Template Polymerization of *N*-Vinylimidazole along Poly(methacrylic acid) in Water. 3. Molecular Weights of the Formed Polymers

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 molecular weights of polymers formed in the template polymerization of *N*-vinylimidazole (VIm) along poly(methacrylic acid) (PMAA) in water at 50 °C using 2,2′-azobis(2-amidinopropane)·2HCl (AAP) as initiator were determined for variable [PMAA] to $[\text{VIm}]_0$ ratios, $[\text{VIm}]_0$, $[\text{AAP}]_0$, and template molecular weight. Molecular weights were up to 70 times higher than those of polymers produced in the absence of the PMAA template, which is probably mainly due to retardation of termination of radicals propagating alongside the template. Longer templates appeared to promote retardation of termination. Frequent radical hopping to other template chains on reaching template ends led to polymers with molecular weights up to 9 times higher than the template molecular weight. From a comparison of molecular weights with corresponding rate enhancements as a function of $[\text{PMAA}]/[\text{VIm}]_0$, it is suggested that the $\bar{M}_v$ of the daughter polymer was further increased by combination termination of two template-associated radicals (template termination), while cross-termination with short radicals and possibly radical occlusion becomes more important at higher $[\text{PMAA}]/[\text{VIm}]_0$. Primary termination may occur because of an enhanced local concentration of the positively charged initiator close to the template chains.

1. Introduction

Template polymerizations are usually studied by determining the rate of polymerization (R_p) as a function of varying template concentrations.[1] Rates are then compared to blank polymerizations in which the template is substituted by a low molecular weight analogue from which a mechanism is deduced pertaining to the specific growth mode of the radical.[1] Generally, one obtains rate enhancements that are attributed to retardation of the termination step due to association of the radicals with the template.[1] Molecular weights of the daugher polymers should be affected in a similar way, since R_p and $\bar{M}_v$ are governed by the same rate coefficients. It may be argued that molecular weights tend to reflect the template polymerization process better since they are determined from polymers produced as a complex with the template, whereas R_p is measured as the overall polymerization rate, thus comprising contributions from both the conventional (nontemplate) and template polymerization process. Unfortunately, it may occur that polymer terminated in the conventional polymerization becomes associated with the template.

Generally, molecular weights of daughter polymers are higher than molecular weights of polymers prepared in the absence of the template, and increases in molecular weight follow increases in rate enhancements.[1–7] In the case of nonaqueous solutions, Koetsier et al. found molecular weights to run parallel with the molecular weights of the template in the polymerization of *N*-vinylpyrrolidone along syndiotactic poly(methacrylic acid) (PMAA).[2] In the polymerization of methyl methacrylate (MMA) along isotactic PMMA,[3] molecular weights of the formed polymers ran parallel to R_p and increased even further when [PMMA] ≥ overlap concentration. This was explained by radical hopping from one template chain to another.[3] In the case of aqueous solutions, the $\bar{M}_v$'s of PMAA were lower than the $\bar{M}_v$ of the template[4] in the template polymerization of methacrylic acid in the presence of poly(*N*-vinylpyrrolidone). Both R_p and $\bar{M}_v$ increased with increasing template molecular weight.[4] According to Ferguson and co-workers, the $\bar{M}_v$ of the formed polymer was equal to the template molecular weight in the polymerization of acrylic acid along poly(*N*-vinylpyrrolidone).[5] Similar results were obtained by Blumstein and Kakivaya for the polymerization of *p*-styrenesulfonic acid in the presence of ionenes.[6] Most of these studies, however, suffer from incomplete isolation of the daughter polymer from the template, leading to the measurement of nonrepresentative samples.[4–8]

We have already reported about the kinetics of the template polymerization of *N*-vinylimidazole (VIm) along PMAA using 2,2′-azobis(2-amidinopropane)·2HCl (AAP) as initiator[9–11] and proved that the template is able to suppress the so-called degradative addition to which VIm is subject at high monomer concentrations.[12] A propagation mechanism of template-associated radicals was deduced,[9] but the main mode of termination could not be inferred unambiguously from the order in initiator concentration.[10]

According to Bamford and Schofield,[12] the presence of degradative addition does not affect the simple relations existing between the degree of polymerization and R_p. Therefore, we will use molecular weights of the polymers formed under various polymerization conditions to obtain additional information about the template polymerization mechanism, in particular, the termination reactions of the template-associated radicals.

2. Experimental Section

2.1. Materials and Polymerizations. *N*-Methylimidazole (Merck) was distilled from KOH, and its molar extinction coefficient was determined to be 1620 L·cm/mol. Al_2O_3 (Activities I and II, 70–230 mesh) was obtained from Aldrich. Other materials and the polymerization procedure have been described.[9–10] Two kinds of complexes were obtained. In the absence of rate enhancements, e.g., at $[\text{PMAA}]/[\text{VIm}]_0 < 0.45$ for $[\text{AAP}]_0 = 0.047$ M, a small amount of transparent sticky material was found, which is believed to be partially complexed PVIm with PMAA. On the other hand, at higher template to monomer ratios, white precipitates were obtained. Molecular weights of PVIm were obtained for both types of complexes. End conversions of template polymerizations varied between 50 and 80% for $[\text{AAP}]_0 = 0.024$ M, except for $[\text{PMAA}]/[\text{VIm}]_0 \leq 0.2$ (30%), and 90 and 100% for $[\text{AAP}]_0 = 0.047$ and 0.072 M except for $[\text{PMAA}]/[\text{VIm}]_0$ below 0.45 (ca. 60%). $\bar{M}_v$'s of the PVIm

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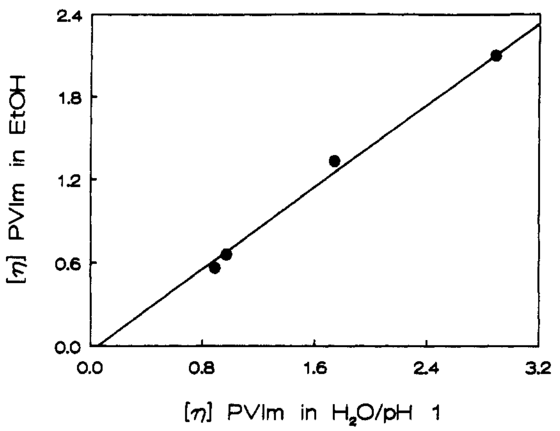


Figure 1. Calibration curve of intrinsic viscosities of PVIm in EtOH at 25 °C ([η] EtOH) versus intrinsic viscosities of PVIm in H_2O/pH 1 at 20 °C ([η] H_2O).

samples used were 81 × 10^3, 100 × 10^3, and 250 × 10^3, and those of PMAA were 89 × 10^3 (PMAA-1), 88 × 10^3 (PMAA-3), 30 × 10^3 (PMAA-4), 128 × 10^3 (PMAA-6), 177 × 10^3 (PMAA-7), and 95 × 10^3 (PMAA-8). PMAA-3 was used for the experiments with $[AAP]_0 = 0.024$ M, and PMAA-1 and PMAA-8 were used for all other experiments except those pertaining to the influence of template molecular weight.

2.2. Viscometric Measurements. Molecular weights of the formed PVIm were obtained by determining $[\eta]_{TC}^{pH\,1}$ of the dissolved template complex (TC) in water at pH 1 and 25 °C. From $[\eta]_{TC}^{pH\,1}$ of the dissociated complex and provided that $[\eta]_{PMAA}^{pH\,1}$ of PMAA at pH 1 and its weight fraction are known, $[\eta]_{PMAA}^{pH\,1}$ of PVIm could be calculated by using the additivity relationship: $[\eta]_{TC}^{pH\,1} = w_{PMAA}[\eta]_{PMAA}^{pH\,1} + w_{PVIm}[\eta]_{PVIm}^{pH\,1}$, with w denoting the weight fraction of the polymer constituents in the complex. The validity of this relation was checked by employing synthetic complexes. In addition, straight Huggins and Kreamer viscosity plots were obtained in all cases, supporting the absence of interactions between PVIm and PMAA at pH 1. Compositions of the complexes were determined by elemental analysis and ^{1}H NMR and corrected for the water content (<5%) of the complexes.

To convert the obtained [η] values to viscosity-average molecular weights, a calibration curve was constructed by measuring [η]'s of ready-made PVIm samples of known $\bar{M}_v$ in both water at pH 1 and 20 °C and in ethanol at 25 °C for which K is 2.45 × 10^{-4} and a is 0.69[13] (Figure 1). Ubbelohde type viscosimeters were used, and the inaccuracy in [η] was ±3%.

Other (absolute) methods, like osmometry, light scattering, ultracentrifugation, and GPC (SEC), are not suitable because of practical and theoretical problems associated with this complicated mixture (polyelectrolytes, extreme pH conditions required for the dissolution of the template complex).

2.3. Separation of the Polycomplex. Though [η] of formed PVIm's could be obtained indirectly according to the above procedure, several approaches were tried for the separation of the synthetic complex consisting of PVIm and PMAA (1:1). In all cases the complex concentration was 2 g/L, which was well below the estimated critical overlap concentration of both synthetic PVIm and template-formed PVIm.

Separation by column chromatography using Al_2O_3 (Activities I and II, 70–230 mesh) as column material and water of pH 12 as solvent and eluent appeared to be unsuccessful despite a large difference in R_f values (PVIm, 0.7; PMAA, 0.05). Similarly, aqueous SEC with water of pH 1 led to adsorption of PVIm onto the column material.

Addition of MeOH to a solution of the complex at pH 1 (HNO_3) caused the precipitation of PVIm–HNO_3, and pure PVIm–HNO_3 could be isolated in a yield of 30%. Addition of DMF to a similar solution caused the precipitation of PMAA, and pure PVIm–HNO_3 in a yield of 60% was obtained from the supernatant solution. PMAA also precipitated at 61 °C upon heating the solution due to the attainment of the lower critical solution temperature.[21] In this way pure PVIm–HNO_3 was obtained again in a 60% yield. However, application of these techniques to dissolved template complexes led to incomplete separation of PVIm contaminated with up to 10% PMAA.

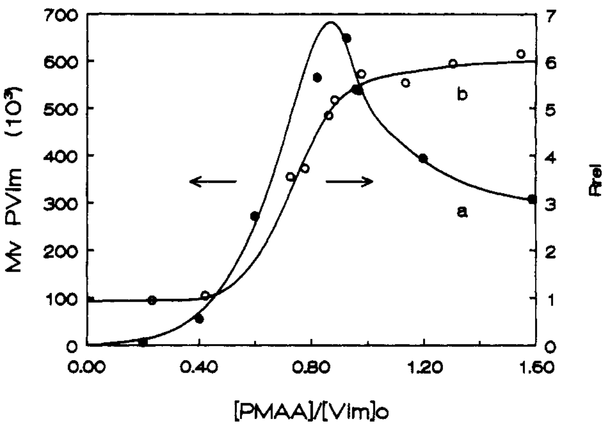


Figure 2. Influence of $[PMAA]/[VIm]_0$ on $\bar{M}_{v,PVIm}$ (curve a, ●) and relative rate (curve b, ○). $[VIm]_0 = 0.41$ M, $[AAP]_0 = 0.047$ M; $\bar{M}_{v,PMAA} = 89 \times 10^3$.

3. Results and Discussion

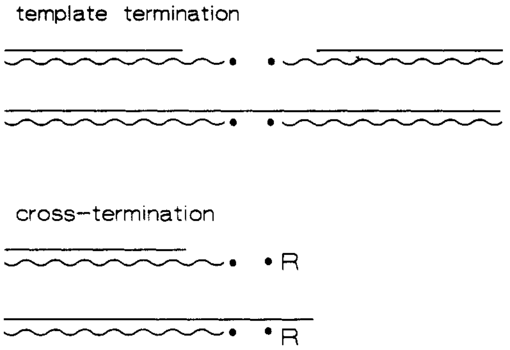
3.1. Influence of Template Concentration. Various attempts were made to separate the two polymer components from their complex (see the Experimental Section). Though in control experiments results looked promising, in handling the template complexes incomplete separation was accompanied by low yields presumably because the presence of very high molecular weight PVIm led to entanglements. In order to avoid the measurement of nonrepresentative samples, it was decided to determine molecular weights of the formed PVIm polymers in an indirect way. The complex, which results after a template polymerization, can be easily dissolved in water at pH 1.[16] Straight Huggins and Kraemer viscosity plots as well as the validity of the additivity relationship of [η]'s proved that interactions do not exist between PMAA and the formed PVIm under these conditions. Calculation of the molecular weights of the formed PVIm from these [η] values is described in detail in the Experimental Section.

It should be mentioned that molecular weights pertain to polymers produced after ca. 90% conversion, whereas rates of polymerization were determined for initial conditions up to 50%. It is assumed that the $\bar{M}_v$ dependence on $[PMAA]/[VIm]_0$ remains qualitatively the same at lower conversions.

In Figure 2, molecular weights of PVIm's together with relative rates of polymerization (R_{rel}), defined[10] as the ratio of $R_p([PMAA]/[VIm]_0)$ to $R_p([PMAA]/[VIm]_0{=}0.2)$, are displayed as a function of $[PMAA]/[VIm]_0$. The molecular weight increases parallel to the rate of polymerization. However, beyond $[PMAA]/[VIm]_0 \simeq 0.85$ the molecular weights decrease in contrast to the nearly constant rate enhancement. All molecular weights are considerably higher than that of the blank polymer ($\bar{M}_v$ = 13.4 × 10^3),[9] and even up to 8-fold the template molecular weight ($\bar{M}_v$ = 89 × 10^3). The latter may be explained by the ability of growing radicals to "hop" to another template chain[3] on reaching the end of the template chain. The provision that template coils should be close to each other for hopping to be possible has been discussed.[9] In this case, a critical chain length of a "hopping" radical is not required for complexation with a neighboring template chain[9] since the already associated radical will lose little entropy on complexation with a next template chain.

The rate profile has been discussed previously.[9–10] Briefly, three regions were identified, viz. region A with

Chart I
Schematic Representation of Termination Reactions of Template-Associated Radicals^a



^{a} (—) denotes template, (∼∼∼) an associated radical, and R• either a primary or an oligomeric radical.

R_{rel} = 1, region B with increasing R_{rel}, and region C with a nearly constant R_{rel}. The AB transition was explained by propagation alongside the template of radicals achieving the critical chain length necessary for complexation with the template. Propagation of template-associated radicals with adsorbed monomer molecules led to rate enhancements mainly due to retardation of the termination step, suppression of degradative addition, and reduction of electrostatic repulsions between a charged radical and a protonated monomer.[9] The BC transition was attributed to complexation of the maximum amount of radicals.

Since the same factors that lead to rate enhancements will influence the $\bar{M}_v$ in a similar way, the increase of $\bar{M}_v$ in region B is obviously caused by growth of radicals alongside the template. Therefore, the decrease of $\bar{M}_v$ beyond $[PMAA]/[VIm]_0 \simeq 0.85$ is puzzling, as well as the fact that it starts at a point where R_p has not attained its maximum value yet.

To rationalize this, we propose that, besides the above-mentioned template effects, the $\bar{M}_v$ profile is also influenced by a shifting balance in termination modes. Template-associated radicals may terminate either by cross-termination or by template termination (Chart I). In both cases no distinction will be made between termination at the template chain or in the surrounding solution. If one assumes termination by combination to be dominant,[11] especially in the case of termination on the template,[14] template termination would increase molecular weights of the formed PVIm's greatly in addition to retardation of termination.[19]

In region B (Figure 2), rate enhancements run parallel with the percentage of template-associated radicals. Beyond the AB transition the number of template-associated radicals will increase relatively more than the number of template chains, leading to a higher number of complexed radicals per template chain. Although this number is smaller than 1, as was inferred from preliminary ESR measurements, radicals are able to grow along more than one template chain by the hopping mechanism, and, therefore, termination of two template-associated radicals is more likely to occur than cross-termination. Eventually, when nearly the maximum amount of radicals has become associated with the template chains, a further increase of the template concentration will raise the number of template chains more than the number of template-associated radicals. This decrease in the average number of template-associated radicals per template chain reduces the probability of an encounter between two complexed radicals. Consequently, cross-termination between a complexed radical and a short noncomplexed radical is more likely to take place. Molecular weights may remain high due to a longer growth period of the template-associated radicals. However, they will be less enhanced compared to the situation whereby template termination dominates.

It is not possible to estimate the relative proportions of template termination and cross-termination from the obtained molecular weights in Figure 2 since there is no direct relationship between molecular weight and percentage of template termination. If the probability of template termination is reduced, radicals are able to grow for a longer period of time, thus decreasing the difference between molecular weights obtained via template termination or cross-termination. Additional complications are created by variation of [PMAA] in Figure 2, which leads to changing concentrations of small radicals in the vicinity of the template. This affects the ratio of template-associated radicals to short radicals in solution, which is essential to the mode of termination as has been discussed. Consequently, the difference by a factor of 2 in the molecular weights of PVIm obtained at a $[PMAA]/[VIm]_0$ of 0.85 and 1.55 (630×10^3 and 325×10^3, respectively) will be regarded as accidental and is not related to 100% template termination and 100% cross-termination, respectively.

According to a kinetic analysis of Smid et al.,[15] template termination leads to a 0.5 order in [initiator] whereas cross-termination leads to a zero-order dependence. Thus, the explanation of the $\bar{M}_v$ profile may be verified by the orders in [initiator] for $[PMAA]/[VIm]_0 = 1$ and 1.55, which were 0.36 ± 0.02 and 0.4 ± 0.02, respectively.[10] At a $[PMAA]/[VIm]_0$ of 1, the order in [initiator] corresponds to a dominating template termination. On the other hand, the order of 0.4 ± 0.02 at a $[PMAA]/[VIm]_0$ of 1.55 does not conform to kinetics with mainly cross-termination, but it does if we take account of radical occlusion as has been proposed in a previous paper.[10] The possibility of primary termination will be discussed in the final section of this paper.

A final remark concerns the influence of the shifting balance in termination modes upon R_p. If the probability of template termination is reduced by the increase of template chains, longer growth periods of the template-associated radicals result, which increase their number and thus R_p. However, termination by cross-termination leads to the removal of radicals from solution and reduces the number of radicals available for association with the template. Apparently, both effects nearly compensate each other since R_p hardly changes between $[PMAA]/[VIm]_0 = 1$ and 1.55 (see Figure 2).

3.2. Influence of Template Molecular Weight. It has been established that the template molecular weight does not affect the profile of R_{rel} versus $[PMAA]/[VIm]_0$.[10] Therefore, the same should apply to the profile of $\bar{M}_v$ versus $[PMAA]/[VIm]_0$ as is illustrated by Figures 2 and 3 for two molecular weights.

Following a similar analysis as applied to R_p,[10] a linear plot was obtained for ln $\bar{M}_{v,PVIm}$ versus ln $\bar{M}_{v,PMAA}$ at $[PMAA]/[VIm]_0 = 1$ (Figure 4), which supports the relation between molecular weights and R_p. The molecular weight of the formed PVIm is determined by the ability of the template to retard termination as long as possible by propagation of radicals alongside the template. This is related to the average length of a template chain and the number of hops by a radical. Obviously, if longer template chains are used, the growth period of the radical alongside each template will increase.

In order to discuss the hopping phenomenon, we define a hop number, H_n, as the average number of templates along which the radical grows. This may be estimated by

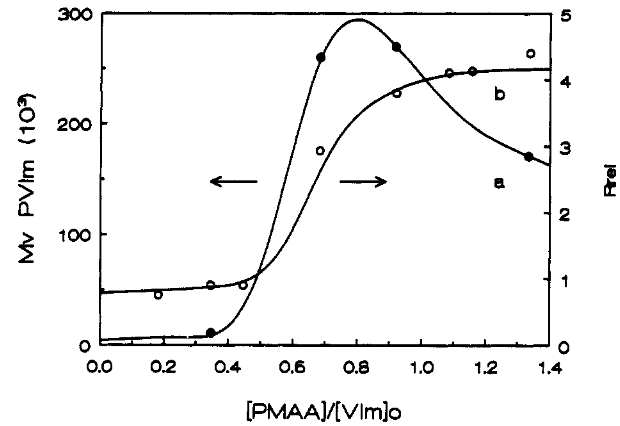


Figure 3. Influence of [PMAA]/[VIm]$_0$ on the molecular weight of the formed PVIm (curve a, ●) and relative rate (curve b, ○), $\bar{M}_{v,PMAA}$ = 30 × 10^3, [VIm]$_0$ = 0.41 M, and [AAP]$_0$ = 0.047 M.

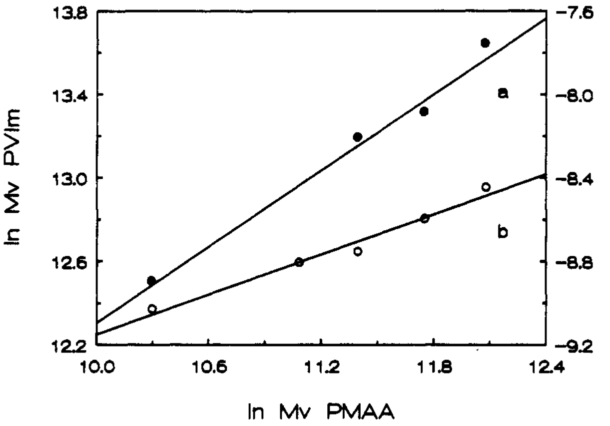


Figure 4. Influence of the template molecular weight on $\bar{M}_{v,PVIm}$ (curve a, ●) and R_p (curve b, ○). [PMAA]/[VIm]$_0$ = 1, [VIm]$_0$ = 0.41 M, and [AAP]$_0$ = 0.047 M.

Table I
Influence of Template Molecular Weight[a]

$\bar{M}_{v,PMAA}$ (× 10^3)	$\bar{M}_{v,PVIm}$ (× 10^3)	R_{rel}[b]	H_n[c]
30	270	4.0 + 0.2	10.3
89	510	5.3 ± 0.3	6.3
128	610	6.2 ± 0.3	5.1
177	800	7.2 ± 0.3	4.9

[a] [PMAA]/[VIm]$_0$ = 1, [VIm]$_0$ = 0.41 M, and [AAP]$_0$ = 0.047 M. [b] Relative rate, R_{rel} is the ratio of R_p([PMAA]/[VIm]$_0$ = 1) to R_p([PMAA]/[VIm]$_0$ = 0.2).[10] [c] Hop number, H_n, was calculated by using $\bar{P}_{n,VIm} = (H_n + 1)(1/2)(\bar{P}_{n,PMAA})$ and by taking account of 50% template termination and 50% cross-termination.[20]

assuming that only termination by combination takes place[12,14] and $\bar{P}_v = 2\bar{P}_n$. Random radical complexation and subsequent growth alongside the template should be considered so that on the average only half the length of the template chain will be used by the radical, i.e.

$$\bar{P}_{n,PVIm} = (H_n + 1)(1/2)(\bar{P}_{n,PMAA})$$

In addition, template termination involves only about half the number of hops per template-associated radical as compared to cross-termination. Hop numbers are therefore calculated assuming 50% template termination and 50% cross-termination.[20] In Table I it can be seen that H_n decreases by a factor of 2 upon increasing the template molecular weight by a factor of 6 from 30 × 10^3 to 177 × 10^3. This suggests that either radicals are able to propagate alongside template macromolecules for a longer period of time, thereby increasing the molecular weights of the resulting polymers, or cross-termination is favored, leading to an apparent reduction of the calculated H_n values.

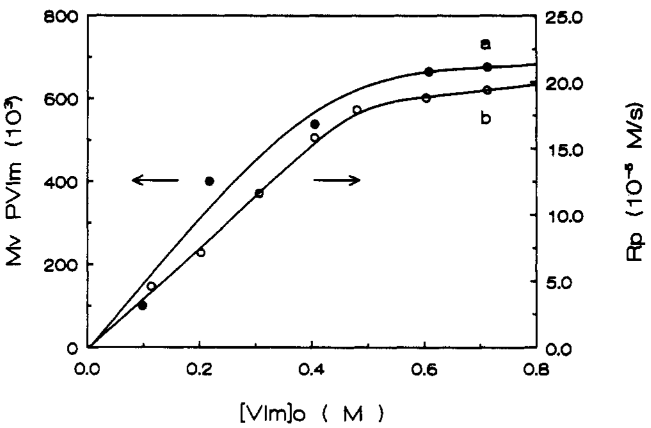


Figure 5. Influence of [VIm]$_0$ on $\bar{M}_{v,PVIm}$ (curve a, ●) and rate of polymerization, R_p (curve b, ○). [AAP]$_0$ = 0.047 M and $\bar{M}_{v,PMAA}$ = 89 × 10^3. [PMMA]/[VIm]$_0$ = 1.

The extent to which $\bar{M}_{v,PVIM}$ is affected by the template molecular weight is reflected by the slope of the linear plot in Figure 4, which is 0.59. This is higher than the 0.31 obtained for ln R_p versus ln $\bar{M}_{v,PMAA}$,[10] signifying that $\bar{M}_{v,PVIm}$ is more sensitive to variation of template molecular weight than R_p. If steady-state conditions are assumed, changes in k_p and k_t should affect the $\bar{P}_n$ of the instantaneously formed polymer to the same extent as R_p.[1] This was found by Koetsier et al.[2] in the polymerization of *N*-vinylpyrrolidone along syndiotactic PMAA. In our case, molecular weights were not determined of the instantaneously formed polymer, and, moreover, the possibility of radical hopping may affect molecular weights of the formed PVIm more than R_p. An alternative explanation may be provided by the possibility that termination in solution does not take place exclusively by combination as is assumed for termination on the template. Then, increasing the template molecular weight reduces the number of hops, which may increase the number of terminations occurring at the template and thus the percentage of termination by combination.

One would expect the number of template-associated radicals per template chain to increase when the template molecular weight is increased, resulting in more template termination. However, this also leads to a reduction of H_n, which decreases the termination probability of the radicals. Since template-associated radicals are most susceptible to termination while in solution,[10] this would lead to a further retardation of the termination step. Therefore, no definite statement can be made with respect to the difference in the dependence of $\bar{M}_v$ and R_p on template molecular weight.

3.3. Influence of Monomer Concentration. The molecular weight of the formed PVIm as a function of [VIm]$_0$ at constant [PMAA]/[VIm]$_0$ = 1 is displayed in Figure 5 together with R_p.

The similarity between the two profiles is obvious. Molecular weights increase up to [VIm]$_0$ = 0.45 M, due not only to suppression of degradative addition[10] but also to the presence of more template chains, which facilitates the hopping process of template-associated radicals. The nearly constant values of $\bar{M}_{v,PVIm}$ at [VIm]$_0$ > 0.45 M support the presence of degradative addition, as has already been concluded from the rate profile.[10]

3.4. Influence of Initiator Concentration. In Figure 6, molecular weight profiles are given for three initiator concentrations. Two things may be noted. First, a reduction of [AAP]$_0$ leads to higher molecular weights, which is in accordance with the higher rate enhancements

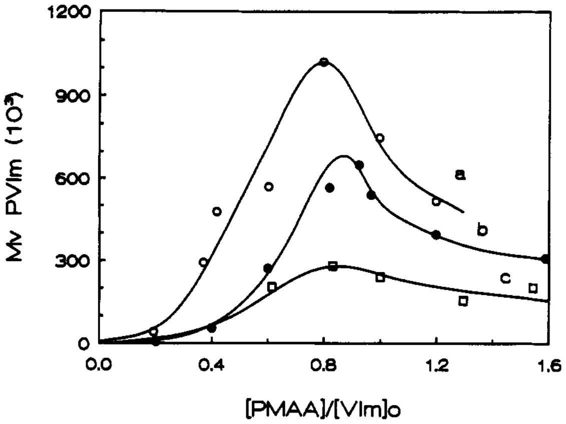


Figure 6. $\bar{M}_{v,PVIm}$ versus $[PMAA]/[VIm]_0$ for three initiator concentrations: $[AAP]_0 = 0.024$ M (curve a, ○), 0.047 M (curve b, ●), and 0.072 M (curve c, □). $[VIm]_0 = 0.41$ M.

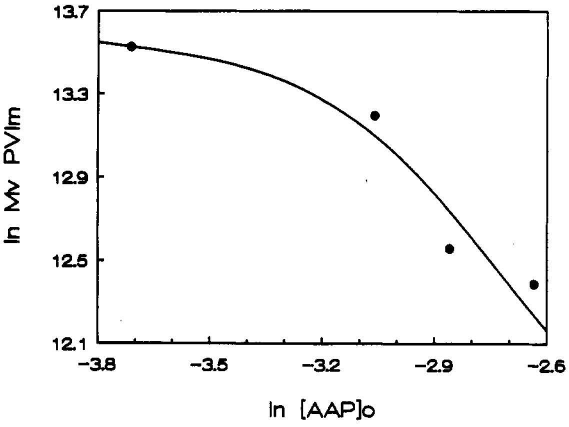


Figure 7. $\ln \bar{M}_{v,PVIm}$ versus $\ln [AAP]_0$ for $[PMAA]/[VIm]_0 = 1$ and $[VIm]_0 = 0.41$ M.

obtained.[9,10] If $[AAP]_0$ is decreased, the probability of termination is reduced and molecular weights of the formed PVIm will increase. Second, the shape of the profiles are rather similar. Therefore, molecular weight profiles may be explained in terms of template termination and cross-termination independent of $[AAP]_0$.

Since AAP is a salt, it is able to interact with the template. This will influence the amount of preferentially adsorbed monomer, the [AAP] in solution, and also termination reactions for $[PMAA]/[VIm]_0 = 1$, since radical dissociation of AAP close to the template could promote cross-termination reactions. The salt effect was observed for the template polymerization at $[VIm]_0 = 0.1$ M, where variation of $[AAP]_0$ led to deviating orders in monomer and initiator concentration.[10] For the higher $[VIm]_0$ of 0.41 M, it is seen that molecular weights become more dependent on $[AAP]_0$ with increasing $[AAP]_0$ (Figure 7). In this case, the effect may be enhanced by different ratios of template termination versus cross-termination as can be deduced from Figure 6.

In order to verify whether the presence of AAP near the template chain would affect termination reactions, rates of polymerization as well as molecular weights of polymers formed by polymerizations in the presence of additional NH_4Cl were measured. The salt ions shield charged sites at the template chain and reduce the local [AAP]. A low initiator concentration was taken since in this case the highest percentage of AAP will be present near the template chain. NH_4Cl was chosen to compensate for AAP because it contains nitrogen like AAP. Although it is not a completely indifferent salt, its interaction with PMAA in water is quite similar to that with NaCl,[17] which was corroborated by preliminary kinetic experiments with NaCl.

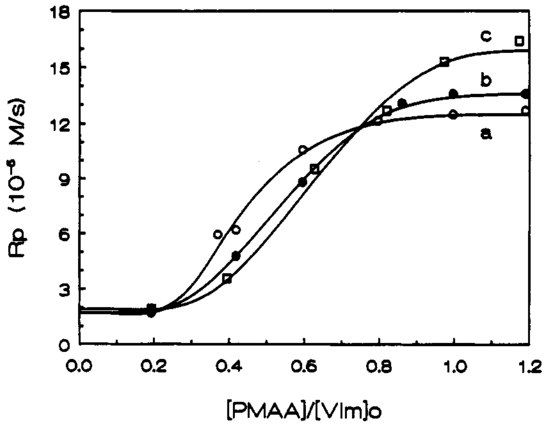


Figure 8. Dependence of R_p on $[PMAA]/[VIm]_0$ at $[AAP]_0 = 0.024$ M for three different salt concentrations: $[NH_4Cl] = 0$ M (curve a, ○), 0.05 M (curve b, ●), and 0.10 M (curve c, □).

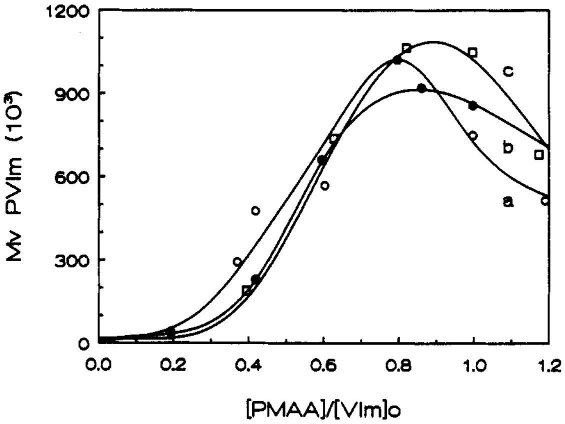


Figure 9. Dependence of $\bar{M}_{v,PVIm}$ on $[PMMA]/[VIm]_0$ at $[AAP]_0 = 0.024$ M for three different salt concentrations: $[NH_4Cl] = 0$ M (curve a, ○), 0.05 M (curve b, ●), and 0.10 M (curve c, □).

Table II
Influences of $[NH_4Cl]$

$[NH_4Cl]$,[a] M	$\bar{M}_{v,PVIm}$ (× 10^3)	R_{rel}
0	750	7
0.05	860	7.6
0.10	1050	8.5
$[MIm] = 0$[b]	510	5.3
$[MIm]_0 = 0.05$ M[b]	500	3.4

[a] $[AAP]_0 = 0.0235$ M, $[PMAA]/[VIm]_0 = 1.0$, and $[VIm]_0 = 0.41$ M. [b] $[AAP]_0 = 0.047$ M, $[PMAA]/[VIm]_0 = 1.0$, and $[VIm]_0 = 0.41$ M.

The rate and corresponding $\bar{M}_v$ profiles for different salt concentrations are shown in Figures 8 and 9. These profiles resemble those obtained for different $[AAP]_0$,[10] indicating the salt-like nature of AAP. The addition of salt will be discussed for three $[PMAA]/[VIm]_0$, i.e. 0.2, 0.4, and 1 at constant $[VIm]_0 = 0.41$ M. At a $[PMAA]/[VIm]_0$ of 0.2, polymerization takes place in solution and R_p is not affected by the addition of salt (Figure 8). At a $[PMAA]/[VIm]_0$ of 0.4, addition of salt leads to shielding of charged sites of both the template and, more important, PVIm radicals, which impairs complexation, as is demonstrated by the reduction of R_p and $\bar{M}_v$. Conversely, at the higher $[PMAA]/[VIm]_0$ of 1, increasing $[NH_4Cl]$ results in higher relative rates (up to 8.5) and molecular weights (Table II). Moreover, a similar shift of the BC transition to higher $[PMAA]/[VIm]_0$ on increasing $[NH_4Cl]$ is observed as for variation of $[AAP]_0$,[10] indicating that complexation of radicals is also affected. The higher molecular weights and rates of polymerization R_p indicate a reduced tendency of template-associated radicals for termination (Table II). This decrease in termination probability can be explained assuming a reduced presence of AAP^{2+} cations near the template due to replacement by salt ions. This affects cross-termination reactions taking place near the template. One may therefore conclude that in the absence of salt, termination reactions are shifted toward more primary termination caused by the presence of AAP near the template chain.

If this enhanced presence of AAP near the template is combined with other factors that determine the probability of termination of a template-associated radical, i.e., H_n, the radical concentration in solution as well as on the template, and termination constants of the termination reactions of template-associated radicals, it is difficult to assess the impact of an enhanced local [AAP] since all factors are interrelated.

In connection with the above, one may expect that shielding of template sites by ions could hinder the propagation of template-associated radicals with adsorbed monomers. Such was found by Blumstein et al.[18] in the polymerization of *p*-styrenesulfonic acid along ionenes in aqueous solution, a polymerization involving mainly propagation along the template with adsorbed monomers. In the present system, obstruction of propagation along the template could be deduced from the addition of 1-methylimidazole (MIm) at standard conditions using $[AAP]_0 = 0.047$ M (Table II). This led to a reduction of R_p by 30%, while the molecular weight appeared not to be influenced (Table II). The small reduction of R_p indicates that the dynamic adsorption/desorption processes at the template chain[9] are able to remove the nonpolymerizable obstacle in a fast way. Therefore, it is not likely that shielding of template sites by counterions will affect the propagation process greatly. The similar values for the molecular weights show that termination reactions are not affected by the addition of MIm.

4. Conclusions

We have demonstrated that molecular weights of the polymers formed can provide additional information about the template polymerization mechanism. Termination reactions of template-associated radicals could be deduced from a comparison of molecular weights of the formed polymers with rate enhancements as a function of $[PMAA]/[VIm]_0$ and appeared to be a combination of template termination, cross-termination, primary termination, and radical occlusion.

The molecular weights of the polymers formed by template polymerization were much higher than polymers produced in the absence of the template and higher than the template molecular weights. This could be satisfactorily explained by retardation of termination for template-associated radicals and by hopping of a radical to a neighboring template after reaching the end of a template macromolecule. Higher template molecular weights increased the $\bar{M}_v$ of the daughter polymer even more.

The local enrichment of AAP near the template seemed to promote cross-termination, which could be reduced by adding NH_4Cl, leading to even larger rate enhancements.

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Registry No. PMMA, 25087-26-7; VIm, 1072-63-5; PVIm, 25232-42-2.