M, as determined by UV, is lower than the 25% for cv-PMAA.[7] This is in agreement with the weaker acidity of it-PMAA.

In the case of the syndiotactic template, the amount of radical complexation appears to be identical to that of cv-PMAA (see Table II). The lower rate enhancements should, therefore, be attributed to a lower rate of propagation and/or higher rate of termination of template-associated radicals caused by conformational constraints (see Influence of the Template Molecular Weight, section 3.4).

3.2. Molecular Weights of the Formed PVIm. Already we established that molecular weights of the formed PVIm grown alongside the template were much higher than those formed in solution.[13] In Figure 4, the profiles of $\bar{M}_{v,PVIm}$ versus $[PMAA]/[VIm]_0$ are shown for st- and it-PMAA. It shows that molecular weights start to increase beyond the AB transition. This result corresponds with that obtained in the case of cv-PMAA,[13] thus supporting the previous conclusion that the polymerization mechanism is independent of template tacticity.

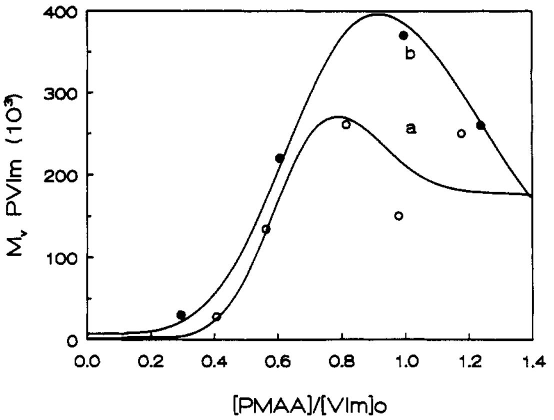

Figure 4. Molecular weights of PVIm formed in the template polymerization; template = it-PMAA-3 (curve a, ○); template = st-PMAA-3 (curve b, ●). $[VIm]_0 = 0.41$ M; $[AAP]_0 = 0.047$ M.

Molecular weights of the formed PVIm at $[PMAA]/[VIm]_0 = 1$ and $[VIm]_0 = 0.41$ M are presented in Table II for the three tactic templates. The differences in molecular weight of PVIm may be attributed to either the template tacticity or the differences in the template molecular weight. Furthermore, it is known that template-associated radicals are able to hop to a neighboring template on reaching template ends and continue their propagation. Therefore, in order to provide for a better comparison between the obtained molecular weights, we use the hop number H_n, which is defined as the number of template chains along which a radical grows.[13] The H_n data in Table II were calculated assuming that the effectiveness of propagation is independent of template tacticity; i.e., the radical will use only half of the template chain on average. Two series of templates of corresponding molecular weights may be compared in Table II: (1) it-PMAA-3, cv-PMAA-4, and st-PMAA-2 with H_n being 2.7, 10.3,[13] and 4.2, respectively; (2) cv-PMAA-8 and st-PMAA-3 with H_n values of 6.3 and 4.2. In the case of the shorter templates, hopping takes place more often due to the availability of more template chains as compared to higher template molecular weights.[13] Interestingly, the H_n values follow the same order as obtained for the rate enhancements (see Table II). This is peculiar since one would expect H_n to be determined by the rate of radical propagation alongside the template (see section 3.4) instead of the amount of template-associated radicals. On the other hand, it was established that high molecular weights of PVIm were additionally enhanced by termination of a template-associated radical with another template-associated radical (termed template termination).[13] Template termination benefits from a larger amount of template-associated radicals and, presumably, causes this trend in H_n.

3.3. Tacticity of the Formed PVIm. The tacticity of PVIm can be determined from the α-C or α-CH resonances which are sensitive to tacticity.[27-29] The three peak groups in the expansion of the methine carbon (Figure 5) of PVIm have been assigned to syndiotactic (rr), heterotactic (mr), and isotactic (mm) triads in downfield direction. Results obtained via either ^{1}H NMR or ^{13}C NMR agreed fairly well with each other. In some occasions, however, ^{1}H NMR was not successful in resolving the isotactic triad peak due to its partial overlap with the β-CH_2 of PMAA.

In order to assess the stereochemical effect in template polymerization, PVIm's were also synthesized at low pH and in the presence of various low molecular weight

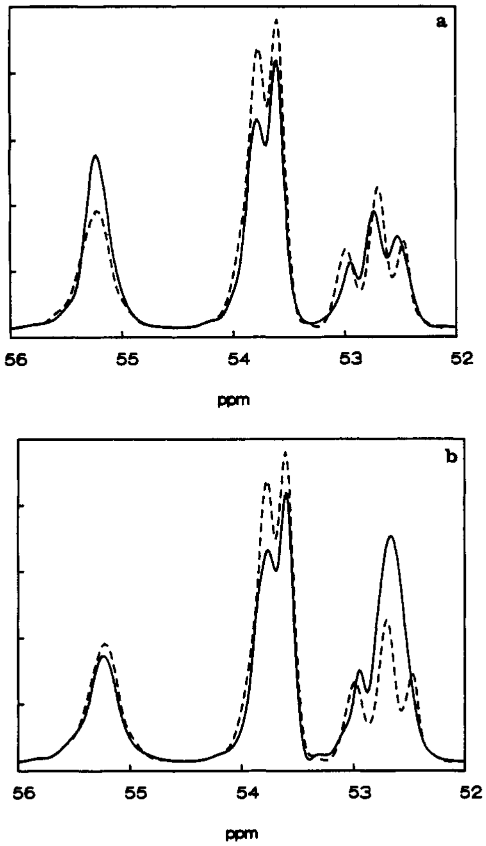

Figure 5. ^{13}C NMR expansion of the α-carbon of PVIm obtained: (a) in the presence of it-PMAA-1 at $[PMAA]/[VIm]_0 = 1$ and (b) in the presence of st-PMAA-1 at $[PMAA]/[VIm]_0 = 0.82$ (—). $[VIm]_0 = 0.41$ M; $[AAP]_0 = 0.047$ M. (- - -) Obtained in the absence of the template at pH 5 or in its presence at $[PMAA]/[VIm]_0 = 0.2$.

Table III
Tactivity of PVIm Synthesized in the Presence of Low Molecular Weight Compounds and as a Function of pH

conditions[a]	(mm):(mr):(rr),[b] %	ρ[c]	convn, %
isobutyric acid	29:50:21	0.99	60
glutaric acid	29:52:19	0.95	
2,3-dimethylglutaric acid	26:54:20	0.92	
2,4-dimethylglutaric acid	30:49:21	1.01	
pH 2	26:52:22	0.96	71
pH 3	26:50:24	1.0	70
pH 4.5	25:52:23	0.96	67
pH 6	25:50:25	1	59
pH 7	22:53:25	0.94	60

[a] Polymerizations conditions: $[COOH]/[VIm]_0 = 1$, $[VIm]_0 = 0.41$ M, $[AAP]_0 = 0.047$ M. [b] All values ±2%. [c] ρ = persistence ratio = $2(m)(r)/(mr)$.

analogues (Table III). The influence of pH upon the tacticity is only slight, in agreement with results obtained by Dambatta et al.[27] On the other hand, a larger effect of the low molecular weight compounds is observed since (mm) becomes larger than (rr). This is probably caused by interactions between the VIm or PVIm radical and the low molecular (di)acids as was observed for the system VIm/isobutyric acid.[7] The ensuing association apparently leads to a slight steric hindrance and will be termed the counterion effect. Values for the persistence ratio ρ in Table III indicate that tacticities generally conform to Bernouillian statistics except in the case of 2,3-dimethylglutaric acid. This may be caused by a different acid–VIm interaction in terms of acid strength and the resulting association of the two components.

The tacticity of the template-formed PVIm may be determined either from samples separated and isolated from the template or from dissolved complexes. The latter was chosen since the mentioned incomplete separation[13] may result in nonrepresentative samples. At a low $[PMAA]/[VIm]_0$ of 0.2, template-formed PVIm's had the same microstructure as PVIm synthesized at pH 6 (cf. Tables III and IV and Figure 5, dashed curves). This is in accordance with the fact that there is no template effect in this region; i.e., polymerization proceeds entirely in solution and not along the template (Figure 1). At $[PMAA]/[VIm]_0 = 1$, however, the tacticity of PVIm appeared to be grossly similar to that of PVIm's produced in the presence of low molecular weight (di)acids (cf. Tables III and IV and Figure 5a, solid curve); i.e., the PVIm's possess an enhanced isotactic triad content. Consequently, a similar steric hindrance is affecting monomer addition in both cases. This effect, which is almost independent of template tacticity, indicates that the reactive radical end has been propagating in close proximity to the template chain. It should be noted that, in the presence of st-PMAA at a $[PMAA]/[VIm]_0$ of 0.82, a PVIm was obtained with an enhanced syndiotacticity, instead (Table IV and Figure 5b, solid curve).

Table IV
Tacticity of Template-Formed PVIm

template	$[PMAA]/[VIm]_0$[a]	mm:mr:rr[b]	ρ[c]	convn, %
it-PMAA-1	0.2	24:51:25	0.98	60
it-PMAA-3	0.2	23:48:29	1.04	60
it-PMAA-1	1.0	31:59:10	0.81	
it-PMAA-3	1.0	30:51:19	0.97	73
it-PMAA-5	1.0	33:47:20	1.05	75
cv-PMAA-4	0.2	23:51:26	0.98	57
cv-PMAA-4	1.0	29:50:21	0.99	90
cv-PMAA-8	1.0	25:57:18	0.87	95
st-PMAA-1	0.25	23:50:27	1.0	55
st-PMAA-1	0.82	22:44:34	1.12	71
st-PMAA-2	1.0	32:51:17	0.96	88
st-PMAA-3	1.0	32:48:20	1.03	93
st-PMAA-4	1.0	31:49:20	1.02	90

[a] Polymerization conditions: $[VIm]_0 = 0.41$ M, $[AAP]_0 = 0.047$ M. [b] All values ±2%. [c] ρ = persistence ratio.

3.4. Influence of the Template Molecular Weight. It has been established that an increase of the template molecular weight leads to a longer growth period of a radical along the same template chain[12] and thus to a higher rate enhancement. Consequently, the extent to which the template is able to influence the polymerization may be deduced from the dependence of R_p and $\bar{M}_v$ on the template molecular weight.[12,13] Linear plots of $\ln R_p$ versus $\ln \bar{M}_{v,PMAA}$ and $\ln \bar{M}_{v,PVIm}$ versus $\ln \bar{M}_{v,PMAA}$ are shown in Figures 6 and 7 for the different tactic templates. The linearity may be described with $\ln R_p = b_1 \ln \bar{M}_{v,PMAA} + c_1$ and $\ln \bar{M}_{v,PVIm} = b_2 \ln \bar{M}_{v,PMAA} + c_2$, respectively. The dependencies of R_p on $\bar{M}_{v,PMAA}$ as derived from these slopes[12] follow the order st < it < cv (Table II), which differs from the order it < st < cv in R_{rel} (Figure 1). The higher b_1 value for cv-PMAA as compared to it-PMAA may be explained by the larger amount of radicals propagating in the case of the former (see section 3.1 and Table II). In the case of the st-PMAA template, a similar amount of propagating radicals ($[R]_T$) was deduced as for cv-PMAA from the discussed complexation experiments. Consequently, since R_p depends on k_p, k_t, and $[R]_T$,[12] one has to assume that radical growth alongside st-PMAA proceeds less easily as compared to it- and cv-PMAA, leading to the lower b_1 value. The differences in b_1 values are larger than those obtained by Koetsier et al.[20] for the polymerization of N-vinylpyrrolidone along various tactic PMAA templates. This may be explained by the higher rate enhancements for the present system.

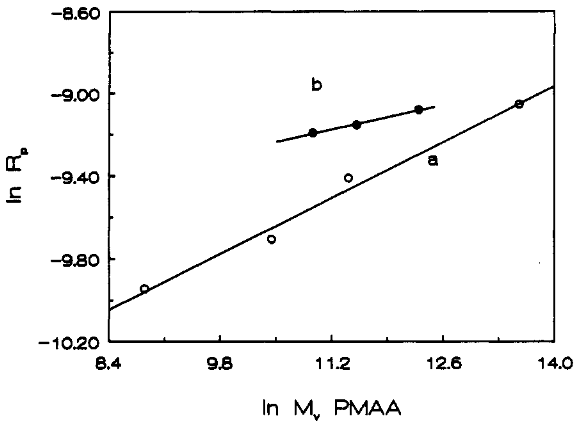

Figure 6. Dependence of the rate of polymerization, R_p, on the template molecular weight; it-PMAA (curve a, ○); st-PMAA (curve b, ●). $[PMAA]/[VIm]_0 = 1$; $[VIm]_0 = 0.41$ M; $[AAP]_0 = 0.047$ M.

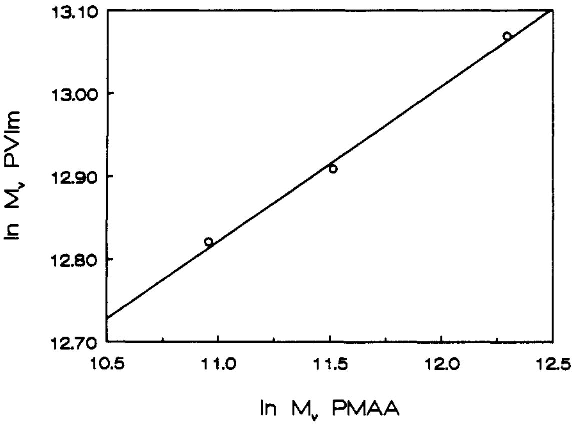

Figure 7. Dependence of $\bar{M}_{v,PVIm}$ on the molecular weight of st-PMAA. For polymerization conditions, see Figure 6.

The dependencies of $\bar{M}_{v,PVIm}$ on the template molecular weight as denoted by b_2 show a similar trend (Table II). No physical interpretation is available so far for the difference between b_1 and b_2 by a factor of 2.[13]

In Table IV, the influence of the template molecular weight upon the tacticities of template-formed PVIm at $[PMAA]/[VIm]_0 = 1$ is given. For all the higher template molecular weights, the effect of (mm) becoming larger than (rr), discussed previously in section 3.3, is observed (Table IV and Figure 5b). However, in the case of the lowest molecular weight templates, i.e., it-PMAA-1 and st-PMAA-1 (Figure 5), the tacticity of the formed PVIm follows the tacticity of the template. Moreover, values for the persistence ratio ρ in Table IV show that Bernouillian statistics are obeyed in most cases, the exceptions being the low molecular weight it- and st-PMAA in addition to the high molecular weight cv-PMAA. If analyzed by first-order Markov statistics, i.e., the adding monomer is influenced by the stereochemistry of the growing chain end, one obtains an isotactic-like chain for it-PMAA-1 and a stereoblock-like or syndiotactic-like chain for st-PMAA-1.[30] Tetrad fractions should be known to verify a first-order Markov and establish the above possibilities.[30] The influence of the tacticity of cv-PMAA will not be discussed further since it seems impossible to relate its stereochemistry to measured tacticities.

No clear definition is available in the literature to assess whether or not the effects obtained result from stereocontrol by the template. If one uses the criterion that a different tacticity should be obtained as compared to a polymerization in the absence of the template, then all results conform to a stereochemical template effect. On the other hand, if the tacticity obtained should be dependent on the tacticity of the template, then the use of the high molecular weight templates does not lead to stereocontrol by the template (Table IV) though the effect may be obscured by the high monomer conversions. In this case, tacticities obtained signify only that the reactive radical end has been propagating in close proximity to the template chain.

Obviously, the low molecular weight templates do lead to a stereochemical effect regardless of the definition used. To rationalize this, let us focus on the stereoregulating properties of the template. Stereoregular polymers may only be expected if ordered templates like st- and it-PMAA are used and, even then, it is required that the growing radical matches the template chain in order to be optimally influenced in a stereochemical way as was discussed in section 3.4. In section 3.1 it was explained that a perfect matching is absent in the system PVIm/PMAA as deduced from the lower rate enhancements and radical complexation. In the case of short template chains, the propagating radical probably reaches the template end before extensive mismatching has occurred. If the template molecular weight is increased and parallel to it is the growth period of the radical along the same template, mismatching between the template and radical is more likely to occur, and monomeric units may be skipped along the template chain by the radical. Consequently, radical growth is now less stereochemically controlled, and the stereoregularity of the resulting PVIm will obviously decrease. Moreover, the longer template chain is less able to adapt its conformation to facilitate radical propagation because of its length. It is possible that model studies or computer simulations may actually prove that the two polymers do not match. However, this has not been done. This mismatching between the template and growing radical may cause the high (mr) values in Table IV, indicating a large number of crossovers.

No data are present in the literature to verify the influence of template molecular weight on the stereochemical effect. It is significant, however, that the largest stereochemical effect in the case of strong interactions between the template and monomer was observed by Blumstein et al.[31] in the polymerization of vinylsulfonic acid along short 2.2.2-ionene templates. The isotacticity and heterotacticity of the resulting poly(vinylsulfonic acid) were strongly increased as compared to a reference polymer.

3.5. Complex Characterization. Template-formed complexes may differ from those formed from ready-made polymer components (synthetic complexes) as has been shown for the case of cv-PMAA in the previous paper.[19] The difference was reflected by a partial suppression of the anhydride formation of PMAA at elevated temperatures. A complex structure was proposed in which short well-complexed chain sections resulting from template propagation alternate with longer sections consisting of noncomplexed and poorly complexed COO units. Complexes with st- and it-PMAA were examined in a similar way by DSC and FTIR, and results are collected in Table V.

The FTIR spectra of template complexes obtained at $[PMAA][VIm]_0 = 1$ and $[VIM]_0 = 0.41$ M together with those of it-PMAA and st-PMAA are presented in Figure 8. The difference in tacticity between it- and st-PMAA may be deduced from absorptions around 1450 and 950 cm^{-1} as described in ref 7.[3,26,32] The percentage of protonation of PVIm (PVImH$^+$) or H-bonded PVIm was calculated from $A_{1573}/(A_{1500} + A_{1573})$[14] and the degree of

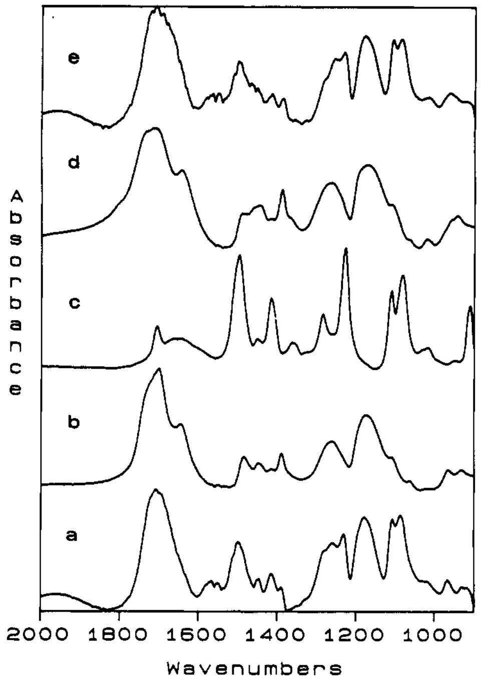

Figure 8. FTIR spectra prior to DSC runs: (a) st-PMAA template complex; (b) st-PMAA; (c) PVIm; (d) it-PMAA; (e) it-PMAA template complex.

Table V
Some Characteristics of PMAA Templates and Their Complexes with PVIm from FTIR and DSC Measurements

	DSC			FTIR	
sample	wt loss,[a,b] %	T_{max},[a] °C	T_g,[c] °C	PVImH⁺, %	COO⁻, %
		Template			
st-PMAA-2	17.3	235	180[15]		0
it-PMAA-4	25.4	190	150 and 168		0
cv-PMAA-8[14]	12	238	163		0
		Template Complex[d,e]			
st-PMAA-2	17	238	190	nd	nd
st-PMAA-3	nd	nd	nd	30	8
st-PMAA-4	18	230	186	27	7
it-PMAA-3	30	194	190	nd	nd
it-PMAA-5	26	190	188	32	10
cv-PMAA-8[14]	15.6	224	194	32	8
		Synthetic Complex[d]			
st-PMAA-2	nd	236	195	34	12
it-PMAA-5	nd	205	193	30	10
cv-PMAA-8	nd	227	196	37	14

[a] After/on the second DSC run. [b] Based on PMAA content. [c] On the third DSC run. [d] [PMAA]/[PVIm] = 1.0 ± 0.1. [e] Polymerization conditions: $[PMAA]/[VIm]_0 = 1.0$, $[VIm]_0 = 0.41$ M, $[AAP]_0 = 0.047$ M. nd = not determined.

ionization of PMAA from the ratio of the asymmetric stretching vibration at 1560 cm^{-1} and the carbonyl absorbance at 1700 cm^{-1} using the ratio of the extinction coefficients.[14,33] The results are compiled in Table V. Again, all values for PVImH⁺ are higher than the α_N of 0.2 of PVIm at pH 6,[7] and the percentages of COO⁻ are all much lower than the degree of neutralization α_N of 0.48 at $[PMAA]/[VIM]_0 = 1$,[7] indicating that charge neutralization by complexation has occurred. FTIR however does not provide conclusive evidence to the extent of charge neutralization.

The temperatures at maximum height of the second endothermic peak (anhydride formation), T_{max}, differ for the various template complexes (Table V). The importance of the spatial orientation of the COOH groups for anhydride formation has been discussed in the previous paper.[14] In the case of cv-PMAA, a shift to lower T_{max} is observed (Table V) which was explained by assuming that the complexation between PVIm and PMAA facilitates anhydride formation by orienting COOH groups. Moreover, this implies that partial dissociation of the complex takes place. The syndiotactic template exhibits an identical behavior (Figure 9 and Table V). it-PMAA, on the other hand, does not show this temperature shift which may be explained from the already perfect orientation of the COOH groups toward one another. It should be noted that the weight loss of it-PMAA and their complexes after anhydride formation is higher than those found for cv- and st-PMAA.

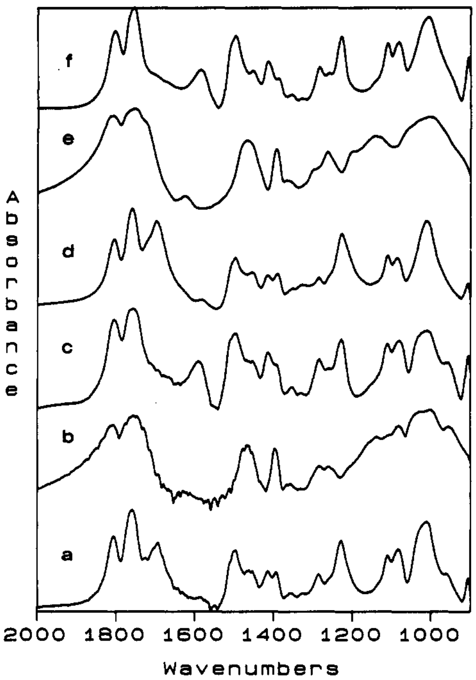

Figure 9. FTIR spectra after anhydride formation: (a) st-PMAA template complex; (b) st-PMAA; (c) st-PMAA complex prepared at pH 6; (d) it-PMAA template complex; (e) it-PMAA; (f) it-PMAA complex prepared at pH 6.

Anhydride formation on heating the samples up to 280 °C was also examined from FTIR spectra (Figure 9). The presence of the PMAA carbonyl absorption at 1700 cm^{-1} indicates that anhydride formation is suppressed to some extent in the template complexes independent of template tacticity. The spectra of the synthetic complexes show that the COO⁻ groups are unable to participate in the anhydride formation as may be deduced from the band around 1570 cm^{-1} which is unchanged relative to the ring vibration of PVIm at 1500 cm^{-1}.

Template complexes of it-PMAA and st-PMAA behave in a similar way as template complexes of cv-PMAA. The partial suppression of anhydride formation may thus be explained by the better interactions in the template complexes as compared to synthetic complexes.[14] These well-complexed chain sections are probably short, since imperfect matching of PVIm and PMAA is likely, as has been discussed in section 3.4. More research will be necessary to quantify the difference in complex structure between the complexes of the various tactic templates.

4. Conclusions

We have established that the mechanism of the polymerization of VIm along PMAA, including suppression of degradative addition, is independent of the tacticity of the template. The tacticity does affect the processes occurring at the template chain, viz., radical complexation and radical propagation, since it determines the acidity of the template and its conformation. With respect to the relation between the kinetic and stereochemical template effect, we conclude that the growing radical is unable to match with the syndiotactic template. Considering the fact that propagation along the isotactic template seems less hindered than in the case of st-PMAA, it is possible that polymerizations with a small pH reduction, leading to extra interactions between the template and monomer/radical, might result in larger stereochemical effects.

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