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Template Polymerization of *N*-Vinylimidazole along Poly(methacrylic acid) in Water. 2. Kinetics of the Template Polymerization

H. T. van de Grampel, Y. Y. Tan,* and G. Challa

Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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ABSTRACT: The template polymerization of *N*-vinylimidazole (VIm) along poly(methacrylic acid) (PMAA) in water at 50 °C with 2,2′-azobis(2-amidinopropane)·2HCl (AAP) as initiator was studied by using variable initiator and monomer concentrations at constant [PMAA]/$[\mathrm{VIm}]_0$. From the order in [VIm] it was concluded that PMAA affected the degradative addition to which the conventional polymerization of *N*-vinylimidazole is subject in three ways: (1) degradative addition is impeded in the case of template-associated radicals due to propagation with adsorbed monomers, (2) [VIm] in solution is reduced below the critical concentration beyond which degradative addition occurs, allowing higher overall monomer concentrations to be used, and (3) under conditions of degradative addition template polymerization still leads to sizable rate enhancements. As compared to conventional polymerizations, the rate of polymerization could be further enhanced by using templates of higher molecular weight, but this did not affect suppression of degradative addition. The order in [initiator] indicated that several termination reactions are possible for the template-associated radicals.

1. Introduction

Polymerizations in which propagation of a radical occurs along a polymeric chain (the template) for the greater part of its lifetime are termed template radical polymerizations.[1] As compared to normal polymerizations, this mode of propagation may influence the rate of polymerization, R_p, and characteristics of the polymers formed.

It is known that the polymerization of *N*-vinylimidazole (VIm) at high monomer concentrations is subject to degradative addition of a chain radical to the 2-position of the imidazole ring of the monomer.[2] This results in deviating kinetics,[2] with R_p being zero order in [monomer] and first order in [initiator]. In conventional polymerization at pH 5 we established that this side reaction becomes important[3] beyond a $[\mathrm{VIm}]_0$ of 0.25 M, but it could be suppressed by protonation of the monomer on reducing the pH to 1. By polymerizing VIm in the presence of equivalent amounts of isobutyric acid (IBA) (termed blank polymerization), which is the low molecular weight analogue of the used PMAA template, degradative addition is postponed to $[\mathrm{VIm}]_0$ of 0.45 M due to interactions between IBA and VIm.

In the case of template polymerization of VIm along poly(methacrylic acid) (PMAA) at a $[\mathrm{VIm}]_0$ of 0.41 M with 2,2′-azobis(2-amidinopropane)·2HCl (AAP) as initiator, the rate was enhanced with respect to the blank or conventional polymerization under comparable conditions.[3,4] A propagation mechanism has been proposed[3] in which monomer adsorption by the template precedes its addition by template-associated radicals in order to explain the obtained profile of R_p versus [PMAA]. Rate enhancements did result from a combination of factors, one of which appears to be suppression of degradative addition.

Additional and more conclusive information with respect to suppression of degradative addition by template polymerization as well as the template polymerization mechanism may be obtained by determination of the order in monomer and initiator concentration at various template concentrations,[5-9] the results of which are described in this paper. Furthermore, the influence of template molecular weight and the different maximal rate enhancements of 4–7 for different polymerization conditions will be discussed.

2. Experimental Section

2.1. Materials. Materials were purified as described in the previous paper,[3] as are the syntheses and characterizations of the PMAA samples. The following templates were used with $\bar{M}_v$'s in brackets: PMAA-1 (89×10^3), PMAA-2 (72×10^3), PMAA-3 (88×10^3), PMAA-4 (30×10^3), PMAA-5 (66×10^3), PMAA-6 (128×10^3), PMAA-7 (177×10^3), PMAA-8 (95×10^3). PMAA-2 was used for the potentiometric measurements, PMAA-3 for the kinetic experiments with $[\mathrm{AAP}]_0 = 0.0235$ M, and PMAA-1 and PMAA-8 for all other experiments except those pertaining to the influence of template molecular weight. All measurements were performed at 50 °C.

2.2. Polymerizations. Procedures for the polymerizations have been described previously.[3] Rates were calculated from the initial straight slopes of the conversion plots. Apparent first-order monomer conversion curves were converted to $-\ln(1-\alpha)$ vs t plots to avoid extrapolation errors in determining the tangent at low conversions.

With respect to rate enhancements, the choice of a suitable reference polymerization is difficult. In the majority of cases[1] the relative rate (R_{rel}) is defined as the ratio of overall rate (R_p) and blank rate ($R_{p,B}$), i.e., $R_{\mathrm{rel}} = R_p/R_{p,B}$, with $R_{p,B}$ equal to the conventional rate ($R_{p,cv}$). In our case there are arguments that may favor either $R_{p,cv}$, $R_{p,B}$, or the rate at $[\mathrm{PMAA}]/[\mathrm{VIm}]_0 = 0.2$. We have chosen $R_p([\mathrm{PMAA}]/[\mathrm{VIm}]_0{=}0.2)$ as the reference polymerization primarily because the blank polymerization behaved differently from the conventional polymerization upon variation of monomer concentration (see ref 3).

3. Results and Discussion

3.1. Influence of Monomer Concentration. The suppression of degradative addition by means of template polymerization can be deduced from reaction orders in [VIm] and [AAP]. On variation of $[\mathrm{AAP}]_0$ and $[\mathrm{VIm}]_0$, two important aspects have to be considered. First, it should be noted that different polymerization conditions could correspond to different stages[10] in the template polymerization process, e.g., the addition of [PMAA] at a constant $[\mathrm{VIm}]_0$ gives rise to template effects differing in magnitude.[3,4] Consequently, one has to verify whether or not direct comparison of obtained R_p's is allowed for the determination of orders. Second, the overall rate of polymerization is the sum of the template polymerization rate and the polymerization rate in bulk solution, i.e., the conventional polymerization rate. In view of abnormal kinetics of the conventional polymerization of VIm due to

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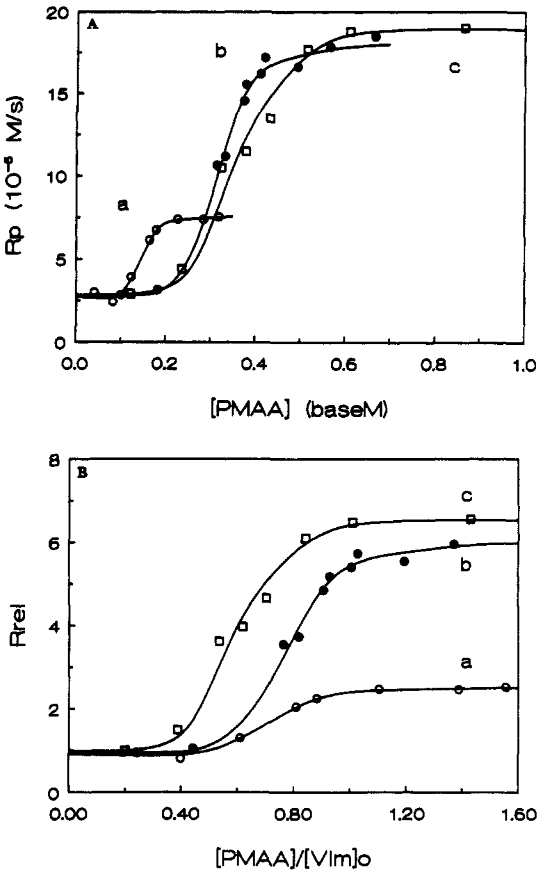

Figure 1. (A) Influence of [PMAA] on R_p for three monomer concentrations: $[\mathrm{VIm}]_0$ = 0.21 M (curve a, ○), 0.41 M (curve b, ●), and 0.61 M (curve c, □). $[\mathrm{AAP}]_0$ = 0.047 M; temperature = 50 °C. (B) Dependence of R_{rel} on $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ for three monomer concentrations: $[\mathrm{VIm}]_0$ = 0.21 M (curve a, ○), 0.41 M (curve b, ●), and 0.61 M (curve c, □). $[\mathrm{AAP}]_0$ = 0.047 M; temperature = 50 °C.

degradative addition, obtained orders must be assessed carefully if one is unable to discriminate between the two contributions.

In Figure 1A, R_p is plotted versus [PMAA] in repeat unit mol/dm^3 (≡baseM) for three monomer concentrations: $[\mathrm{VIm}]_0$ = 0.21, 0.41, and 0.61 M. Three regions can be discerned in all profiles, namely, region A with a constant R_p, region B with R_p increasing, and region C with R_p having a nearly constant but higher value. The profiles differ in the positions of the AB and BC transitions and in the (maximal) rate enhancement at the BC transition.

The rate profile obtained for $[\mathrm{VIm}]_0$ = 0.41 M has already been discussed[3] in terms of a critical chain length, l^*, of the radical required for complexation with the template. This critical chain length is determined by both the length and charge density of the radicals, the latter of which is strongly influenced by the gradual decrease of pH in regions A–C due to the increasing PMAA concentration.[3] In region A, polymerization takes place in solution due to the inability of radicals to complex with the template chain (chain length smaller than l^*). Beginning complexation of these radicals with the template is feasible at the AB transition, subsequently followed by propagation alongside the template. The increase of R_p in region B is explained by the increasing number of radicals that become associated with the template upon achieving l^*. By arguing that propagation of template-associated radicals proceeds with adsorbed monomers only (modified type Ia mechanism[1,3]), we can assign the BC transition to the onset of maximal radical complexation.

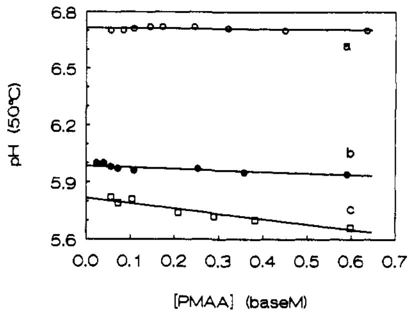

Figure 2. Influence of [PMAA] on pH (50 °C) at a constant $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ of 0.2 (curve a, ○), 1.0 (curve b, ●), and 1.55 (curve c, □).

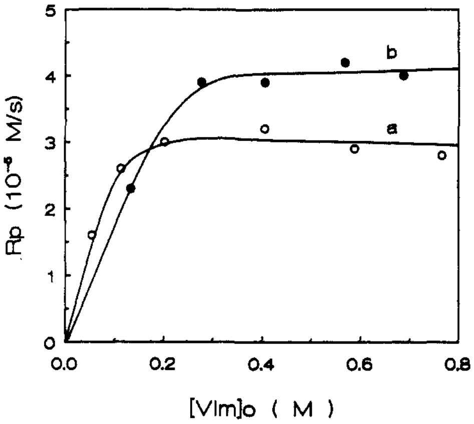

Figure 3. Dependence of R_p on $[\mathrm{VIm}]_0$ for $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ = 0.2 (curve a, ○) and for the conventional polymerization at pH 5 (curve b, ●).[3] $[\mathrm{AAP}]_0$ = 0.047 M; temperature = 50 °C.

The pH, which controls the number of template-associated radicals through their charge density, is inherently determined by the ratio of [PMAA] to $[\mathrm{VIm}]_0$. Surprisingly, the pH appeared to be nearly constant for each definite template–monomer ratio, i.e., irrespective of template concentration (Figure 2). This is probably caused by the mixture of a weak polyacid (PMAA) and a weak base (VIm) at intermediate pH values. If one now plots R_{rel} against $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ (Figure 1B) instead of R_p versus [PMAA] (Figure 1A), it is apparent that the template to monomer ratios of the AB and BC transitions nearly coincide with each other, further supporting the mechanism as outlined in ref 3. Moreover, determination of the order in [VIm] seems possible at a constant template to monomer ratio, since they seem to pertain to similar stages of the template process.[10]

The order in VIm was determined for a $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ of 0.2, 1.0, and 1.55, the first two of which relate to conditions without and with a (maximal) template effect, respectively. Though a $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ of 1.55 was studied to provide information on the template process at high template concentrations, results appeared to be rather similar to those for the ratio of unity (see Figure 1A). It is reminded that the order in $[\mathrm{VIm}]_0$ is dependent on the monomer concentration due to the possibility of degradative addition.

In the case of $[\mathrm{PMAA}]/[\mathrm{VIm}]_0$ = 0.2, where polymerization takes place exclusively in solution, a rather similar profile of R_p versus $[\mathrm{VIm}]_0$ was obtained as the one for the conventional polymerization (Figure 3, curves a and b). R_p increases with $[\mathrm{VIm}]_0$ up to $[\mathrm{VIm}]_0$ = 0.2 M, after which it assumes a constant value. The order in [VIm] below a $[\mathrm{VIm}]_0$ of 0.2 M was approximately 1, but the curvature of the rate profile hampered an accurate determination. However, the invariance of R_p on monomer concentration

Table I
Order in $[VIm]_0$ for Different $[PMAA]/[VIm]_0$[a]

	$[PMAA]/[VIm]_0$		
$[VIm]_0$, M	0.2	1.0	1.55
<0.20	*b*	0.98 ● 0.05	0.95 ● 0.05
>0.20	ca. 0		
<0.45		0.98 ● 0.05	0.95 ● 0.05
>0.45		0.2 ± 0.03	0.2 ± 0.03

[a] $[AAP]_0$ = 0.047 M. [b] See Figure 3.

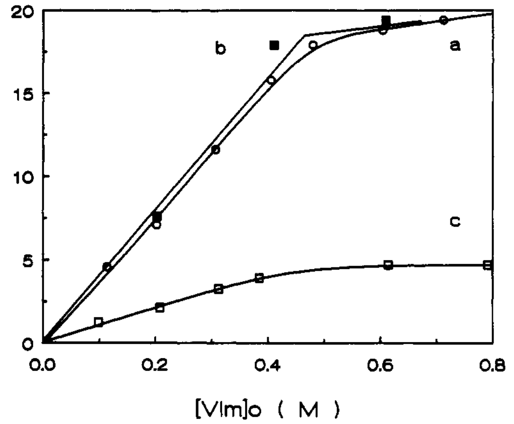

Figure 4. Dependence of R_p on $[VIm]_0$ for $[PMAA]/[VIm]_0$ = 1.0 (curve a, ○), for $[PMAA]/[VIm]_0$ = 1.55 (curve b, ■), and for the blank polymerization in the presence of IBA (curve c, □).[3] $[AAP]_0$ = 0.047 M; temperature = 50 °C.

at $[VIm]_0 > 0.2$ M signifies the presence of degradative addition (Table I). Similarly, degradative addition became dominant in the conventional polymerization beyond a $[VIm]_0$ of 0.15 and 0.25 M for pH 8 and pH 5, respectively.[3] The value of ca. 0.2 M for $[PMAA]/[VIm]_0$ = 0.2 at pH 6.7 (see Figure 2) is in accordance with these values. As compared to the conventional polymerization, the R_p for $[PMAA]/[VIm]_0$ = 0.2 is slightly lower, which can be attributed to preferential adsorption of VIm by and an enhanced local AAP concentration near the template chain.[11] This reduces their concentrations in solution where polymerization takes place.[3]

In the cases of $[PMAA]/[VIm]_0$ of 1.0 and 1.55, the obtained rate profiles are different. The order in [VIm] is 0.98 ● 0.05 up to a $[VIm]_0$ of 0.45 M, beyond which it changes to 0.2 ± 0.03 (see Figure 4 and Table I). The first-order dependence in monomer concentration at $[VIm]_0 < 0.45$ M indicates classical kinetics and, thus, absence of degradative addition to monomer. However, rate profiles for these $[PMAA]/[VIm]_0$, albeit much higher, have shapes rather similar to the one obtained for the blank polymerization, since they all level off beyond a $[VIm]_0$ of 0.45 M (cf. curves a and b with c in Figure 4). This suggests the presence of degradative addition for $[VIm]_0 > 0.45$ M as was identified for the blank polymerization.[3] Nevertheless, conversion–time curves for these polymerizations are distinctly different from linear plots anticipated in the case of degradative addition[3] (Figure 5). However, they tend to become linear with increasing monomer concentration, demonstrating an increasing contribution of degradative addition of the conventional (nontemplate) polymerization to the overall process.

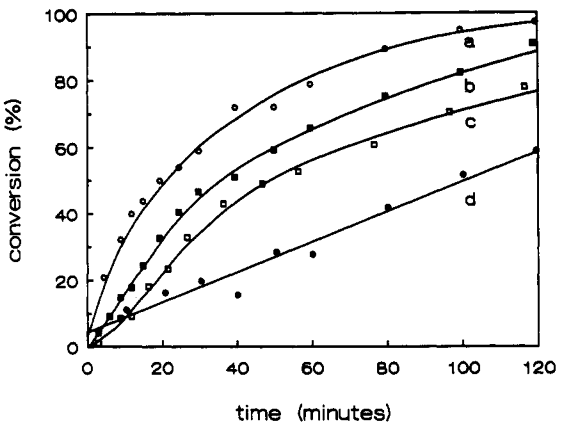

Figure 5. Conversion–time plots for three monomer concentrations at $[PMAA]/[VIm]_0$ = 1.0 and $[AAP]_0$ = 0.047 M: $[VIm]_0$ = 0.41 M (curve a, ○), 0.61 M (curve b, ■), and 0.72 M (curve c, □). Curve d (●) pertains to a blank polymerization for $[VIm]_0$ = 0.41 M and $[IBA]/[VIm]_0$ = 1. (See ref 3).

It has already been mentioned that the overall rate of polymerization (R_p) comprised contributions from polymerization in solution ($R_{p,sol}$) and alongside the template ($R_{p,T}$): $R_p = R_{p,sol} + R_{p,T}$. These rates are related to each other in two ways. First, radicals produced in solution will participate in the template process after complexation with the template. Second, monomer molecules are either free in solution or adsorbed on the template; i.e., $[VIm]_{total} = [VIm]_{sol} + [VIm]_T$. Since it has been established that degradative addition takes place in solution at a $[VIm]_0$ beyond 0.25 M at pH 5 and that there is a preferential monomer adsorption of 34 ± 9% at $[PMAA]/[VIm]_0$ of unity,[3] degradative addition should occur in solution at a $[VIm]_{total}$ of 0.38 ± 0.06 M for the template polymerization. This concentration corresponds nicely with the bend in the obtained rate profiles at $[VIm]_0$ = 0.45 M (Figure 4, curves a and b). Evidently, radicals that have become inactive due to degradative addition prior to complexation with the template cannot be reactivated.

This leaves the question of the specific influence of the template in suppressing degradative addition. Propagation along the template by template-associated radicals with adsorbed monomer molecules does not suffer from this side reaction as was demonstrated by a first-order dependence of R_p in $[VIm]_0$ (Table I). Apparently, adsorbed monomer molecules are protonated, which prevents degradative addition.[3] Also, PMAA decreases $[VIm]_{sol}$ by preferential adsorption, allowing higher monomer concentrations to be used before degradative addition takes place. Theoretically, the occurrence of degradative addition may be shifted to even higher monomer concentrations by reducing the pH of the solution.

Furthermore, it should be pointed out that R_p slightly increases with increasing $[VIm]_0$ at $[VIm]_0 > 0.45$ M (Figure 4 and Table I). Since the higher monomer concentration leads to an increasing number of inactive radicals, no rate increase should have been observed (see, e.g., blank polymerization). Consequently, not only do reactive radicals still complex with the template but also part of the radicals, which are destined to become inactive due to degradative addition, will associate with the template. Thus, the template is able to reduce the number of inactive radicals, which may be caused by a smaller critical chain length l^* rather than kinetic radical chain length. The critical chain length l^* at $[PMAA]/[VIm]_0$ = 1 may be calculated[3] by using the degree of neutralization of PVIm (0.2) and the minimal amount of six electrostatic interactions necessary to complex with the template. This leads to a $\bar{M}_v$ of 5.6×10^3 for l^*, which is lower than the $\bar{M}_v$ of ca. 11×10^3 obtained for polymers in the conventional polymerization at high pH.[3]

Therefore, the influence of the template is not limited to the prevention of degradative addition by propagation of radicals alongside the template with adsorbed mono-

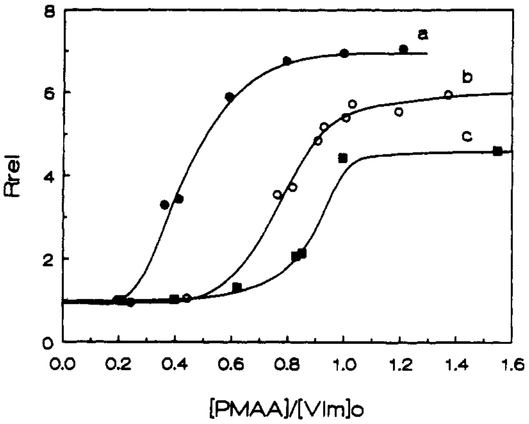

Figure 6. Influence of initiator concentration on R_{rel} versus $[PMAA]/[VIm]_0$: $[AAP]_0 = 0.024$ M (curve a, ●), 0.047 M (curve b, ○), and 0.072 M (curve c, ■). $[VIm]_0 = 0.41$ M; temperature = 50 °C.

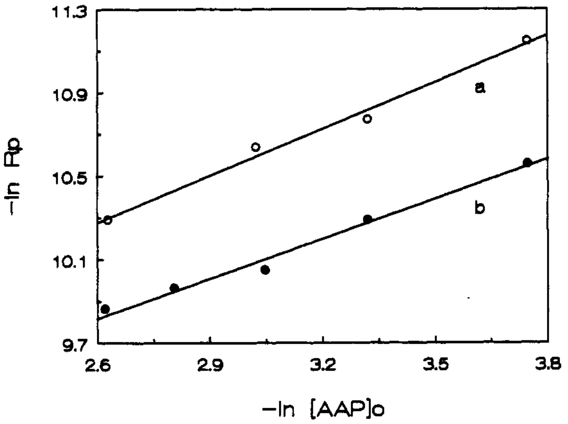

Figure 7. $-\ln R_p$ versus $-\ln [AAP]_0$ for $[VIm]_0 = 0.12$ M and $[PMAA]/[VIm]_0 = 0.2$ (curve a, ○) and 1.0 (curve b, ●).

mers; it is also able to reduce the number of inactive radicals in solution under conditions of degradative addition.

3.2. Influence of Initiator Concentration. Likewise, the order in AAP was determined at constant template to monomer ratios after it was deduced from Figure 6 that comparison between obtained rates was allowed. Obviously, the AB transition shifts to higher $[PMAA]/[VIm]_0$ when $[AAP]_0$ is increased, since shorter radicals require a higher charge density and thus a lower pH to achieve complexation with the template.[3] At a $[PMAA]/[VIm]_0$ of 0.2, polymerization primarily takes place in solution instead of alongside the template, provided $[AAP]_0 > 0.024$ M.

The BC transition is also shifted to higher $[PMAA]/[VIm]_0$ on increasing $[AAP]_0$, again due to the aforementioned reason. The differences between initiator concentrations become smaller with increasing $[AAP]_0$ since the length of the radical is proportional to $[AAP]^{-0.5}$, if classical kinetics holds.

Polymerizations at $[PMAA]/[VIm]_0$ of 1.0 and 1.55 appear to correspond to similar stages[10] of the template process as they did for variation of $[VIm]_0$. The order in [AAP] was determined for different monomer concentrations because it is rather sensitive to $[VIm]_0$.[3]

Orders were calculated from linear $\ln R_p$ versus $\ln [AAP]_0$ plots (as illustrated by Figures 7 and 8) and are presented in Table II. The results for $[VIm]_0 = 0.12$ M deviate from orders expected for classical kinetics as was deduced from the order in monomer concentration (Table I). Though unexpected, it is presumably caused by the high initiator concentration used in comparison with the template concentration. AAP is a salt and consequently will have interactions with PMAA, leading to contraction of PMAA coils due to shielding of the charged sites and reduction of preferential adsorption of VIm and possibly even influencing initiation/termination reactions. Therefore, we will not pay attention to this anomaly. The influence of salt will be discussed in a next paper.[15]

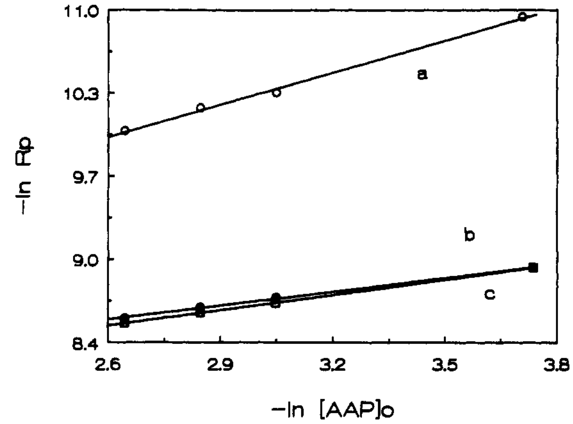

Figure 8. $-\ln R_p$ versus $-\ln [AAP]_0$ for $[VIm]_0 = 0.41$ M and $[PMAA]/[VIm]_0 = 0.2$ (curve a, ○), 1.0 (curve b, ●), and 1.55 (curve c, □).

Table II
Order in $[AAP]_0$

	$[PMAA]/[VIm]_0$		
$[VIm]_0$, M	0.2	1.0	1.55
0.12	0.85 ± 0.1[a]	0.62 ± 0.04[a]	
0.21	0.54 ± 0.05	0.38 ± 0.02	
0.41	0.84 ± 0.04	0.36 ± 0.02	0.40 ± 0.02
0.61	0.98 ± 0.03	0.68 ± 0.1	

[a] Salt effect by initiator; see text.

At $[PMAA]/[VIm]_0 = 0.2$ and $[VIm]_0 \geq 0.2$ M, the increasing order in $[AAP]_0$ with increasing $[VIm]_0$ demonstrates the emergence of degradative addition, eventually becoming 1 at $[VIm]_0 = 0.61$ M (Table II). This is in line with the results obtained for the order in monomer concentration. For the higher ratios of 1.0 and 1.55, the obtained orders of ca. 0.4 in $[AAP]_0$ at $[VIm]_0 = 0.21$ and 0.41 M are lower than the expected 0.5 for classical kinetics, which holds for $[VIm]_0$ (see the preceding section). This apparent contradiction seems peculiar but is related to the concept of template polymerization as will be discussed later on. The order of 0.68 ± 0.1 at a $[VIm]_0$ of 0.61 M confirms the presence of degradative addition as was deduced from the order in $[VIm]_0$ (Table I and Figure 4) and the shapes of conversion curves in Figure 5.

In the case of template polymerization, the order in [initiator] is dependent upon the principal termination reactions. Two bimolecular termination reactions for the template-associated radicals can be distinguished:[1] termination with another template-associated radical ("template termination") or with a radical from solution ("cross-termination"). In either case, no distinction will be made as to whether termination reactions occur on the template or in solution. At $[PMAA]/[VIm]_0 \geq 1$, these cross-termination reactions will take place with small oligomeric radicals due to the existence of a small l^*, while termination with primary radicals is also possibly caused by the elevated local [AAP] near the template chain.[3]

According to a general kinetic mechanism for template polymerization developed by Smid et al.,[12] the termination reaction depends on the ability of radicals to complex with

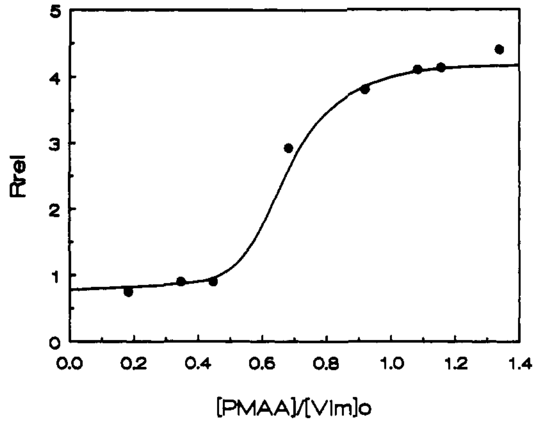

Figure 9. Dependence of R_{rel} on [PMAA]/[VIm]$_0$ for PMAA-4 with $\bar{M}_v$ = 30 × 10^3 (cf. Figure 1B). [VIm]$_0$ = 0.41 M.

the template as defined by

$$T + P_b \xrightarrow{k_c} P_T$$

with P_b signifying either a radical or terminated polymer in solution and P_T a radical or terminated polymer associated with the template. Obviously, a larger k_c leads to a higher probability of template termination. Assuming that at [PMAA]/[VIm]$_0$ = 1 the rate of complexation is equal to the rate of initiation,[13] one finds the following relations for R_p:[12]

$$\text{cross-termination} \quad R_p \simeq [I]^0$$

$$\text{template termination} \quad R_p \simeq [I]^{0.5}$$

The obtained order of 0.36 ± 0.02 does not point to only one mode of the termination reactions but to the presence of a mixture of termination reactions. In our case, template termination is feasible since it is possible that growing radicals hop to a next template chain upon reaching the end of the template macromolecule.[14] This is supported by molecular weights of the formed PVIm, which are 6- to 8-fold the molecular weights of their parent template macromolecules.[15] Also, cross-termination is possible either by radicals diffusing to the template chains or during a hop of a template-associated radical to a neighboring template chain. The enhanced presence of the positively charged AAP^{2+} cation near the template chain will contribute to cross-termination reactions by increasing the probability of primary termination.

The addition of more template macromolecules to the system should not substantially increase the number of complexed radicals but certainly should reduce the probability of an encounter between two template-associated radicals. Consequently, one would expect cross-termination to become more dominating at [PMAA]/[VIm]$_0$ = 1.55, but this cannot be deduced from the order in initiator. However, radical occlusion can no longer be excluded, since this takes place in the extreme situation of no termination and leads to a first-order dependence in [AAP]. Theoretically, this would compensate for the expected reduction of the order in [AAP]$_0$ due to an anticipated larger contribution of cross-termination reactions at [PMAA]/[VIm]$_0$ = 1.55.

3.3. Influence of Template Molecular Weight. The peculiar analogy between PMAA and IBA with respect to the similar monomer concentration where degradative addition starts to occur (see Figure 4) was elaborated by determination of R_p as a function of the template molecular weight. The profile of R_{rel} vs [PMAA]/[VIm]$_0$ appears to be independent of the template molecular weight as is illustrated by comparing the profiles for $\bar{M}_v$ = 89 × 10^3 (Figure 1B) and 30 × 10^3 (Figure 9).

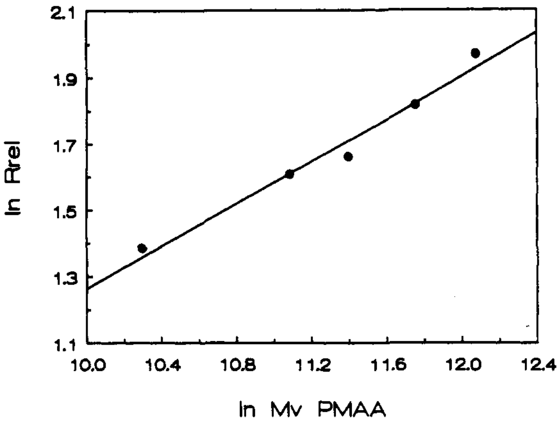

Figure 10. Influence of template molecular weight on R_{rel} for [PMAA]/[VIm]$_0$ = 1, [VIm]$_0$ = 0.41 M, and [AAP]$_0$ = 0.047 M.

The dependence of R_{rel} on the template molecular weight at [PMAA]/[VIm]$_0$ = 1 fits the linear relationship ln R_{rel} = b ln $\bar{M}_{v,PMAA}$ + ln c, with b and c constants (Figure 10). Following the analysis of critical chain lengths by Bartels et al.,[16] the intersection at R_{rel} of unity would correspond to the minimal template length that is required for template polymerization. The abscissa equals an $\bar{M}_v$ of ca. 350. By taking account of a broad molecular weight distribution at high conversions, we could expect a $\bar{M}_v/\bar{M}_n$ > 2, and hence a limiting M_n value approximating that of IBA. Therefore, the previously encountered similarity between the rate profiles of PMAA and IBA (Figure 4) is not coincidental. Suppression of degradative addition up to [VIm]$_0$ = 0.45 M is apparently independent of template molecular weight, provided that [COOH]/[VIm] = 1. This may be rationalized by assuming that [VIm]$_{sol}$ is reduced below the critical value of 0.25 M by adsorption or complexation (in the case of IBA) of monomer molecules in which case it is independent of the template molecular weight. This supports the adsorption equilibrium

$$T_n + M \overset{K_M}{\rightleftarrows} T_n\cdots M$$

with n the number of monomeric units of the template, to be of the Langmuir type; i.e., monomer adsorption is independent of the degree of occupancy of the template.

No physical interpretation has been established for the slope of ln R_{rel} versus ln $\bar{M}_{v,PMAA}$ as yet. In the polymerization of N-vinylpyrrolidone (NVP) along syndiotactic PMAA,[17] a value of 0.15 for b was determined, whereas it ranged from 0.09 to 0.12 in the polymerization of NVP along isotactic and atactic PMAA.[16] In these cases, relative rates varied between 2 and 2.5. For the present system, b is 0.31 and relative rates vary between 4 and 7. Thus, it suffices to note that b is related to the magnitude of the template effect, i.e., the influence of the template upon the polymerization, as is reflected by k_c, the template propagation rate constant ($k_{p,T}$), the termination rate constant ($k_{t,T}$), and the concentration of template-associated radicals.

3.4. Rate Enhancements. The rate enhancements R_{rel}, defined as the ratio of R_p([PMAA]/[VIm]$_0$ = 1) to R_p([PMAA]/[VIm]$_0$=0.2) (see the Experimental Section), were calculated for three cases: influence of template molecular weight, influence of [AAP]$_0$ at [VIm]$_0$ = 0.41 M, and influence of [VIm]$_0$ at [PMAA]/[VIm]$_0$ = 1.0 (Table III).

From Figure 10, it is obvious that R_{rel} increases with increasing template molecular weight. In order to ratio-

Table III
Influence of $[AAP]_0$ and $[VIm]_0$ on R_{rel}

$[VIm]_0$, M	R_{rel}[a] for $[AAP]_0$ (M)		
	0.023	0.047	0.072
0.12		1.8 ± 0.1	
0.21		2.2 ± 0.1	
0.41	7.0 ± 0.2	5.3 ± 0.2	4.4 ± 0.1
0.61		6.5 ± 0.2	
0.72		6.9 ± 0.3	

[a] R_{rel} is the ratio of $R_p([PMAA]/[VIm]_0=1)$ to $R_p([PMAA]/[VIm]_0=0.2)$.

nalize this, we assume that the primary function of the polymerization in solution is to generate radicals for the template propagation process and we neglect its contribution to the overall rate. Consequently, R_p reduces to $R_{p,T} = k_{p,T}[M]_T[R]_T$, with $[M]_T$ and $[R]_T$ the concentration of monomer and radicals on the template, respectively. $[R]_T$ is partially determined by the termination constant $k_{t,T}$; i.e., retardation of termination leads to a longer radical lifetime and thus to an increase of the number of template-associated radicals provided that the complexation rate of new radicals is not affected. The invariance of $[M]_T$ to the template molecular weight has already been discussed. Any increase in $k_{p,T}$ could result from a reduced hopping of template-associated radicals from one to another template, during which they grow in solution. However, the growth period in solution is short compared to the period of template growth, and, therefore, $k_{p,T}$ will hardly change when hopping is reduced by increasing the template molecular weight. This leaves $k_{t,T}$ and/or $[R]_T$ as factors responsible for the enhanced R_p. This conclusion may be substantiated if one considers that template-associated radicals are most susceptible to termination (both template and cross-termination reactions) during a hop between template chains. Consequently, if a radical hops less frequently due to an increase in the template molecular weight, its chances on becoming terminated are reduced. Molecular weights of the formed PVIm indeed proved that the number of hops decrease with increasing template molecular weight.[15]

A similar line of reasoning may be applied to the variation of the initiator concentration (Table III); a lower $[AAP]_0$ reduces the probability of termination, leading to a prolonged radical growth period alongside the template, and, thus, R_{rel} will increase. This appears to be quite general in the case of template polymerizations.[18]

In Table III, rate enhancements are also presented for a variation of $[VIm]_0$ at $[PMAA]/[VIm]_0$ of unity (see also Figure 4). An increase in rate enhancement with $[VIm]_0$ at $[VIm]_0 < 0.45$ M results from the increasing number of radicals that participate in the template process. At $[VIm]_0 > 0.45$ M, rate enhancements increase less since the number of active radicals is affected by degradative addition.

4. Concluding Remarks

In this paper we established that the presence of PMAA suppresses degradative addition in the polymerization of VIm by influencing the polymerization in three ways. First, growth of template-associated radicals alongside the template with adsorbed monomers effectively impedes degradative addition to monomer. Second, PMAA reduces the monomer concentration in solution below a critical value, allowing higher monomer concentrations to be used before degradative addition occurs. Third, the template is able to reduce the number of inactive radicals in solution under conditions of degradative addition, probably because of a lower critical chain length for complexation compared to the kinetic chain length of the radicals. In addition, template polymerization gives rise to rate enhancements up to a factor of 7, which is dependent on the template molecular weight. Suppression of degradative addition, on the other hand, is not dependent on the molecular weight of the template.

The order in initiator did not provide conclusive evidence with respect to the dominating termination reaction. So far, termination may take place by template termination, cross-termination, or no termination at all (radical occlusion).

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References and Notes

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