

TEMPLATE POLYMERIZATION

G. Challa and Y.Y. Tan

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

Abstract - Template polymerizations (TP) are divided into two types. In type I we are concerned with initiation and propagation of monomer preadsorbed by or complexed to template macromolecules. In type II active oligomers created in "free" solution complex with template macromolecules and continue to propagate along the template by adding monomer "picked up" from the surrounding solution. The discussion is confined chiefly to two systems, viz. the radical TP of methylmethacrylate (MMA) along isotactic poly-MMA and that of N-vinylpyrrolidone along syndiotactic poly(methacrylic acid). Experimental evidence and arguments are given to support the view that these systems belong to TP's of type II.

INTRODUCTION

The term template polymerization (TP), also called replica or matrix polymerization, will be applied to those systems in which polymer chains propagate along macromolecular templates for at least the greater part of their growth. Such propagation may affect not only the reaction rate but also the average molar mass and the microstructure of the formed polymer as compared to the situation in absence of a template, i.e. the blank polymerization. In most cases the presence of a template leads to rate enhancement. This phenomenon has been referred to as "chain effect" by Ballard and Bamford (1) who pioneered in this field. Many template systems have since been investigated in various laboratories over the world. A non-exhaustive list is given in Tables 1A and B.

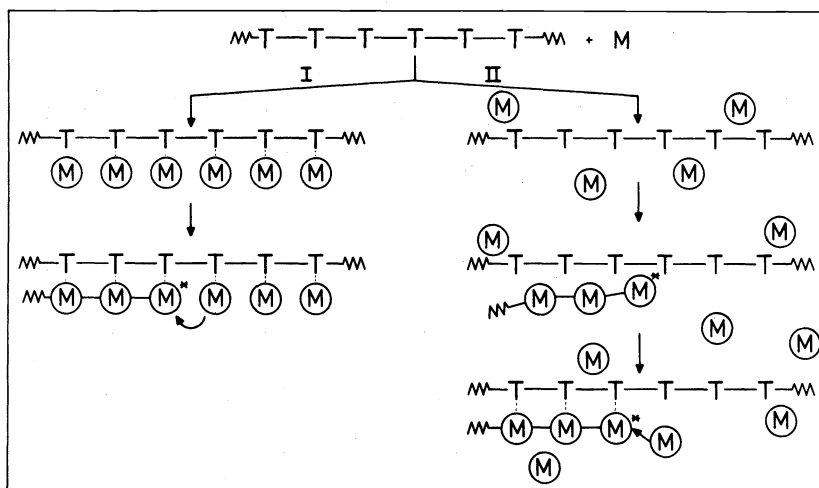


Fig. 1. Schematic presentation of template polymerization mechanisms.

The majority of TP systems can be classified into two main types, one being characterized by polymerization of template-associated monomer (type I), the other by propagation of template-associated polymer chains that are initiated in "free" solution (type II). The mechanisms are presented schematically in Fig. 1.

TABLE 1A. Template polymerizations of type I

Monomer	Template	Solvent	Initia-Temp. tor*) (°C)	Ref.
Phenylalanine-NCA	Poly(sarcosine)-dimethylamide	nitrobenzene	- 25	1-4
Phenylalanine-NCA	Poly(2-vinylpyridine)	nitrobenzene	spont. 35	5
4-Vinylpyridine	Various polyacids	H ₂ O	spont. 20;25	6-10
4-Vinylpyridine	Poly(4-vinyl-oxy-carboxylphthalic acid)	acetone, DMF	BPO 70	11
4- and 2-Vinylpyridine	Poly(maleic anhydride)	acetone, DMF	spont. 50	12
2-Vinylpyridine	Poly(methacrylic acid)	H ₂ O	spont. 64	13
N-vinyloxazolidone	Poly(methacrylic acid)	H ₂ O	K ₂ S ₂ O ₈ 60	14
Acrylic acid	Poly(ethylene imine)	acetone/H ₂ O	AIBN/hν 25	15
Acrylic acid	Poly(ethylene imine)	H ₂ O	K ₂ S ₂ O ₈ 31	16
(Meth)acrylic acid	Ionenes	H ₂ O	K ₂ S ₂ O ₈ 50	17
p-Styrene sulfonic acid	Ionenes	isopropanol/H ₂ O	AIBN 60-70	18,19
Propargylchloride	Poly(4-vinylpyridine)	methanol	spont. 50	10,20
Methacrylic acid	Poly(N-vinyl-5-methyloxazolidone)	H ₂ O	K ₂ S ₂ O ₈ 60	21
N-β-methacryloyl-oxyethyl of adenine (MAO-A)	Poly(MAO-T= thymine)	pyridine	AIBN 20-70	22
Acrylic acid	Poly(N-vinylpyrrolidone)	H ₂ O	K ₂ S ₂ O ₈ 74	23

*) AIBN = azobisisobutyronitrile, BPO = benzoylperoxide; spont. = spontaneous initiation.

An important consequence of mechanism II is that growing template-associated polymer chains add monomer from the surrounding solution, whereas growing chains in mechanism I add neighbouring template-associated monomer molecules. Both types have in common that they end up with a polymer complexed to the template. The separation from the template often poses a problem, which hampers accurate characterization of the polymer formed.

It is seen from Table 1A that the TP systems of Bamford, Kabanov, Blumstein and others, which are based on strong ionic interactions, conform to mechanism I. This group can be called TP's of the first type. TP systems of Ferguson, Shavit, Kargin, our group and others, involving weaker interaction forces, conform to mechanism II; these belong to TP's of the second type and are listed in Table 1B.

It should be stressed, however, that the distinction between the two types is not always sharp, and borderline cases may exist. The chain effect, currently more often called template or matrix effect, can also be caused by a polymer template formed in situ. This effect has been demonstrated by Chapiro to occur during polymerization of acrylic acid in certain solvents (34) and bulk polymerization of acrylonitrile (35). These systems presumably belong to type I.

TABLE 1B. Template polymerizations of type II

Monomer	Template	Solvent	Initiator*)	Temp. (°C)	Ref.
Acrylic acid	Poly(N-vinyl-pyrrolidone)	H ₂ O	K ₂ S ₂ O ₈	74	24
(Meth)acrylic acid	Polyethylene-glycol	(methanol)/H ₂ O	K ₂ S ₂ O ₈	31;50	16,25
Methacrylic acid	Poly-(L-lysine)	H ₂ O	AIBN	80	26
Methacrylic acid	Poly(N-vinyl-pyrrolidone)	H ₂ O	K ₂ S ₂ O ₈	65	27
Methacrylic acid	it-PMMA	DMF	TBCP	-10-25	28
N-vinyl-pyrrolidone	st-PMAA	DMF	AIBN	50-70	29
Methyl-methacrylate	it-,st-PMMA	DMF	TBCP	-10-100	30-33

*) AIBN = azobisisobutyronitrile; TBCP = t. butyl-cyclohexylperoxydicarbonate. it = isotactic; st = syndiotactic.

To be absolutely certain that one is dealing with a TP of type I, the monomer can be attached to a template by covalent bonds (Ref. 36 & 37), or one can complex stoichiometrically the monomer to the template by electrostatic forces prior to polymerization (Ref. 18). Sometimes it is possible to observe the interaction of monomer with the template but isolation of the complex is prevented by the ensuing spontaneous polymerization (Ref. 5-10, 12, 13 & 20). The formation of monomer-template complexes can be established by spectroscopic means (Ref. 2 & 20) but if weak interaction forces play a role it may be necessary to resort to other methods to establish unequivocally the existence or non-existence of preferential adsorption of monomer by the template.

In addition to such evidence, one can often deduce the type of mechanism from kinetic studies of the polymerization. To this end one examines the reaction rate as a function of two parameters, one being the (base) molar ratio of template to monomer concentration, $[T]/[M]_0$ (or $[M]_0/[T]$), the other being the ratio of template concentration to its critical concentration for homogeneous segmental distribution, $[T]/C^*$. On approaching C^* template macromolecules start to overlap each other.

Consider a polymerization system where the blank rate V_B is not zero and the template propagation rate V_T is higher than V_B , i.e. the relative rate $V_R = V_T/V_B$ is greater than unity. Let $[T]$ be varied at constant $[M]_0$ in a series of experiments. If the polymerization conforms to mechanism I the rate will increase with increasing $[T]$ until a maximum rate is reached at $[T]/[M]_0 = 1$. At this ratio all monomer is adsorbed by or associated with the template, provided this happens in a 1:1 fashion. At higher ratios the "filling" degree of template molecules is reduced, the absorbed monomer sequences become shorter and hence the rate will drop. This is illustrated in Fig. 2, curve I. If mechanism II is involved, the rate will also increase with increasing $[T]$ due to the growing contribution of template propagation. This increase stops only at a stage when the whole reaction volume is homogeneously occupied by template coils, i.e. at $[T] = C^*$. Above C^* only template propagation takes place, hence the rate will remain constant: $V_T = V_{max}$ (see Fig. 2, curve II).

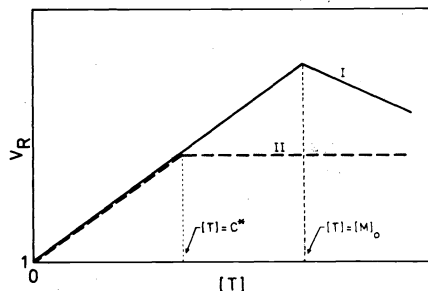


Fig. 2. Schematic diagram of relative rate V_R against template concentration $[T]$ for TP's of type I (curve I) and type II (curve II) at constant initial monomer concentration $[M]_0$ with $[M]_0 > C^*$ (C^* is critical concentration for overlap of template macromolecules).

If $[T]$ is kept constant instead and $[M]_0$ is varied we shall obtain diagrams as shown in Fig. 3. Again in case of mechanism I there will be a change of rate at $[M]_0/[T] = 1$ because of simultaneous blank polymerization of excess monomer, whereas in case of mechanism II the rate will rise up to much higher $[M]_0$.

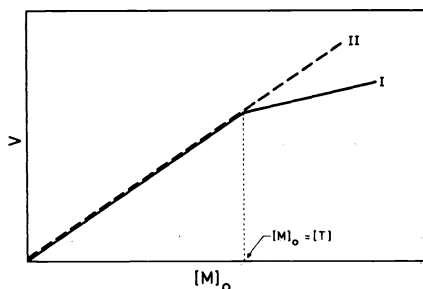


Fig. 3. Schematic diagram of polymerization rate V against initial monomer concentration $[M]_0$ for TP's of type I (curve I) and type II (curve II) at constant template concentration $[T]$.

In this review we shall limit the discussion chiefly to two of our investigated systems, viz. the radical polymerization of methylmethacrylate (MMA) in dimethylformamide (DMF) in the presence of it-PMMA templates and that of N-vinylpyrrolidone (NVP) in DMF in the presence of st-poly(methacrylic acid) (st-PMAA) templates. As we shall presently demonstrate these systems can be classified as TP's of type II.

ABSENCE OF MONOMER ADSORPTION

Determination of preferential adsorption by or solvation of polymers in mixed solvents can be done by a variety of methods (Ref. 38), one of which is interferometry combined with equilibrium dialysis (Ref. 39). This method is based on measurements of refractive index increments of solutions of polymer in a solvent mixture c.q. monomer solvent mixture. By applying thermodynamics (Ref. 38 & 40) we obtain for the so-called preferential adsorption coefficient λ the simplified expression:

$$\lambda = \frac{1}{1 - \bar{v}_M c_M} \cdot \frac{(dn/dc_p)_\mu - (dn/dc_p)_m}{(dn/dc_M)}$$

The refractive index increments $(dn/dc_p)_\mu$, $(dn/dc_p)_m$, and (dn/dc_M) are related to polymer solutions at constant chemical potential of monomer, to solutions at constant molality of monomer, and to monomer solvent mixtures,

respectively; \bar{v}_M is the partial specific volume of monomer at the monomer concentration c_M . The quantity $(dn/dc_p)_\mu$ is obtained after dialysis equilibrium against an excess of the monomer solution.

It appeared that (dn/dc_M) for MMA-DMF and NVP-DMF mixtures are positive and constant over the whole composition range. For it-PMMA solutions in MMA/DMF, it is seen from Fig. 4 that $(dn/dc_p)_\mu = (dn/dc_p)_m$. Hence $\lambda = 0$, which means that preferential adsorption of MMA (and DMF) by it-PMMA is completely absent. In this respect an nmr study on the temperature dependence of chemical shifts of CH_2 -protons of MMA in DMF- d_7 in the absence or presence of PMMA ($-d_8$) by Schneider and Spěváček (41) is of interest. Their experiments showed that interaction between MMA and DMF was somewhat affected by the presence of PMMA, irrespective of its tacticity. One interpretation was that this might be caused by a somewhat stronger interaction of MMA with PMMA than with DMF. Obviously, such effect does not necessarily lead to a noticeable preferential adsorption of MMA by PMMA.

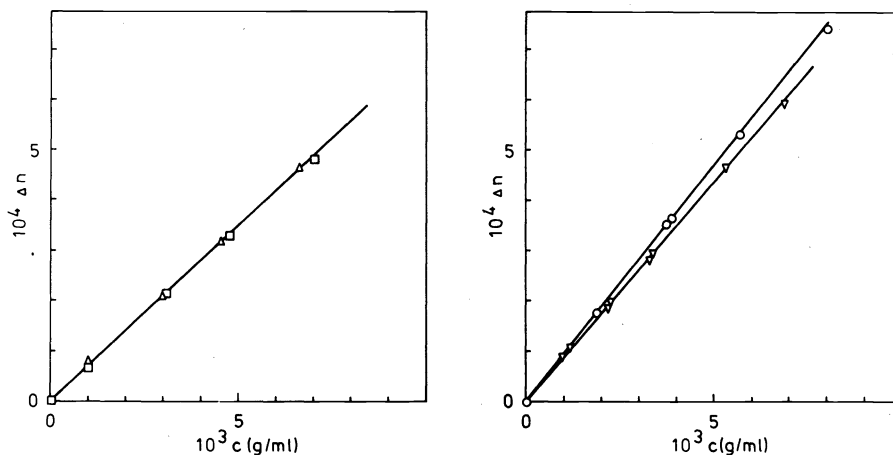


Fig. 4. (left). Refractive index difference Δn between it-PMMA solutions and the "solvent" mixture MMA/DMF (20.6/79.4 by weight) against it-PMMA concentration c at constant molality (\square) and at constant chemical potential (Δ) of MMA. Temperature: 20°C. PMMA: $\bar{M}_v = 1.3 \times 10^5$, $\bar{M}_n = 0.4 \times 10^5$, $(mm) = 0.92$.

Fig. 5. (right). Refractive index difference Δn between st-PMAA solutions and the "solvent" mixture NVP/DMF (8/92 by volume) against st-PMAA concentration c at constant molality (\circ) and at constant chemical potential (∇) of NVP. Temperature: 20°C. PMAA: $\bar{M}_v = 1.6 \times 10^5$, $(rr) = 0.95$.

Fig. 5 shows that for solutions of st-PMAA in NVP/DMF $(dn/dc_p)_\mu < (dn/dc_p)_m$. This leads to $\lambda < 0$ meaning that the solvent DMF rather than the monomer NVP is preferentially adsorbed by PMAA.

According to these results one should expect these TP systems to behave like TP's of type II.

TEMPLATE POLYMERIZATIONS BY COMPLEXATION OF GROWING CHAINS

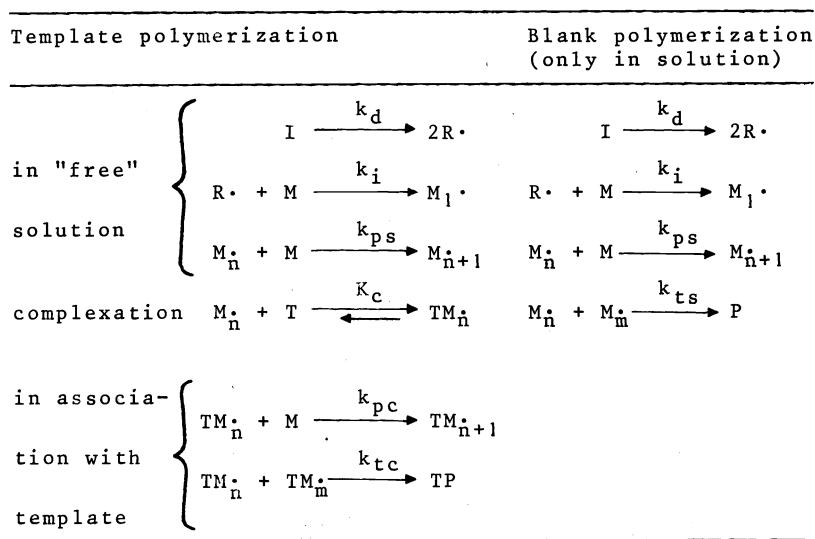
Complex formation between two polymers is the starting-point for selecting such TP-systems. Because of this dependency, complexation and TP are both governed by the same factors such as solvent, temperature, and chain length, chemical structure, and microstructure of the polymer components.

The TP systems MMA/it-PMMA is based on stereocomplex formation between it- and st-PMMA (Ref. 42 & 43). Although the interacting forces are of a Van der Waals nature, complexation is feasible due to cooperative action coupled with stereocomplementarity.

The TP systems NVP/st-PMAA is derived from the 1:1 complexation between polyvinylpyrrolidone (PVP) and st-PMAA (Ref. 44). The two components are held together by hydrogen bonds between the carbonyl groups of the pyrrolidone rings and the carboxyl groups of the MAA-units (Ref. 23, 44 & 45).

In aqueous solutions hydrophobic interactions may play an additional role (Ref. 44 & 45). The stronger interaction in this system leads to an insoluble complex between NVP-monomer and PMAA in water, but the adsorbed monomer is rapidly hydrolyzed into acetaldehyde and pyrrolidone (Ref. 29). In DMF, however, NVP adsorption by PMAA is largely obstructed by preferential adsorption of the solvent, as mentioned before. Only PVP can associate with PMAA by cooperative interaction.

In general these TP's require a minimum or critical chain length of either of the polymer components due to the cooperative nature of their interaction. This critical chain length is decisive for a template effect (Ref. 27). If the chain length of the growing polymer radical remains too short, no TP can occur. Neither can a TP be expected if the chain length of the chosen template macromolecule is too short. Generally, if interactions are favourable the critical chain lengths are in the oligomer region and the proper conditions can therefore be achieved easily (Ref. 46). Based on mechanism II the following reaction schemes are applicable:



The stationary polymer radical concentration for blank polymerization is $[M\cdot]_B = (v_i/2k_{ts})^{1/2}$ and those for TP are $[M\cdot]_C = (v_i/2k_{tc})^{1/2}$ in complexed state and $[M\cdot]_S = [M\cdot]_C/K_c[T]$ in "free" solution; v_i is the rate of initiation. For the blank polymerization we can write the well known equation:

$$V_B = k_{ps} \cdot (2k_{ts})^{-1/2} [M] v_i^{1/2} \quad (1)$$

The TP rate is expressed by:

$$V_T = \frac{k_{ps}}{(2k_{tc})^{1/2}} \cdot \frac{1}{K_c} \cdot \frac{[M]}{[T]} \cdot v_i^{1/2} + \frac{k_{pc}}{(2k_{tc})^{1/2}} [M] v_i^{1/2} \quad (2)$$

This first term on the right hand side of (2) consists of the contributions of initial "free" propagation before complexation and "free" propagation after complex dissociation. If the complexation "constant" K_c is very large, this term can be neglected and hence Eqn. (2) becomes:

$$V_T = k_{pc} \cdot (2k_{tc})^{-1/2} \cdot [M] v_i^{1/2} \quad (3)$$

The instantaneous degree of polymerization $\bar{P}_{n,T}$ of polymer formed during TP is given by:

$$\bar{P}_{n,T} = k_{pc} \cdot (2k_{tc})^{-1/2} \cdot [M] v_i^{-1/2} \quad (4)$$

In fact an extra term on the right hand side should be added to take account of the critical chain length for complexation of "free" propagating chains, but for true TP application of this term can usually be omitted. In the following paragraphs we shall discuss various aspects of TP's, namely

stereoregulation, kinetics, effect of molar mass, and effect of template concentration.

STEREOREGULATION

Stereoregulation has been observed in TP's of MMA along stereoregular PMMA. This is ascribed to the tendency of it- and st-PMMA to form stereocomplexes (Ref. 43) having the composition of 1 it/2 st (Ref. 47). The extent of association is strongly dependent on the solvent (Ref. 48). In DMF, for example, the strong interaction between it- and st-PMMA is manifested by a substantial drop of the reduced viscosity η_{sp}/c , especially at the composition 1 it/2 st (Fig. 6a).

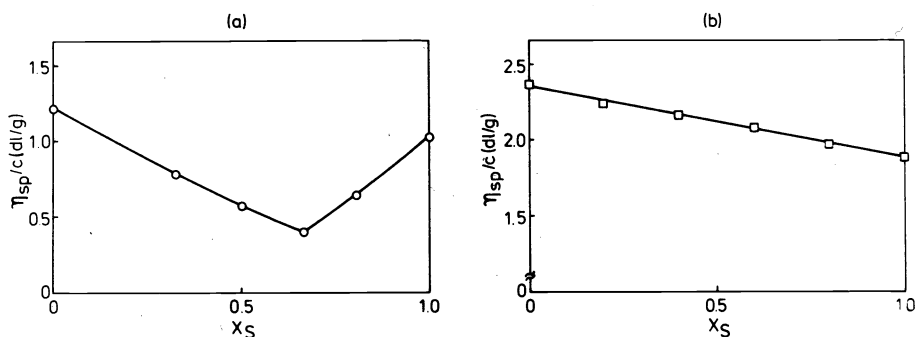


Fig. 6. Reduced viscosity η_{sp}/c against weight (mol) fraction X_s of st-PMMA for it/st-PMMA mixtures in (a) DMF, (b) CHCl_3 as solvent. Temperature: 20°C . Total polymer concentration: 0.2 g/dl. Polymers: it-PMMA of $\bar{M}_v = 5 \times 10^5$, $(mm) = 0.95$ and st-PMMA of $\bar{M}_v = 5 \times 10^5$, $(rr) = 0.90$.

On the contrary, in a solvent like chloroform, η_{sp}/c is additive over the whole composition range (Fig. 6b), indicating the complete absence of any association. In accord with this observation no template effect could be detected in chloroform.

If MMA is polymerized in the presence of it-PMMA in e.g. DMF, acetonitrile, or acetone, stereoassociation promotes syndiotactic growth of PMMA radicals along it-PMMA chains (Ref. 31). Prior to association, however, the initial oligomeric PMMA radicals consist of 65% racemic (syndiotactic) triads at 25°C . The critical chain length has been estimated at less than 50 monomer units. In order to obtain highly syndiotactic PMMA, "template" propagation, i.e. growth along the template, should proceed for a long enough period. This implies adjustment of monomer $[M]$ and initiator $[I]$ concentrations, together with the use of highly isotactic PMMA templates of reasonably high molar masses.

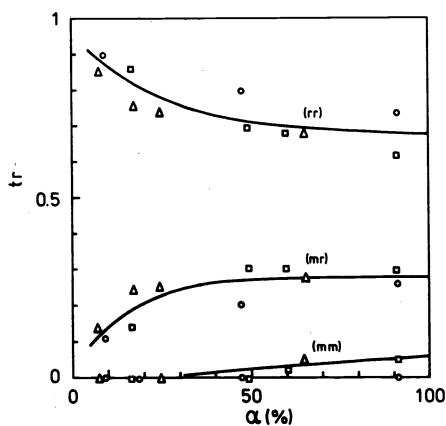


Fig. 7. Triad content tr (tacticity) of PMMA's formed in the presence of it-PMMA templates ($\bar{M}_v = 7.6 \times 10^3$, $(mm) = 0.90$) and complexed in the insoluble fractions against MMA conversion α in (o) DMF, (Δ) acetone, and (\square) acetonitrile. $[M]_0 = [\text{MMA}]_0 = 2.06 \text{ M}$, $[T] = [\text{it-PMMA}] = 0.34 \text{ base-M}$, $[I]_0 = [\text{t-butylcyclohexylperoxydicarbonate}]_0 = 0.01 \text{ M}$. Polymerization temperature: 25°C .

The syndiotacticity of formed PMMA decreases with increasing conversion of the excess monomer as shown in Fig. 7. This may be due to the influence of the formed st-PMMA, which occupies the it-PMMA templates and in turn acts as a template promoting the formation of meso(isotactic) sequences. Indeed, stereoblock polymers could be isolated (Ref. 31 & 49). Moreover, separate experiments confirmed the template effect caused by st-PMMA although it was smaller than that exerted by it-templates (Ref. 31).

From the temperature dependence of the tacticity of formed PMMA's it has been concluded that the stereoregulation is chiefly determined by the difference in activation entropy for meso and racemic addition, $\Delta S_{r/m}^\ddagger - \Delta S_{m/r}^\ddagger$ (Ref. 31). If it-templates were used this difference was negative, meaning that the complexed growing chain end is forced in such a configuration by the template that the monomer addition takes place in a syndiospecific manner.

KINETICS

The influence of solvent, temperature and template microstructure on the relative rate V_R of TP's of MMA in the presence of PMMA, is clearly demonstrated in Fig. 8 (Ref. 32).

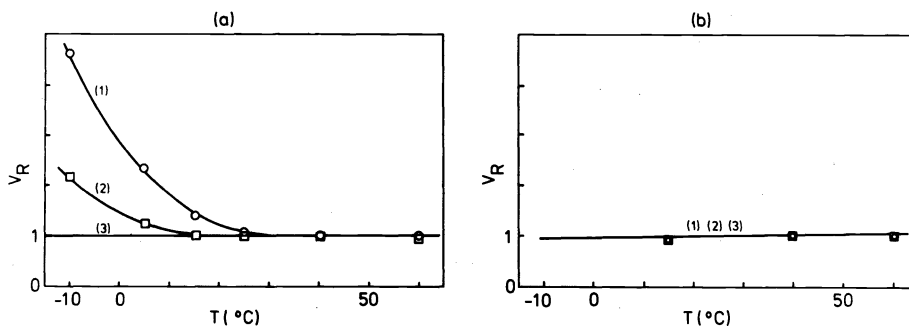


Fig. 8. Relative initial rate V_R against polymerization temperature T for polymerizations of MMA in the presence of (1) it-PMMA, (2) st-PMMA, (3) at-PMMA in the solvent (a) DMF, (b) CHCl_3 . Blank polymerizations $V_R = 1$. Polymers: it-PMMA with $\bar{M}_v = 6 \times 10^5$, $(mm) = 0.95$ and st-PMMA with $\bar{M}_v = 3.4 \times 10^5$, $(rr) = 0.89$. For concentrations, see under Fig. 7.

In agreement with results concerning stereoregulation, the template effect appears to be optimal in the presence of it-PMMA of high molar mass in a strongly complex-promoting solvent (DMF) at low temperatures.

Normal viscosity effects do not affect the kinetics since in chloroform all types of PMMA led to $V_R = 1$, i.e. the same rates as the blank, although the viscosity of the reaction mixtures increased strongly. This is equally true with respect to polymerization in DMF in the presence of non-complexing atactic PMMA.

Raising the temperature increases the rate of TP but decreases V_R due to less complete stereoassociation of growing PMMA chains with it-PMMA template. This follows also from the temperature dependence of η_{sp}/c of the 1 it/2 st-stereocomplex in DMF as illustrated in Fig. 9, where the relative reduced viscosity $(\eta_{sp}/c)_R$ is defined as the ratio of experimental and additive η_{sp}/c . By elevating the temperature compact stereocomplexes transform into loose network-like structures that result in enhanced η_{sp}/c . Enhancement of η_{sp}/c has also been found in toluene, a solvent that promotes stereocomplexation only weakly (Ref. 48).

TP of MMA in the presence of it-PMMA in DMF has been investigated in detail at 5°C by the rotating-sector method (Ref. 32). The results are collected in Table 2. It appeared that the radical lifetime τ_s increased 8-fold as compared to a corresponding blank polymerization. In combination with stationary state experiments k_p and k_t can be calculated. From Table 2 it is seen that k_p and k_t are both reduced by the template, but because k_t is much more reduced (about 80 times) than k_p (about 5 times), the polymerization rate is enhanced as compared to the blank rate ($V_R \approx 2$).

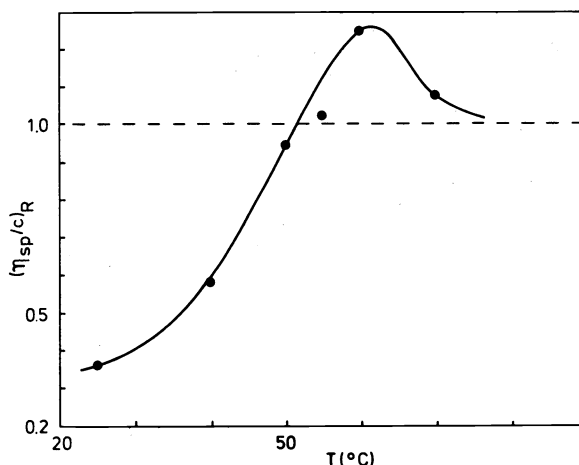


Fig. 9. Relative reduced viscosity $(\eta_{sp}/c)_R$ with respect to additive value against temperature T for 1:it/2:st-PMMA stereocomplex in DMF. Total polymer concentration: 0.2 g/dl. Polymers: it-PMMA of $\bar{M}_v = 5.5 \times 10^5$, $(mm) = 0.94$ and st-PMMA of $\bar{M}_v = 5 \times 10^5$, $(rr) = 0.89$.

TABLE 2. Some kinetic results of blank and template polymerizations in DMF at 5°C*).

Quantity	Template polymerization	Blank polymerization
V ($M \cdot s^{-1}$)	4.03×10^{-6}	2.02×10^{-6}
τ_s (s)	64	8.3
k_p ($M^{-1} \cdot s^{-1}$)	5.8	26.3
k_t ($M^{-1} \cdot s^{-1}$)	1.7×10^4	1.4×10^6

*) Template: it-PMMA of $\bar{M}_v = 5 \times 10^5$, $(mm) = 0.95$; $[MMA] = 2.16 M$; $[MMA]/[it-PMMA] = 6$.

Under these reaction conditions it is permissible to divide Eqn. (3) by Eqn. (1) to obtain:

$$V_R = V_T/V_B = (k_{pc}/k_{ps}) \cdot (k_{tc}/k_{ts})^{-\frac{1}{2}} \quad (5)$$

Furthermore, a study of the temperature dependence revealed that the overall activation energy ΔE^\ddagger and overall activation entropy ΔS^\ddagger were both decreased by it-PMMA (Ref. 32). This is illustrated by the Eyring plot in Fig. 10 according to:

$$\ln(k/T) = -\Delta H^\ddagger/RT + \{\Delta S^\ddagger/R + \ln(k_B/h)\}$$

where $k \equiv k_p k_d^{1/2}/k_t^{1/2}$, ΔH^\ddagger is the overall activation enthalpy, k_B is the Boltzmann constant, and h is the Planck constant. The decrease in ΔE^\ddagger is ascribed mainly to increase of the activation energy for the termination step ΔE_t^\ddagger and the decrease in ΔS^\ddagger to decrease of the activation entropy of the propagation step ΔS_p^\ddagger .

By combining these results, one comes to the conclusion that the kinetics of this TP system are primarily governed by hindered segmental mobility of associated chain radicals delaying their termination, and that the stereoregulation is determined by stereoselection during the somewhat retarded propagation.

Such a conclusion may be generally valid for TP's of type II. But when NVP was polymerized in the presence of st-PMAA at various temperatures, activation parameters were obtained that were approximately identical with those of the blank polymerization, despite $V_R \approx 2$ and a higher molar mass of the formed PVP as compared to the blank polymer (Ref. 29). This unexpected

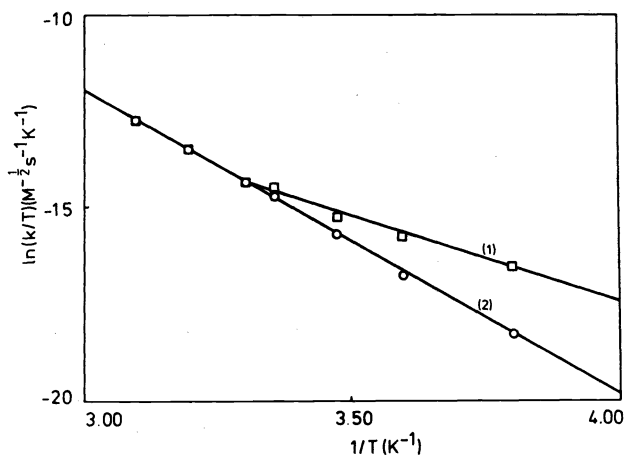


Fig. 10. Eyring plot for the overall rate constant k of (\square) template and (\circ) blank polymerization in DMF. Template: it-PMMA of $\bar{M}_v = 15 \times 10^5$, $(rr) = 0.92$. For concentrations, see under Fig. 7.

result can be explained by assuming that desolvation of PMAA templates plays a role during "template" propagation of PVP radicals. Expected decreases in ΔE^\ddagger and ΔS^\ddagger may be compensated by the enthalpy and entropy of desolvation, ΔH_{desolv} , and ΔS_{desolv} , respectively. To be more precise, the anticipated drop in ΔS^\ddagger may be fully compensated by ΔS_{desolv} , which has a positive value signifying an entropy driven process.

Desolvation is reasonable in view of the preferential solvation of PMAA by DMF as mentioned before. Moreover, it has been established recently that volume expansion occurs on complex formation between PVP and PMAA in DMF (Ref. 50). The drop in $(\eta_{\text{sp}}/c)_R$ on raising the temperature up to about 80°C (Fig. 11), which is due to the formation of more compact complexes, additionally supports the view that the driving force for complexation is increase of entropy by desolvation (Ref. 50).

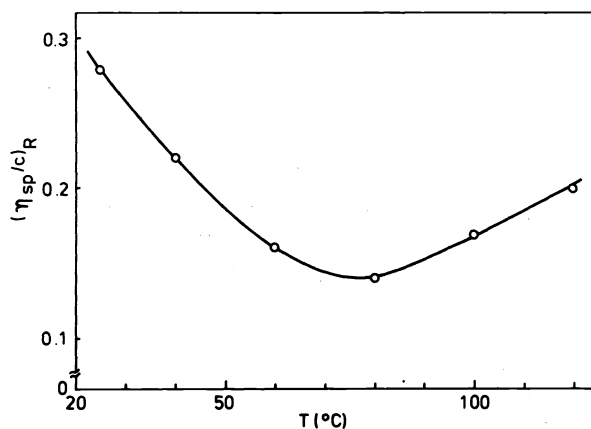


Fig. 11: Relative reduced viscosity $(\eta_{\text{sp}}/c)_R$ with respect to additive value against temperature T for 1:1 complex of poly-(N-vinylpyrrolidone) and st-PMAA. Total polymer concentration: 0.25 g/dl . Polymers: PVP of $\bar{M}_v = 6.4 \times 10^5$ and st-PMAA of $\bar{M}_v = 1.9 \times 10^5$, $(rr) = 0.92$.

MOLAR MASS EFFECTS

The effect of molar mass of the template, $\bar{M}_{v,t}$, on the molar mass of polymer formed, $\bar{M}_{v,f}$, has been examined for template systems containing moderate concentrations of the template. In order to obtain $\bar{M}_{v,f}$ of PMMA produced

during TP of MMA in the presence of it-PMMA, \bar{M}_v of the total polymer including the template, was measured in the "nonassociating" solvent chloroform. As the $\bar{M}_{v,t}$ and weight of it-PMMA were known, $\bar{M}_{v,f}$ of the formed PMMA could be calculated by means of the additivity rule (Réf. 31).

Fig. 12 shows that the chain length of the formed PMMA is related to that of the it-PMMA template (Ref. 31 & 32).

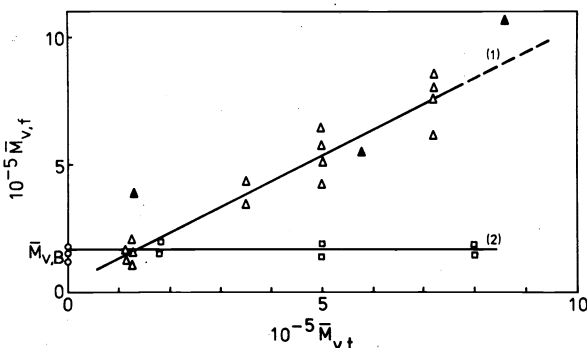


Fig. 12. \bar{M}_v of total polymer formed $\bar{M}_{v,f}$ against \bar{M}_v of templates $\bar{M}_{v,t}$ for polymerizations of MMA in DMF in the presence of (Δ) it-PMMA's and (\square) at-PMMA's. (\circ) Blank polymer with $\bar{M}_{v,B} \approx 1.5 \times 10^5$. For reaction conditions, see under Fig. 7. (\blacktriangle) Polymers from polymerizations at $[\text{it-PMMA}] \approx 0.5 \text{ C}^*$ and -5°C ($\bar{M}_{v,B} = 10.6 \times 10^5$). at = atactic.

Even in cases where $\bar{M}_{v,B}$ of the blank polymer was higher than $\bar{M}_{v,t}$, the $\bar{M}_{v,f}$ tended to follow $\bar{M}_{v,t}$. This tendency can be explained by assuming that termination of chain ends can take place only after their leaving the covered template chains. In other words, growing chain ends leaving template macromolecules are more susceptible to termination or possibly also to transfer, than chain ends within coils of blank polymerization systems. Presumably as a consequence of the formation of compact and rather stiff stereocomplexes protruding radical chain ends are less screened. $\bar{M}_{v,f}$ can be decreased also by taking high initiator concentrations or by adding a chain transfer agent such as carbontetrabromide in increasing quantities (Ref. 31). Because of their small size, initiator as well as CBr_4 molecules are able to penetrate into the template coils and to terminate growing chains. This leads to the formation of less syndiotactic PMMA (Ref. 31), diminishing the amount of stereocomplex. The template efficiency is reduced accordingly.

The correlation between $\bar{M}_{v,f}$ and $\bar{M}_{v,t}$ has been found also with the TP of NVP in the presence of st-PMAA. The effect is less conspicuous, probably because of chain transfer to monomer which cannot be suppressed by template growth (Ref. 29).

Of course, in case of less complete association of growing oligomer radicals with the template, the overall polymerization rate is composed of contributions of pure template and "free", non-template (identical to blank) polymerization. To study this, one could polymerize either at higher temperatures or in a weakly complex-promoting solvent. A third way is to lower the template concentration below C^* .

THE EFFECT OF TEMPLATE CONCENTRATION

The critical concentration C^* can be estimated from viscometric measurements either by employing the empirical equation $\text{C}^*[\eta] = 1$ (Ref. 51) or by detecting the break point in the course of absolute viscosity with polymer concentration (Fig. 13). By lowering $[\text{T}]$ below C^* we arrive at situations where separate template coils are surrounded by "free" solution. If $[\text{T}]$ is increased from 0 to C^* the volume occupied by template coils increases gradually and so does the contribution of TP. As discussed earlier, at $[\text{T}] > \text{C}^*$ the whole reaction system is homogeneously filled with template macromolecules and "free" (blank) polymerization no longer contributes.

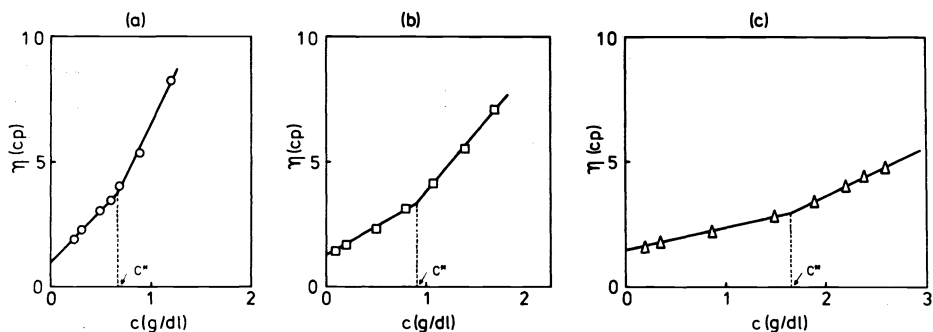


Fig. 13. Viscosity η against it-PMMA template concentration $[T]$ in a MMA/DMF (1:4 wt/wt) mixture at -5°C for it-PMMA's of various \bar{M}_v 's: (a) 9.6×10^5 , (b) 5.8×10^5 , (c) 1.3×10^5 .

If ϕ is the volume fraction occupied by templates, i.e. $\phi = [T]/C^*$, we can write for the overall rate (Ref. 29):

$$V = \phi V_T + (1 - \phi)V_B \quad (6)$$

$$\text{or } V_R = V/V_B = \phi V_{R,\max} + (1 - \phi) \quad (6a)$$

with $V_{R,\max} = V_{\max}/V_B$ i.e. V_T/V_B at $[T] \geq C^*$

This relation is found to be valid for the TP of NVP along st-PMAA (Fig. 14a) (Ref. 29). It is obvious that the average molar mass of the formed PVP will also increase gradually from the value of the blank polymer at $[T] = 0$ to a

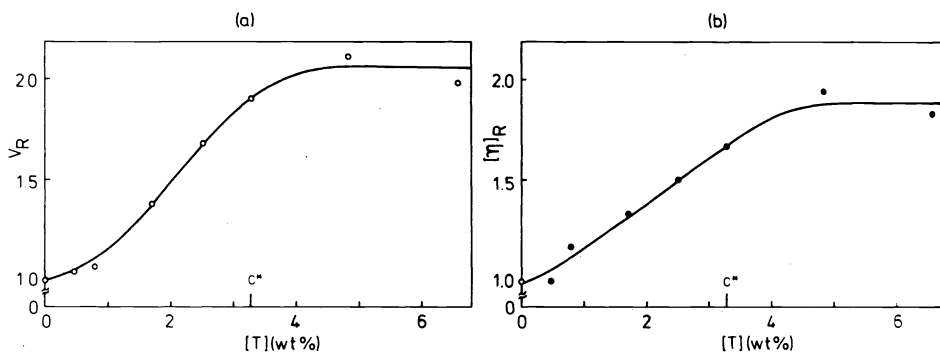


Fig. 14. (a) Relative polymerization rate V_R against st-PMAA template concentration $[T]$ for TP of NVP in DMF at 60°C ; (b) Relative intrinsic viscosity $[\eta]_R$ with respect to blank value against template concentration $[T]$. $[\text{NVP}]_0 = 0.75 \text{ M}$, $[\text{AIBN}]_0 = 0.01 \text{ M}$.

maximum value for pure TP at $[T] > C^*$. In Fig. 14b the relative intrinsic viscosity $[\eta]_R$, defined as the ratio of $[\eta]_f$ of the PVP formed in the presence of template and $[\eta]_B$ of the blank PVP, is given instead of molar mass because the constants for the Mark-Houwink relation in the solvent dimethylsulfoxide (DMSO) are unknown. DMSO had to be used in order to obtain $[\eta]_f$ by means of the additivity rule as no complexation occurs in this solvent. At $[T] > C^*$ we have $[\eta]_{R,\max} = [\eta]_{\max}/[\eta]_B$ where $[\eta]_{\max}$ is $[\eta]$ of the polymer formed by pure TP. Although the chain lengths of PVP were always longer after template than after blank polymerization, they were still shorter than those of the PMAA templates (Ref. 29). This is probably caused by chain transfer to monomer inside template coils.

If chains can grow to a size longer than that of template macromolecules one would expect termination to be more postponed near $[T] = C^*$ because of the possibility for the growing chains to "jump" from the end of one template to

another yet unoccupied template, thus avoiding the relatively fast termination of a free protruding radical chain end. Such a "jumping" mechanism (Ref. 31 & 32) leads to an additional enhancement of V_R on passing C^* as illustrated in Fig. 15, found for the TP of MMA along it-PMMA (Ref. 32).

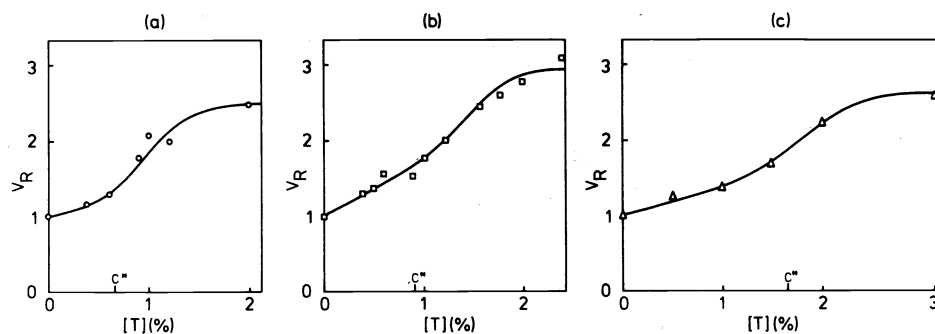


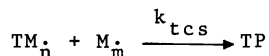
Fig. 15. Relative polymerization rate V_R against it-PMMA-template concentration $[T]$ for TP of MMA in the presence of the it-PMMA's from Fig. 13, in DMF at -5°C . For $[M]_0$ and $[I]_0$ see under Fig. 7.

A corresponding rise of $(\bar{M}_{v,f})_R = \bar{M}_{v,f}/\bar{M}_{v,B}$ found around C^* is in full agreement with this conception. The described transitory changes in V_R and $(\bar{M}_{v,f})_R$ or $[\eta]_R$ as a function of $[T]$ at constant $[M]_0$ do not occur at $[T] = [M]_0$ but rather at $[T] = C^*$. Therefore the behaviour of these two systems is a strong support of mechanism II as accepted before from the absence of monomer adsorption. Another indication in favour of mechanism II shows up when TP's were performed with $[T] < [M]_0$ and followed to high conversions. One may expect that after the template becomes fully covered with polymer formed by "template" propagation, the excess monomer can also polymerize in the "free" solution and the rate will drop to that of the blank polymerization. This has been found for both TP systems (Ref. 29 & 32). A new critical point, i.e. a critical conversion, is exhibited at $([M]_0 - [M]) \approx 2[T]$ for the MMA/it-PMMA system and at $([M]_0 - [M]) \approx [T]$ for the NVP/st-PMAA system.

CONCLUDING REMARKS

Equations (3) and (6) can be used for TP's of type II provided there is a strong interaction between propagating chains and template macromolecules. If this is not the case we have to take into account the formation of "free" chain ends M_s^* on dissociation of the complex. The complexation "constant" K_C is not a real constant because it increases as the chains grow in length due to the cooperative effect. For our present purpose it suffices to assign to K_C an average value which is related to the average chain length of the polymer formed.

Since for TP $[M]_c = K_C[M]_s[T]$, a fraction $K_C[T]/(1 + K_C[T])$ of the chain ends is growing by "template" propagation and a fraction $1/(1 + K_C[T])$ by "free" (blank) propagation inside template coils. This is in fact an alternative way of interpreting Eqn. (2). Equation (2) is restricted to polymerizations without "free" termination, i.e. it does not contain k_{ts} . Moreover, we have neglected the mixed termination reaction:



If we include these possibilities we obtain for the overall rate under steady state conditions the general expression:

$$v = \frac{(k_{ps} + k_{pc}K_C[T])[M]v_i^{1/2}}{(2k_{ts} + 2k_{tcs}K_C[T] + 2k_{tc}K_C^2[T]^2)^{1/2}} \quad (7)$$

If K_C is (very) large, Eqn. (7) transforms into Eqn. (2) c.q. Eqn. (3), which means $v = V_T$. If K_C is practically zero, it is easily seen that even at

[T] > C*, Eqn. (7) is replaced by Eqn. (1), i.e. $V = V_p$. In other words, if the initial chains do not associate at all, then "free" propagation will continue until its termination and no template effect will be detected. An example is the already mentioned polymerization of MMA in the presence of at-PMMA. Another one is based on the system PMMA/PMAA where only it-PMMA can associate with st-PMAA in e.g. DMF (Ref. 52). From this stereospecific interaction one may expect isotactic growth of MMA along st-PMAA. No template effect was detected whatsoever (Ref. 28). The reason is that the initially formed "free" growing PMMA radicals possessing an atactic microstructure are not able to associate with the st-PMAA template.

Therefore, association of initially "free" growing oligomer radicals with template chains is a strict prerequisite for TP of the second type. It is not sufficient to establish merely complex formation of two polymers without considering the initial conditions under which a derived TP can be accomplished.

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