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A STUDY OF RADICAL POLYMERIZATION OF N-VINYLPYRROLIDONE IN THE PRESENCE OF POLY(METHACRYLIC ACID) TEMPLATES BY DSC

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Abstract—The template polymerization of N-vinylpyrrolidone (NVP) along syndiotactic poly(methacrylic acid) (st-PMAA) templates has been studied by differential scanning calorimetry (DSC) using the scanning as well as the isothermal technique. The resulting Arrhenius plot covers a temperature range between 65 and 120°C and two parts can be distinguished. Below 80°C the overall activation energy, E_a, and entropy $\Delta S^{\neq}$, are $76\,\mathrm{kJ\cdot mol^{-1}}$ and $-79\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ respectively, in excellent agreement with previous dilatometric results. These values differ slightly from those of the blank polymerization leading to rate enhancement by a factor of only two. The small difference in activation parameters is explained by the occurrence of desolvation of st-PMAA chains during propagation of the polyvinylpyrrolidone (PVP) radicals along the template. Above 80°C, the decreasing tendency to form complexes between PVP and st-PMAA results in a decreasing template effect and a gradual change of apparent E_a and $\Delta S^{\neq}$ values towards those of the blank polymerization. Similar results were obtained with atactic and isotactic PMAA templates, but smaller rate enhancements were observed due to weaker complex formation.

INTRODUCTION

The kinetics and mechanism of the radical polymerization of N-vinylpyrrolidone (NVP) along poly(methacrylic acid) (PMAA) templates of various tacticities (especially along syndiotactic (st-)PMAA) in dimethylformamide (DMF) have been studied by varying several reaction variables [1–3], including the temperature. By applying the conventional technique of dilatometry, the influence of temperature could be examined only over a limited interval of 50–70°C [2]. In order to extend the range to higher temperatures, differential scanning calorimetry (DSC) was used. This technique had been successfully applied to the blank polymerization [4] i.e. polymerization without a PMAA template. It was shown that, by combining the scanning and isothermal methods, one could cover a temperature range of 70–110°C, provided that proper evaluation of the scanning thermograms was made. This paper reports the results and evaluation of such a study of NVP polymerization in particular along st-PMAA, because it induces a larger rate enhancement than the atactic or isotactic templates [1].

EXPERIMENTAL

Materials

The syntheses, purifications and characterizations of atactic (at-) and st-PMAA samples have been described [1, 2]. Isotactic (it-)PMAA was obtained by acid hydrolysis of it-poly(methyl methacrylate) [5, 6]. Its purification was slightly modified: after dialysing the aqueous suspension of it-PMAA, the polymer was isolated by centrifugation and freeze dried. Reprecipitations from a DMF solution in diethylether and subsequently from a methanolic solution in diethylether yielded it-PMAA of good quality. Its molar mass and tacticity were deduced from the original it-poly(methyl methacrylate). Data on the template polymers are presented in Table 1. The purifications of DMF, NVP and azobisisobutyronitrile (AIBN) have been described [4].

Polymerizations

Isothermal measurements at 65–90°C and scanning DSC experiments at scan speeds of 1.25, 5 and 10°C/min were performed in a Perkin–Elmer DSC-2 apparatus under conditions already described [4]. The composition of the reaction mixtures was: $[\mathrm{NVP}] = 0.75\,\mathrm{mol/dm^3}$; $[\mathrm{PMAA}] = 0.75$ base $\mathrm{mol/dm^3}$, and $[\mathrm{AIBN}] = 0.01\,\mathrm{mol/dm^3}$. All measurements were carried out at least in triplicate.

DATA ANALYSIS AND RESULTS

Scanning experiments

As the template polymerization of NVP in the presence of PMAA is first order in monomer, the overall reaction rate constant k_{ov} at any temperature can be

Table 1. Data on PMAA templates

Code PMAA	$\overline{M}_v \times 10^{-3}$	Triad tacticity I	H	S
st-123	58	0	8	92
st-112	109	0	7	93
at	313	10	39	51
it	244	94	5	1

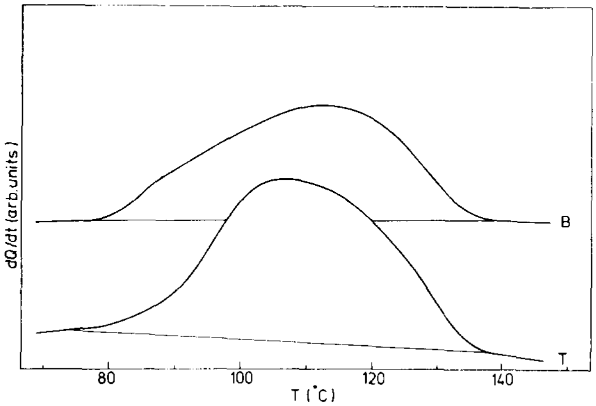

Fig. 1. Typical DSC thermograms of blank (B) and template (T) NVP polymerization along st-PMAA in DMF. [NVP] = 0.75 mol·dm^{-3}; [st-PMAA 123] = 0.75 base mol·dm^{-3}; [AIBN] = 0.01 mol·dm^{-3}; scan speed 5°C/min.

computed by the use of equation:

$$k_{ov} \equiv k_p\left(\frac{fk_d}{k_t}[\mathrm{AIBN}]_0\right)^{1/2} = (\mathrm{d}H/\mathrm{d}t)/(A - a) = f(T) \quad (1)$$

where k_p, k_t and k_d are the rate constants for propagation, termination and initiator decomposition, f is the initiator efficiency (assumed independent of temperature and presence of template), $[\mathrm{AIBN}]_0$ the initial initiator concentration, $\mathrm{d}H/\mathrm{d}t$ the rate of heat evolution, $\mathrm{d}t$ being coupled to the scan speed $\mathrm{d}T/\mathrm{d}t$, A is the area under the total DSC curve, a its partial area up to temperature T, and $f(T)$ is a function of temperature of the Arrhenius type. Typical scanning thermograms for a template and a blank polymerization are given in Fig. 1. The maximum of the curves shifts to higher temperatures with increasing scan speed due to the dependence of monomer conversion on time and temperature [4]. The maxima of the "template" curves are shifted to a lower temperature relative to the maxima of the "blank" curves indicating a higher rate of the template polymerization.

The heats of polymerization, ΔH_p, computed from the areas A decreased with increasing scan speed (Fig. 2). This effect has been ascribed to premature exhaustion of AIBN [4]. The weaker dependency of the template curve with respect to the blank curve reflects the higher rate of template polymerization. Nevertheless, the extrapolated values of polymerization heat*, $\Delta H_{p,0}$, are approximately identical, viz. 63 kJ·mol^{-1}.

Apparently the heat of complexation between the growing polyvinylpyrrolidone (PVP) chain and the PMAA template is very small. Indeed, Abe et al. [7] found a negative value of only about 1 kJ·mol^{-1} in the PVP/atactic (at-)PMAA system in DMF.

Because of the dependency on scan speed, areas A have to be corrected by a factor $\Delta H_{p,0}/\Delta H_p$ [4]. Furthermore, due to initiator consumption, instantaneous AIBN concentrations should be taken instead of $[\mathrm{AIBN}]_0$ [4]. By introduction of these corrections, Eqn (1) transforms into:

$$k'_{ov} \equiv \left(\frac{k_p^2 f k_d}{k_t}\right)^{1/2} = \frac{\mathrm{d}H/\mathrm{d}t}{\left(\frac{\Delta H_{p,0}}{\Delta H_p}A - a\right)[\mathrm{AIBN}]^{1/2}} = Z\mathrm{e}^{-E_a/RT} \quad (2)$$

where E_a is the overall activation energy and Z the pre-exponential factor. A typical Arrhenius plot is given in Fig. 3. It shows two distinct linear parts. Part I spans a conversion range of about 1–10%, part II that of 23–65%. Part I gives an overall activation energy, E_a, that is extremely high. It is related to an induction period as found previously by dilatometry [2]. Such initial retardation has no connection with a

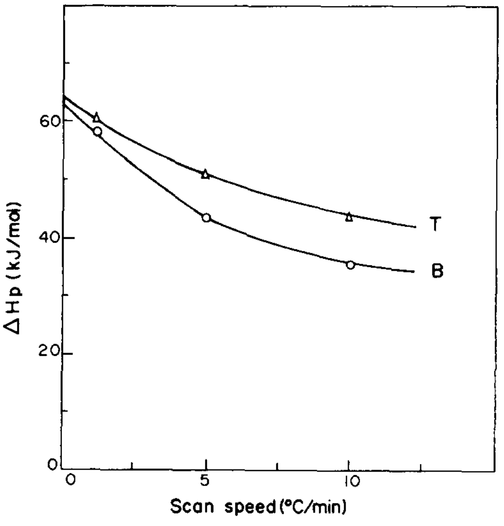

Fig. 2. Heat of polymerization of NVP in DMF for blank (B) and template (T) polymerization along st-PMAA as a function of scan speed. For concentrations see Fig. 1.

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* According to convention, heats of exothermic reactions should in fact be given as negative values, i.e. $\Delta H_{p,0} = -63$ kJ·mol^{-1}.

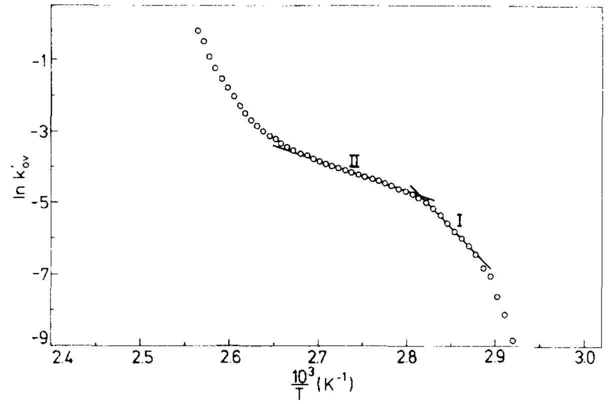

Fig. 3. Arrhenius plot derived from a DSC scanning thermogram obtained at scan speed 1.25°C/min for the NVP polymerization along st-PMAA in DMF. For concentrations see Fig. 1.

template effect but is caused by impurities in the PMAA [2]. The relevant activation parameters are derived from part II of the curves. In contrast to the NVP blank polymerization [4], activation parameters for template systems depend on the scan speed, as shown in Table 2 for polymerization in the presence of st-PMAA. Overall activation entropies are included, computed from the relation:

$$\Delta S^{\neq} = R\left(\ln Z - \ln\frac{k_B T}{h} - 1\right)$$

where k_B and h are Boltzmann's and Planck's constant, respectively.

Isothermal experiments

From the thermograms, kinetic curves (see Fig. 4) can be derived by means of the expression:

$$\ln(A/(A - a)) = k_{ov}t \qquad (3)$$

where A is the sum of the areas enclosed by the isothermal thermogram and the subsequent scanning curve for residual monomer conversion.

The overall rate constants k_{ov} at various temperatures are computed from the slopes of the linear parts. If these are divided by $[\text{AIBN}]_0^{\frac{1}{2}}$, values for k'_{ov} are obtained. Overall activation parameters are collected in Table 3.

It should be noted that at 90°C some error is introduced by temperature lag due to the rapid start of the reaction. The value of 61 kJ·mol^{-1} for E_a may therefore be too low. The value of 76 kJ·mol^{-1} over the interval 65–80°C is in excellent agreement with the value of 77 kJ·mol^{-1} found by dilatometric measurements [2].

A composite Arrhenius plot from the isothermal and scanning experiments is given in Fig. 5. For comparison, the scanning plot for the blank polymerization is included.

Table 2. Overall activation parameters for NVP template polymerization along st-PMAA-123 in DMF from scanning experiments

Scan speed (°C/min)	T interval (°C)	Conversion interval (%)	E_a (kJ·mol^{-1})	$\Delta S^{\neq}$* (J·mol^{-1}·K^{-1})
1.25	85–100	23–65	69	−101
5	100–110	22–50	76	−83
10	110–120	20–40	83	−64

* At $T = 373$ K.

Table 3. Overall activation parameters for NVP template polymerization along st-PMAA-123 from isothermal experiments

T interval (°C)	Conversion interval (%)	E_a (kJ·mol^{-1})	$\Delta S^{\neq}$* (J·mol^{-1}·K^{-1})
65–80	15–60	76	−79
80–90	15–60	61	−124

* At $T = 353$ K.

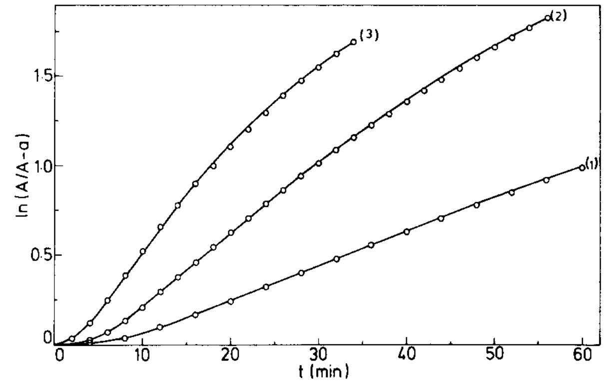

Fig. 4. Conversion vs time curves for the polymerization of NVP along st-PMAA template in DMF at (1) 70; (2) 80; (3) 90°C. For concentrations see Fig. 1.

DISCUSSION

The composite Arrhenius plot (Fig. 5) for the template polymerization along st-PMAA shows a break around 80°C. Below this temperature the plot runs approximately parallel to that for the blank polymerization. This means that the rate enhancement by the presence of the template remains about the same, viz. a factor two (the relative rate $v_R \simeq 2$), and that the difference in E_a is small, viz. approx. 7 kJ·mol^{-1}. Also $\Delta S^{\neq}$ for the template reaction differs only by 19 J·mol^{-1}·K^{-1} from that for the blank reaction. Within experimental error these results agree reasonably well with those obtained by dilatometry over the range 50–70°C [2]. These marginal differences contrast with other template systems of the same type where substantial decreases in E_a (of the order of 25–35 kJ·mol^{-1}) and $\Delta S^{\neq}$ (of the order of 90–100 J·mol^{-1}·K^{-1}) were found [8, 9], despite weaker interactions between the template chain and the growing polymer radical than in the present case. The decrease in E_a was ascribed mainly to retardation of termination, and the decrease in $\Delta S^{\neq}$ to a sterically hindered propagation. Such an interpretation would be valid in the present case, but the anticipated large decreases in E_a and $\Delta S^{\neq}$ are supposed to be partly compensated

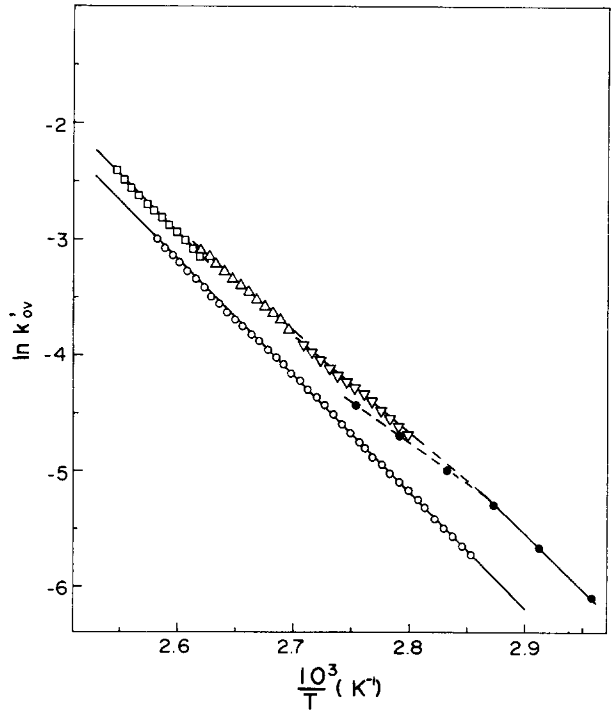

Fig. 5. Composite Arrhenius plot of the overall polymerization rate constants for blank and template NVP polymerization in DMF obtained from scanning and isothermal thermograms. Scanning exp.: blank, 1.25 and 5°C/min (○); template, 1.25 (▽), 5 (△) and 10°C/min (□). Isothermal exp.: template (●). For concentrations see Fig. 1.

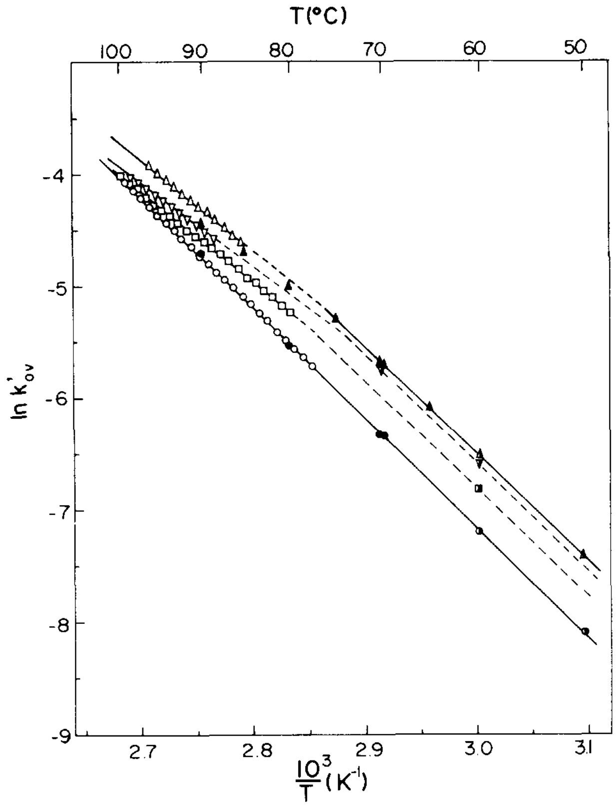

Fig. 6. Composite Arrhenius plots of the overall rate constants for blank and template NVP polymerization in DMF obtained from scanning and isothermal DSC experiments and from dilatometry. Scanning at 1.25°C/min: blank (○), template: st-PMAA (△); at-PMAA (▽); it-PMAA(□). Isothermal: blank (●); st-PMAA (▲). Dilatometry: blank (◑); template: st-PMAA (▲); at-PMAA (▼); it-PMAA (◨). For concentrations see Fig. 1.

desolvation of the PMAA macromolecules during propagation of PVP radicals along them. Indeed, the occurrence of desolvation could be substantiated by the preferential adsorption of DMF by st-PMAA in a mixture of DMF and NVP [11] and by the volume expansion on complex formation between PVP and st-PMAA [10] which is also indirectly manifest during template polymerizations in dilatometers [2, 10]. Moreover, the fact that the heats of polymerization, $\Delta H_{p,0}$, in the presence and absence of st-PMAA, were approximately identical (Fig. 2) points to a small heat of complexation. This can be explained if one assumes that the energy required for the desolvation of the st-PMAA chains compensates for the liberated energy on complexation.

Therefore, an additional term for desolvation should be added to the overall activation parameters of the template polymerization:

$$E_a = E_p + \tfrac{1}{2}E_d - \tfrac{1}{2}E_t + \Delta H_{\text{des.}}$$

$$\Delta S^{\neq} = \Delta S_p^{\neq} + \tfrac{1}{2}\Delta S_d^{\neq} - \tfrac{1}{2}\Delta S_t^{\neq} + \Delta S_{\text{des.}}$$

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

It should be noted that the contribution of polymer complex formation (via $\Delta H_{\text{compl.}}$ and $\Delta S_{\text{compl.}}$) is incorporated in the activation parameters for the propagation step.

From the positive value of $\Delta S_{\text{des.}}$ the process can be regarded as being partly entropy driven. The continuing decrease in reduced viscosity and increase in turbidity on complex formation between PVP and st-PMAA in DMF by elevating the temperature points in the same direction [10].

Above 80–85°C however, there was a reversal ascribed to a diminishing tendency to form complexes [10]. Therefore, the reason for the deflection of the Arrhenius plot for template polymerization around 80°C (Fig. 5) must not be sought in a change of polymerization mechanism but rather in a diminishing complex stability above this temperature and a consequent decreasing template effect. This means that, on average, propagation along the template takes place for shorter and shorter times until, at some temperature where no complex can be formed, template polymerization ceases and the reaction rate would become essentially identical to that of the blank polymerization. The plots above 80°C in Fig. 5 show this tendency. Therefore, only apparent activation parameters could be obtained from Arrhenius plots at each scan speed.

Some results, using the scanning technique, have also been obtained with at- and it-PMAA as templates. They are given in Fig. 6, supplemented with data from dilatometric measurements.

The course of the Arrhenius plots is generally the same as that of the st-PMAA system. It becomes less pronounced as the template is less syndiotactic, in accordance with the decreasing complexation strength between PVP and PMAA in the order of st > at > it-PMAA, provided molar masses are comparable and not too low [1]. Apart from this difference, one may therefore conclude that template polymerization of NVP occurs according to one kind of mechanism irrespective of the tacticity of the PMAA.

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