A DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF THE RADICAL POLYMERIZATION OF N-VINYLPYRROLIDONE IN DIMETHYLFORMAMIDE

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Abstract—Polymerization of N-vinylpyrrolidone (NVP) in dimethylformamide was studied by differential scanning calorimetry (DSC). The concentration of NVP was 0.75 M, that of the radical initiator (azobisisobutyronitrile) 0.01 or 0.02 M. For proper evaluation of scanning thermograms, it was necessary to correct for incomplete monomer conversion due to premature initiator exhaustion and to consider the instantaneous initiator concentration. If these points were allowed for in the computations, activation parameters agree well with those obtained from isothermal thermograms. The values for the overall activation energy were $E_a = 82$ and $84\,kJ/mol$, and those for the pre-exponential factor $Z = 6 \times 10^{-9}$ and 13×10^{-9} $(mol/l)^{-\frac{1}{2}}.sec^{-1}$, obtained from the scanning (dynamic) and the isothermal method, respectively.

INTRODUCTION

For a number of years the polymerization of N-vinylpyrrolidone (NVP) in the presence of poly(methacrylic acids) (PMAA) of various tacticities has been investigated in this Laboratory [1, 2]. One of the features of this so-called template polymerization is the enhanced reaction rate as compared to a polymerization of NVP in the absence of PMAA.

Kinetic studies of these polymerizations were performed using conventional techniques, viz. dilatometry, titrimetry, and gravimetry. However, during the last 10 years or so, differential scanning calorimetry (DSC) [3] has been applied with success to the study of polymerization systems. Studies include curing of resins [4, 5c, 9, 10, 12–14, 15a, e, 16, 17, 19], homopolymerization [5a, 6, 7, 11, 15b–d, f, 18–21] and copolymerization [5b, d] of vinyl monomers, using either the isothermal [4–11, 13a, 14, 15b, c, e, f, 16, 18–21] or the scanning [4, 7, 9–14, 15a, d, 16, 17] method. By modifying the sample chamber and sample pans to allow illumination of the sample with a u.v.-light source, photoinduced curing or polymerizations can be examined also [19–21].

Because of its advantages such as small sample size, handiness of manipulation, rapidity of performance and versatility, DSC seemed to be attractive for studying our polymerization system. In this paper an evaluation of the technique is given as applied to the polymerization of NVP in dimethylformamide (DMF) without PMAA (blank polymerization); in the following paper the kinetic data of the template polymerization as obtained by DSC will be discussed.

EXPERIMENTAL

Materials

N-vinylpyrrolidone (NVP) from Fluka (Switzerland) was distilled under reduced N_2 pressure and stored at $-20°C$. Dimethylformamide (DMF) from Merck (W. Germany) was dried over P_2O_5 and distilled under reduced N_2-pressure. Azobisisobutyronitrile (AIBN) from AKZO-Chemie (Netherlands) was recrystallized from methanol.

Measurements

Polymerizations of NVP as well as decomposition of AIBN in DMF were examined with a Perkin–Elmer DSC-2 apparatus equipped with a scanning auto-zero device for obtaining a straight baseline.

Reaction mixtures were prepared in round-bottom flasks of 25 or 50 ml and degassed by a freeze-thaw procedure combined with vacuum-N_2 alternation at freezing temperature. The composition of the polymerization reaction mixtures was: [NVP] = 0.75 mol/dm³ and [AIBN] = 0.01 - mol/dm³ or 0.02 mol/dm³. For decomposition experiments for AIBN, a concentration of 0.1 mol/dm³ in DMF was taken.

Standard Perkin–Elmer volatile sample pans were filled with 7–10 mg of the reaction mixture in a N_2 atmosphere of a dry-box, each sealed with a cover, and stored at 4°C until used. Each pan was checked for tightness by weighing before and after the measurement. Leaky pans were discarded. DSC measurements were run at least in triplicate.

Temperature calibration of the calorimeter for chosen scan speeds was performed with the ICTA (The International Confederation for Thermal Analysis) certified reference materials indium ($T_m = 429.7$ K) and o-terphenyl ($T_m = 329.4$ K). The heat of fusion of indium (28.0 J/g) was used for area calibration.

For scanning experiments, scan speeds of 1.25, 5 and 10°C/min, were used. Each sample was placed in the sample holder assembly of the DSC at room temperature and scanned up to 150°C.

For the isothermal experiments each sample was placed in the holder, preset at the chosen temperature. When no more reaction was indicated by the recorder, a heating program of 5°C/min up to 150°C was applied in order to determine the amount of residual monomer. For all measurements an empty reference pan was used as a reference.

DATA ANALYSIS AND RESULTS

Scanning experiments
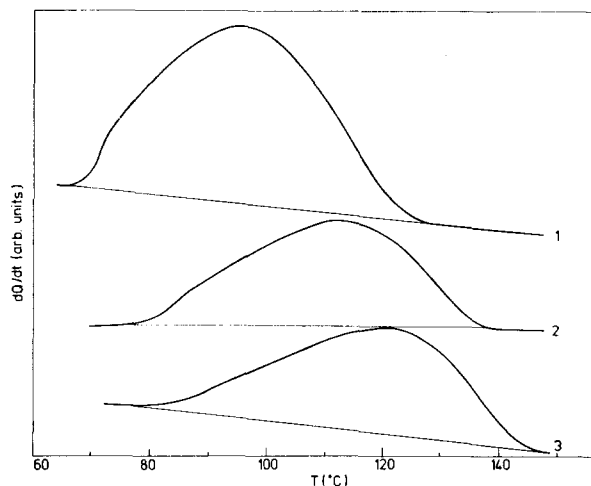
If it is assumed that the heat evolved is propor-

Fig. 1. Typical DSC thermograms of the polymerization of NVP and DMF with heating rates (1) 1.25; (2) 5; and (3) 10°C/min. [NVP] = 0.75 mol/dm^3; [AIBN] = 0.01 mol/dm^3.

tional to the number of moles reacted, n, one can compute the rate constant k of simple reactions from a thermogram through the equation [22]:

$$k = \frac{(A V/n_0)^{x-1}(dH/dt)}{(A - a)^x} \quad (1)$$

where A (in mJ) is the total area under the DSC curve on a time axis, which is proportional to the total heat of reaction (in kJ/mol), a (in mJ) is the area corresponding to the heat evolved up to any time t, dH/dt (in mJ/sec), is the rate of heat evolution at time t, n_0/V is the initial concentration of the reactant in mol/dm^3 and x is the order of the reaction.

The polymerization rate of NVP up to reasonable conversions is expressed by:

$$-\frac{d[NVP]}{dt} = k_{ov}[NVP] \quad (2)$$

Fig. 2. The heat of polymerization of NVP in DMF as a function of scan speed. (1) [NVP] = 0.75 mol/dm^3, [AIBN] = 0.01 mol/dm^3; (2) [NVP] = 0.75 mol/dm^3, [AIBN] = 0.02 mol/dm^3.

with the overall rate constant:

$$k_{ov} = k_p\left(\frac{f k_d}{k_t}[AIBN]_0\right)^{1/2} \quad (3)$$

where k_p and k_t are the rate constants for propagation and termination, respectively, k_d is the rate constant for decomposition of AIBN, f the initiator efficiency (which is assumed to be independent of temperature), and [AIBN]$_0$ the initial initiator concentration. As the polymerization is first order, Eqn (1) reduces to

$$k_{ov} = (dH/dt)/(A - a) \quad (4)$$

Since on scanning, the temperature of the reaction mixture is rising continuously, the time axis is coupled to the temperature through the scan rate dT/dt and consequently each run yields a set of rate constants as a function of temperature.

By applying the Arrhenius equation:

$$k_{ov} = Z e^{-E_a/RT} \quad (5)$$

the activation energy E_a (kJ/mol) and the pre-exponential factor Z can then be computed.

Figure 1 shows three thermograms for the NVP polymerization obtained at scan speeds of 1.25, 5 and 10°C/min, respectively. The maximum of the curves shifts to higher temperature with increasing scan speed due to the dependence of monomer conversion on time and temperature [4]. It appeared that the heat of polymerization ΔH_p (in kJ/mol), calculated from the area A, (and also E_a and Z) is strongly dependent on the scan speed (Fig. 2, curve 1). The lowering of ΔH_p on increasing the scan speed may be caused by premature exhaustion of the initiator, leading to incomplete monomer conversion and too small areas of A. This explanation is supported by the somewhat less dependency of ΔH_p on scan speed by doubling the initiator concentration (Fig. 2, Curve 2). Extrapolation of the heat of reaction to zero scan speed is supposed to yield values of $\Delta H_{p,o}$ corresponding to complete monomer conversion. The values found were 63 and 65 kJ/mol [23] for polymerization using [AIBN]$_0$ = 0.01 and 0.02 mol/dm^3, respectively. Measured areas, A, should therefore be multiplied by a ratio $\Delta H_{p,o}/\Delta H_p$ in order to obtain correct areas.
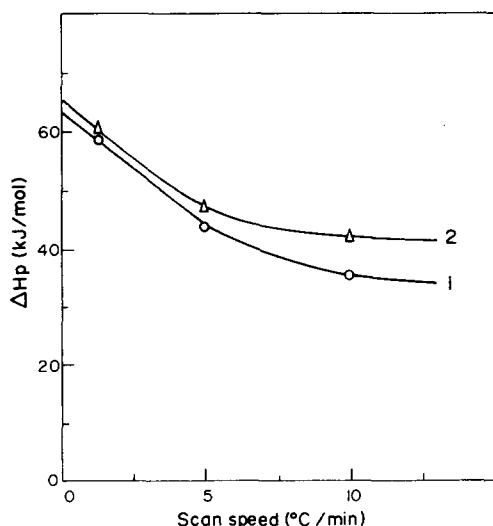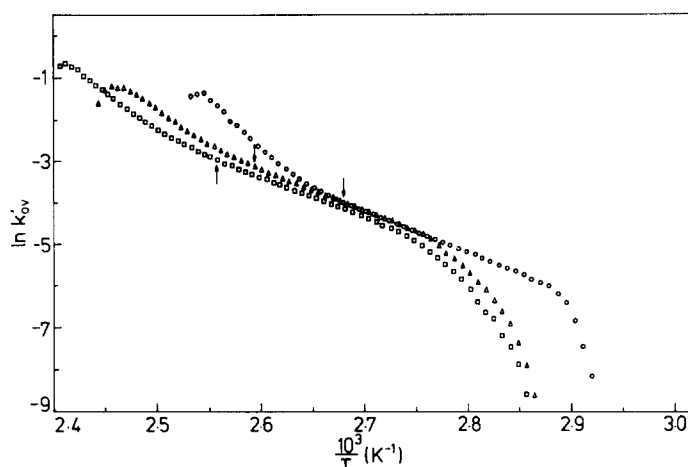
Fig. 3. Arrhenius plots of corrected overall polymerization rate constants for NVP polymerization in DMF. Scan speeds: (O) 1.25; (△) 5; (□) 10°C/min. [NVP] = 0.75 mol/dm^3; [AIBN] = 0.01 mol/dm^3. For meaning of arrows, see text.

It has been assumed before that k_{ov} is constant. However, this is only (approximately) valid at not too high conversions and temperatures when initiator consumption is still very low so that [AIBN] $\simeq$ [AIBN]$_0$. As these conditions are not fulfilled for a large part of scanning traces, the initiator concentration at any instant should be computed and the corrected rate constant $k_{ov}^{corr} = (k_p^2 f k_d/k_t)^{\frac{1}{2}} \cdot$[AIBN]$^{\frac{1}{2}}$ be used or rather $k'_{ov} = k_{ov}^{corr}/$[AIBN]$^{\frac{1}{2}}$.

Instantaneous AIBN-concentrations can be computed as follows. The dissociation rate of the initiator is given by:

$$\frac{d[\text{AIBN}]}{dt} = -Z_d \cdot e^{-E_d/RT} \cdot [\text{AIBN}] \qquad (6)$$

where Z_d and E_d are the frequency factor and activation energy for AIBN decomposition, respectively. By substituting

$$\frac{dt}{dT} \cdot dT = \frac{1}{\beta} \cdot dT,$$

where β is the scan speed in K/sec, for dt in Eqn (6) and integration, one finally obtains:

$$\ln \frac{[\text{AIBN}]_0}{[\text{AIBN}]} = \frac{Z_d}{\beta} \int_{T_0}^{T} e^{-E_d/RT} \cdot dT. \qquad (7)$$

The integral can be solved numerically and [AIBN] computed at any temperature accordingly.

E_d and Z_d for the decomposition of AIBN in DMF

were determined by DSC. There was neither dependence of the heat of decomposition ΔH_d nor of E_d and Z_d on scan speed. The values found were: $\Delta H_d = 208.5 \pm 3$ kJ/mol [23], $E_d = 142.5 \pm 3$ kJ/mol and ln $Z_d = 39.5 \pm 1$ sec^{-1}. The activation parameters are generally higher than those found by other workers [7, 24, 25].

In Fig. 3 Arrhenius plots for the NVP polymerization at the three scan speeds are shown, obtained after corrections for ΔH_p and [AIBN]. Each curve consists of 3 parts. The low temperature non-linear part of the curve is ascribed to (large) errors introduced by small heat generations. The high temperature non-linear part (up from the arrows in Fig. 3) is caused by yet unknown factors. The intermediate linear part is considered to be the relevant one from which the activation parameters were calculated (see Table 1). The values appeared to be essentially independent of scan speed and initiator concentration. The average value for $E_a = 82 \pm 4$ kJ/mol and ln $Z = 22.4 \pm 1.5$ (mol/l)$^{-\frac{1}{2}}$.sec^{-1} or $\Delta S^{\neq} = -69 \pm 12$ J.mol^{-1}.K^{-1}. Overall activation entropies were computed from the relation $\Delta S^{\neq} = R(\ln Z - \ln k_B T/h - 1)$ where k_B and h are the Boltzmann and Planck constant, respectively.

Isothermal experiments

Figure 4 shows three typical isothermal thermograms of NVP polymerizations with 0.01 mol/dm^3 AIBN recorded at 70, 80 and 90°C. At low degrees of

Table 1. Activation parameters for NVP polymerization in DMF

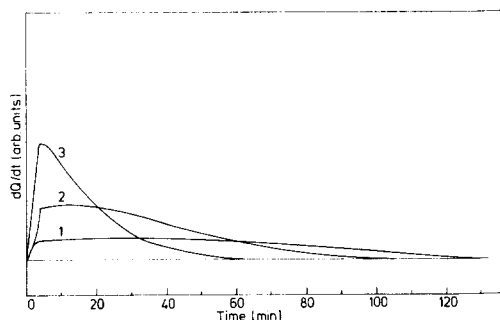| Scan speed (°C/min)	[AIBN]$_0$ (mol/dm^3)	Conversion intervals (mol%)	T-intervals (K)	E_a (kJ/mol)	ln Z [(mol/l)$^{-\frac{1}{2}}$ sec^{-1}]	$\Delta S^{\neq}$* (J.mol^{-1}.K^{-1})
1.25	0.01	12–57	350–370	81 ± 3	22.2 ± 1.5	−71 ± 12
5	0.01	6–40	360–380	82 ± 2.5	22.4 ± 1	−69 ± 8
10	0.01	5–35	365–390	80 ± 4	21.7 ± 2	−75 ± 17
1.25	0.02	15–47	358–373	81.5 ± 5	22.0 ± 1.5	−72 ± 12
5	0.02	15–35	370–383	84.5 ± 5	22.7 ± 2	−66 ± 17
10	0.02	11–32	373–388	85.5 ± 3	23.2 ± 1	−62 ± 8

* At $T = 373$ K.

Fig. 4. Thermograms of the NVP polymerization of DMF recorded isothermally at (1) 70; (2) 80; (3) 90°C.

conversion, the relation:

$$\ln \frac{[NVP]_0}{[NVP]} = k_{ov} \cdot t \qquad (8)$$

applies. $[NVP]_0$ and $[NVP]$ are the concentrations at the beginning and at time t, respectively. As $[NVP]$ is directly proportional to the area of the thermogram, Eqn (8) can be expressed as:

$$\ln\left(\frac{A}{A-a}\right) = k_{ov} \cdot t. \qquad (9)$$

For the total area A corresponding to complete monomer conversion ($= [NVP]_0$) the sum of areas enclosed by the isothermal thermogram and the proceeding scanning curve has been taken. The areas of the scanning part, corresponding to the amount of the residual monomer, decreased with increasing temperature in agreement with the observation by Malavasic et al. for the polymerization of methyl methacrylate [15b]. The derived kinetic curves are given in Fig. 5. From the slopes, k_{ov} at the various temperatures can be computed. To compare these results with those of the dynamic experiments, k_{ov} was divided by $[AIBN]_0^{\frac{1}{2}}$. E_a was found to be 84.5 kJ/mol and ln $Z = 23.3$ (mol/l)$^{-\frac{1}{2}}$.sec^{-1} (or $\Delta S^{\neq} = -61$ J.mol^{-1}.
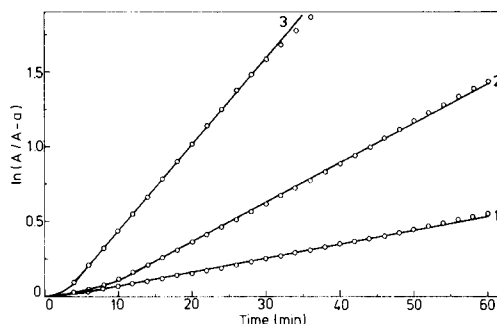

Fig. 5. Conversion vs time curves for the polymerization of NVP in DMF at (1) 70; (2) 80; (3) 90°C. $[NVP] = 0.75$ mol/dm^3; $[AIBN] = 0.01$ mol/dm^3.

K^{-1}), in good agreement with values found from scanning experiments (cf. Table 1). The agreement can be illustrated by a composite Arrhenius plot for the isothermal and scanning experiments at 1.25 and 5°C/min (Fig. 6), from which $E_a = 83$ kJ/mol and ln $Z = 23$ (mol/l)$^{-\frac{1}{2}}$ sec^{-1} ($\Delta S^{\neq} = -64$ J.mol^{-1}.K^{-1}).

DISCUSSION

Most of the investigations on kinetics of vinyl-(co-)polymerizations by DSC have involved the isothermal method [5-7, 15b, c, f, 18-21] rather than the scanning technique [7, 11, 15d]. This is so because of the more straightforward and simpler interpretation of isothermal traces. However, measurements at several temperatures are required for obtaining activation parameters.

In contrast, an Arrhenius plot can be constructed, at least in principle, from one scanning trace. For its full evaluation, however, the effect of scan speed must be examined. From such a study it appeared that not only should one take account of the change in initiator concentration but also of premature initiator exhaustion which introduced an error in the total
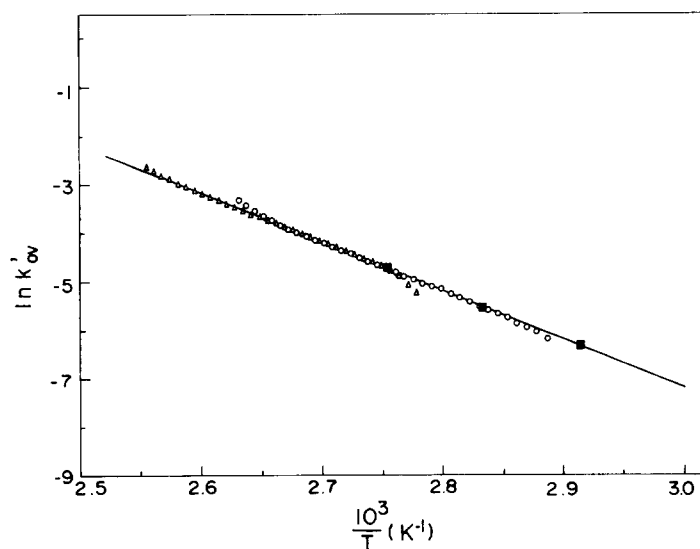

Fig. 6. Composite Arrhenius plot of the overall polymerisation rate constants resulting from scanning and isothermal thermograms. Scan speeds: (O) 1.25; (△) 5°C/min. Isothermal experiments: (■). $[NVP] = 0.75$ mol/dm^3; $[AIBN] = 0.01$ mol/dm^3.

area A of the DSC trace. This error, which reflects the portion of unconverted monomer, becomes larger at higher scan speeds because the average reaction temperature shifts to higher regions resulting in increasing decomposition rate of AIBN and increasing lag of NVP monomer conversion. Surprisingly no such dependence of A on scan speed was found for bulk polymerization of NVP [26] from which an average reaction heat of 57 ± 1 kJ/mol could be computed. Apparently bulk polymerizations could proceed to completion probably because of the occurrence of the gel effect [26, 27] or thermal polymerization [26, 28], neither of which was observed in the solution polymerizations. It should be noted that in these considerations the efficiency factor f has been assumed not to change with temperature.

A small error, not mentioned before, is introduced by the heat of decomposition of AIBN, which is incorporated in the DSC scanning thermograms. Because this heat contribution amounts to no more than a few percent, it was neglected. It could be subtracted automatically by employing a solution of initiator as the reference during measurements [7].

The fact that activation parameters found by the scanning and isothermal methods agree fairly well ($E_a = 82$ and 84 kJ/mol; $Z = 5 \times 10^{-9}$ and 13×10^{-9} (mol/l)$^{-\frac{1}{2}}$ sec^{-1} or $\Delta S^{\neq} = -69$ and -61 J. mol^{-1}.K^{-1}) [29], justifies the analysis of scanning curves.

Although the analysis of scanning thermograms is rather elaborate, the scanning technique employing several scan speeds expands the Arrhenius plot to higher temperatures, thereby supplementing results from isothermal measurements. The latter cannot be applied at high temperatures due to the rapidity with which the reaction starts giving unavoidable temperature lags. The merits of utilizing both methods to supplement each other have already been stressed by Fava [4].

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