Kinetics of Azo-Initiated 1-vinyl-2-pyrrolidone Polymerizations at Low Conversions in Aqueous Media

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ABSTRACT: The free-radical polymerization behavior of 1-vinyl,2-pyrrolidone (NVP) was studied at low conversions, using capillary dilatometry. The aqueous media were kept at neutral pH and the studies were conducted isothermally, at 40 or 45°C. The azo-type initiators used were 4,4′-azobis-4-cyanopentanoic acid (ACPA), 2,2′-azobisisobutyronitrile (AZBN), and 2,2′-azobis[2-(2-imidazolin-2-yl)propane dihydrochloride] (ABDH). The monomer concentration and initiator concentration ranges were 1.17–2.34 mol L^{-1} and 1–8 mmol L^{-1}, respectively. The rates of polymerization (R_p) and orders of reaction with respect to NVP and the initiator were evaluated and the kinetic equations were found to be $R_p \propto$ [NVP] [ACPA]$^{1.2}$; $R_p \propto$ [NVP] [AZBN]$^{1.1}$; and $R_p \propto$ [NVP]$^{2.2}$ [ABDH]$^{1.1}$. The polymers obtained were characterized by their viscosity numbers and correlation of the viscosity average molecular weights made with the type and amount of the azo initiator. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 239–246, 2000

Key words: azo initiators; 1-vinyl-2-pyrrolidone; solution polymerization; free-radical kinetics; termination by nonradical substrate

INTRODUCTION

1-Vinyl,2-pyrrolidinone

CH$_2$=CH=N with ring CH$_2$—CH$_2$ and CO—CH$_2$ (NVP)
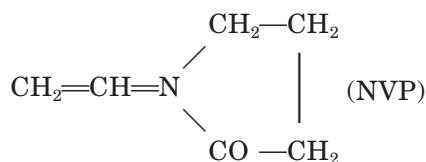
is the building block for a variety of water-soluble polyvinylpyrrolidones and copolymers of commercial value. An early patent describing the production of this monomer dates back to 1943.[1] Nowadays, homopolymers and copolymers of NVP are value-added specialties used in applications as diverse as pharmaceuticals, textiles, and fiber–glass treatments, adhesives, pigment and colloid stabilization in aqueous and nonaqueous dispersions, cosmetics, detergents, and toiletries, and as flocculation agents in beverage clarification processes among others.[2] Industrial polymers based on the NVP monomer are produced in aqueous media by a free-radical mechanism; an early patent[3] cites potassium sulfite—the reducing component of a redox pair—as an initiator presumably in the presence of oxidizing transition-metal residues. NVP is stabilized with nonvolatile amine inhibitors. It is particularly sensitive to oxygen retardation as noted by Kaplan and Rodriguez[4]: It is not clear whether this is due to an accumulative effect of monomer peroxidation and subsequent transfer of the peroxidized NVP rad-

ical fragment's H-abstraction reactions from another NVP (leading to inactivated primary radicals) and/or is the peroxy-NVP radical fragment's inability to add-on to a monomer. This monomer is also susceptible to acidolysis, producing $CH_2=CH-NH-(CH_2)_3COOH$ by ring opening.

CH_3CHO and $CH_2=CH-N(Me)-CH_2OH$ are also products of undesirable cleavage reactions of the monomer under acidic conditions. These agents potentially interfere with the polymerization as chain-transfer agents and may have to be avoided in efforts to keep up the linearities of polymer molecules, the high average kinetic chain lengths particularly at high conversions, and the overall rate of polymerization. Bamford and coworkers cited the presence of other species in the monomer.[5] NVP is maintained under basic conditions and usually polymerized in alkali-buffered media.[6]

Diazo compounds are well known in generating primary radicals of equal and moderated reactivities at predictable rates, depending on their thermal decomposition kinetics.[7] These features enable their wide applicability in industrial free-radical polymerizations. For free-radical polymerizations, the ideal kinetic model is well established in the literature.[8] The expression for the rate of polymerization is

$$R_p = \frac{k_p}{k_t^{1/2}} \{2fk_d\}[M_0][I_0]^{1/2} \qquad (1)$$

where k_d, k_p, and k_t are the initiator decomposition, propagation, and termination rate constants, respectively; f, the initiator efficiency factor (a constant for an initiator–monomer–solvent system); and $[M_0]$ and $[I_0]$, the initial monomer and initiator concentrations, respectively. A factor of 2 arises from generation of 2 mol of primary radicals from the decomposition of a mol of the initiator.

Here, we report on the polymerization behavior of 1-vinyl-2-pyrrolidone in aqueous media using dilatometry in the presence of commercially available azo initiators. The measurements are found to be practical and informative in the establishment of cause–effect relationships from exploratory polymerization runs in an industrial setting. The adopted experimental protocol enables rapid correlations of polymerization with the molecular structure.
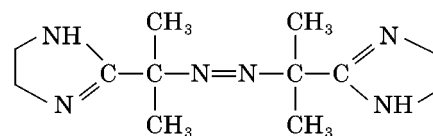
Table I Chemical Formulas of Diazo Compounds Used as Initiators
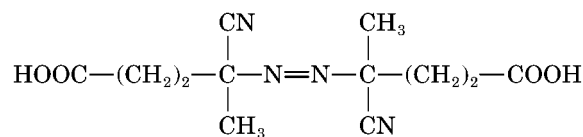
4,4′-Azobis-4-cyanopentanoic acid (ACPA)
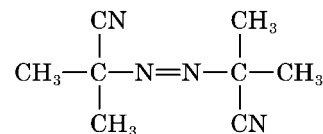
2,2′-Azobisisobutyronitrile (AZBN)

2,2′-Azobis[2-(2-imidazolin-2-yl)propane-dihydrochloride (ABDH)

EXPERIMENTAL

1-Vinyl-2-pyrrolidinone was obtained from Fluka AG (Buchs, Switzerland). It was purified by thorough deoxygenation at room temperature followed by fractional distillation under reduced pressure and collection of the middle fraction. The purified monomer was stored at 5–8°C (mp = 13.5°C). 4,4′-Azobis-4-cyanopentanoic acid (ACPA), 2,2′-azobisisobutyronitrile (AZBN), and 2,2′-azobis[2-(2-imidazolin-2-yl)propane dihydrochloride] (ABDH) were used as supplied. The chemical formulas of the azo initiators are given in Table I. Water used was deionized (specific conductance = 3.33×10^{-5} Ω^{-1} cm^{-1} at 30°C). The dilatometer used was similar to that used by Voeks and Crane.[9]

A typical polymerization run is as follows: 1.170 mol L^{-1} of NVP and 4.00 mmol L^{-1} of the initiator were placed in the 50-mL capacity reservoir of the dilatometer. The solution was checked for pH and purged with oxygen-free nitrogen for 15 min at a flow rate of 0.1 m^3/min using a gas dispersion tube fitted with a 170–220-μm fritted tip at ambient temperature. The dilatometer was then assembled and placed in a thermostatted bath at 40.00 + 0.02°C. The precision capillary bore measured 2.80 + 0.01 mm. The height of the fluid level in the capillary was monitored using a
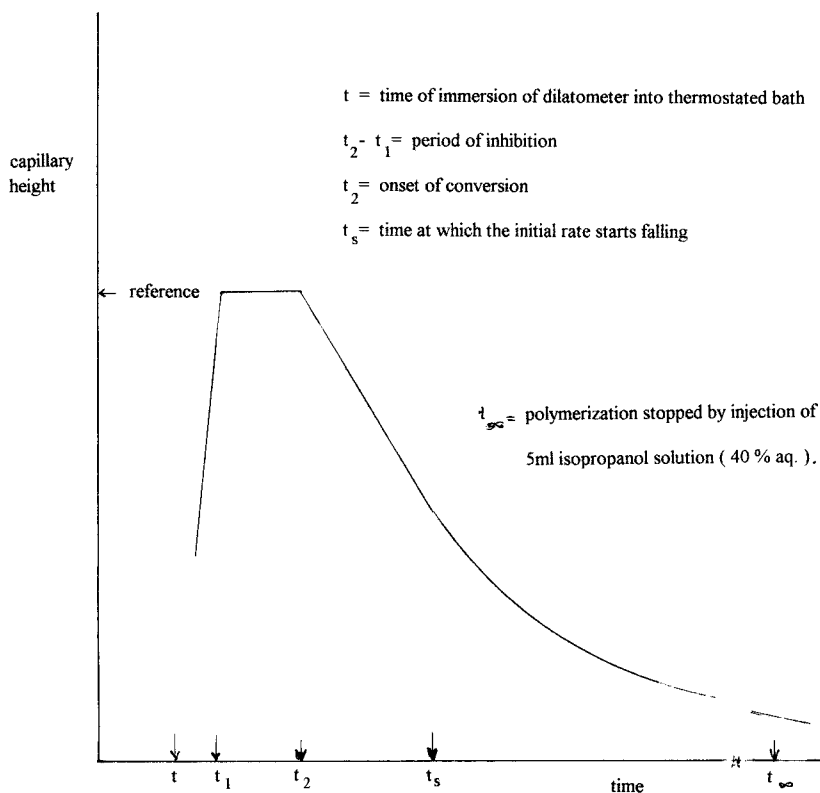
t = time of immersion of dilatometer into thermostated bath

$t_2 - t_1$ = period of inhibition

t_2 = onset of conversion

t_s = time at which the initial rate starts falling

t_∞ = polymerization stopped by injection of 5ml isopropanol solution (40 % aq.).

Figure 1 Profile of change in meniscus with time in the course of kinetic measurements above ambient temperature.

cathetometer to the nearest one-fifteenth of a millimeter. Profiles of decreases in the capillary height with time are similar to that shown in Figure 1. Examples on the actual course of dilatometric runs are given in Figure 2. An initial dilatometric conversion rate, R_p, is obtainable according to

$$R_p \propto \frac{\Delta h[M_0]}{\Delta t} \qquad (2)$$

where Δt is the time lapse from $t = 0$; Δh, the change in the capillary height at Δt; and $[M_0]$, the initial concentration of the monomer. Accurate determination of the shrinkage factor $d[M_0]/\Delta h$ in mol/mm for a given capillary and the change in capillary height corresponding to full conversion (Δh_∞) enable the expression of monomer conversions in mol L^{-1} s^{-1} and percent conversions, respectively.

Capillary viscometry was conducted using Ubbelohde-suspended level instruments with a 0.4-mm precision bore at T (°C) = 30.00 + 0.02. The conversion of intrinsic viscosity values to vis-

cosity average molecular weights was made using the relationship $[\eta]_{H_2O}^{30} = 3.93 \times 10^{-4} M_v^{0.59}$.[10]

RESULTS AND DISCUSSION

The ideal model of free-radical polymerization accounts only for the initiator to generate initiating free-radical fragments, the monomer to add-on to a radical, and the termination being by mutual deactivation between two macroradicals; other competitive reactions, for example, H-abstraction reactions of the free radicals, are ignored. Often, one needs to validate the agreement between experimental observations from a specific initiator–monomer–solvent system with ideal behavior and/or give meaning to deviations from such reference kinetic models. A simple approach to achieve this would be to express eq. (1) as

$$\ln R_p = \ln K + \ln[M_0] + \tfrac{1}{2}\ln[I_0] \qquad (3)$$

where K is constant, and keeping any one of the second or third terms on the rhs of eq. (3) constant
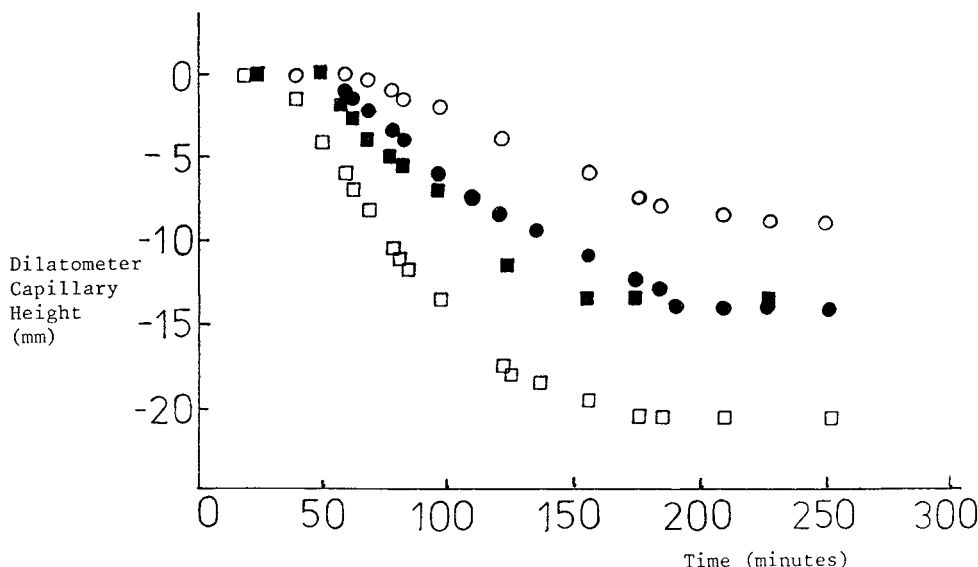
Figure 2   Course of isothermal solution polymerizations of NVP [ACPA] by weight on monomer (%): (○) 0.3; (●) 0.5; (■) 0.7; (□) 0.9. pH 7; [NVP] = 13.0%; temperature (°C) = 45.00 + 0.02.

at a time and with the other follow the change in $\ln R_p$. $\ln R_p$ versus $\ln [M_0]$ plots at constant $[I_0]$ and $\ln R_p$ versus $\ln [I_0]$ plots at constant $[M_0]$ are shown in Figures 3 and 4, respectively. At the NVP concentration of 1.170 mol L^{-1}, azo-initiator concentrations were varied within the range 1 and 8 mmol L^{-1} (Fig. 3).

Polymerizations Using ACPA or AZBN Initiator

In these cases, the dependence of the polymerization rate with respect to the initiator concentration is found to be near first order. To account for the observed kinetic data, one works out elementary steps that make up a mechanistic description of the kinetics of the reaction. Here, the inactivation of the macroradicals occurs by a nonradical substrate, instead of a bimolecular termination mechanism. Therefore, one assumes a steady-state polymerization condition where

$$2fk_d[I_0] = k_t[\square\square\square\square\square\square\square\square\square\square*][N] \quad (4)$$

where $[\square\square\square\square\square\square\square\square\square*]$ is the steady-state concentration of macroradicals, and $[N]$, the concentration of the nonradical terminator.

Since the

rate of propagation

$$= k_p[\square\square\square\square\square\square\square\square\square*][M_0] \quad (5)$$

the combination of eqs. (4) and (5) with the elimination of the steady state [macroradical] term gives

$$R_p = \frac{K'[M_0][I_0]}{[N]} \quad (6)$$

where K' is a constant. Thus, macroradical deactivation by a nonradical may account for the first-order dependence of the reaction rate with respect to the [initiator]. In fact, the kinetics of AZBN-based polymerizations of an acrylamide monomer have been interpreted similarly to that represented by eq. (6), albeit with high concentrations of about $5M$ of the acrylamide monomer.[11] The supplementary 0.1 order in the initiator dependence observed here could be tied to the limited solubilities of ACPA and AZBN in water at pH 7 (see also Polymerizations Using ABDH Initiator). It is also credible that even at very low conversions far from conditions of "high viscosities/diffusion control" a propagating macroradical end becomes threaded-in and inaccessible as not to undergo bimolecular termination.

As evident from Figure 4, the first order in NVP dependence of the reaction rate is kept up in the case of AZBN and ACPA initiations, in accordance with simple kinetics. Also, high kinetic chain lengths (as inferred from the high intrinsic viscosities—Table II) point to conditions of polymerization conducive to high molecular weights with any of these azo compounds.
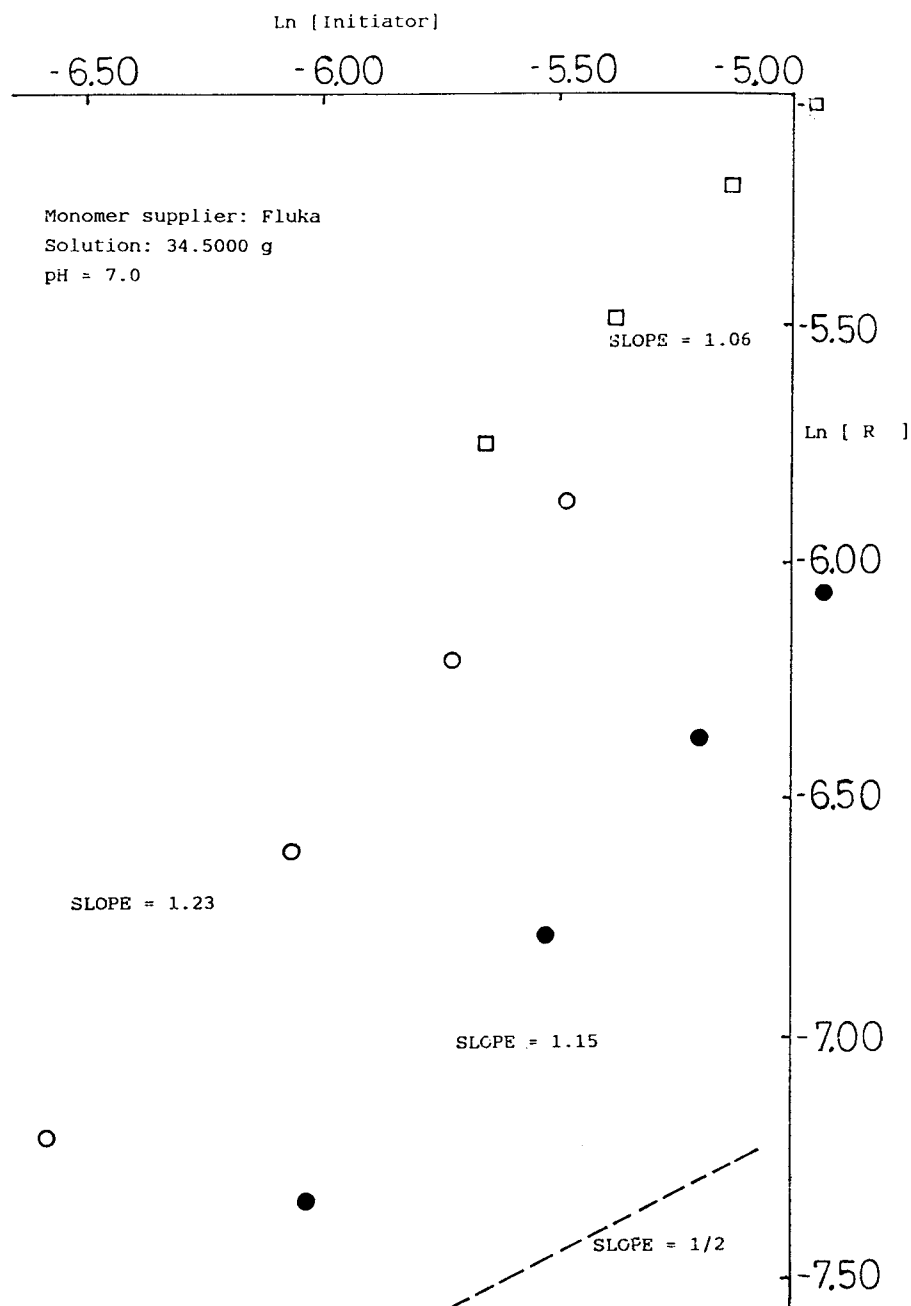
Figure 3 Isothermal solution polymerization of NVP at pH 7: variation of $\ln[R]$ with $\ln[\text{initiator}]$ with constant $[\text{NVP}] = 1.170$ mol L^{-1}. ($\bigcirc$) [ACPA] at 45°C; ($\bullet$) [AZBN] at 45°C; ($\square$) [ABDH] at 40°C.

An early reference to NVP polymerizations to high conversions in aqueous nonbuffered solutions[12] used AZBN in the concentration range of 4.5–13 mmol L^{-1} and found $\frac{1}{2}$-order [AZBN] dependence of the rate of polymerization; also, it reported the absence of any significant change of the average degree of polymerization (DP) with the variation of [AZBN] in the range considered.

Here, the effect of initiator concentration on the viscosity-average DP is significant as observed from Table II for both AZBN- and ACPA-initiated systems, respectively.

Polymerizations Using ABDH Initiator

In the case where termination of polymer-radical growth is exclusively by a primary radical with
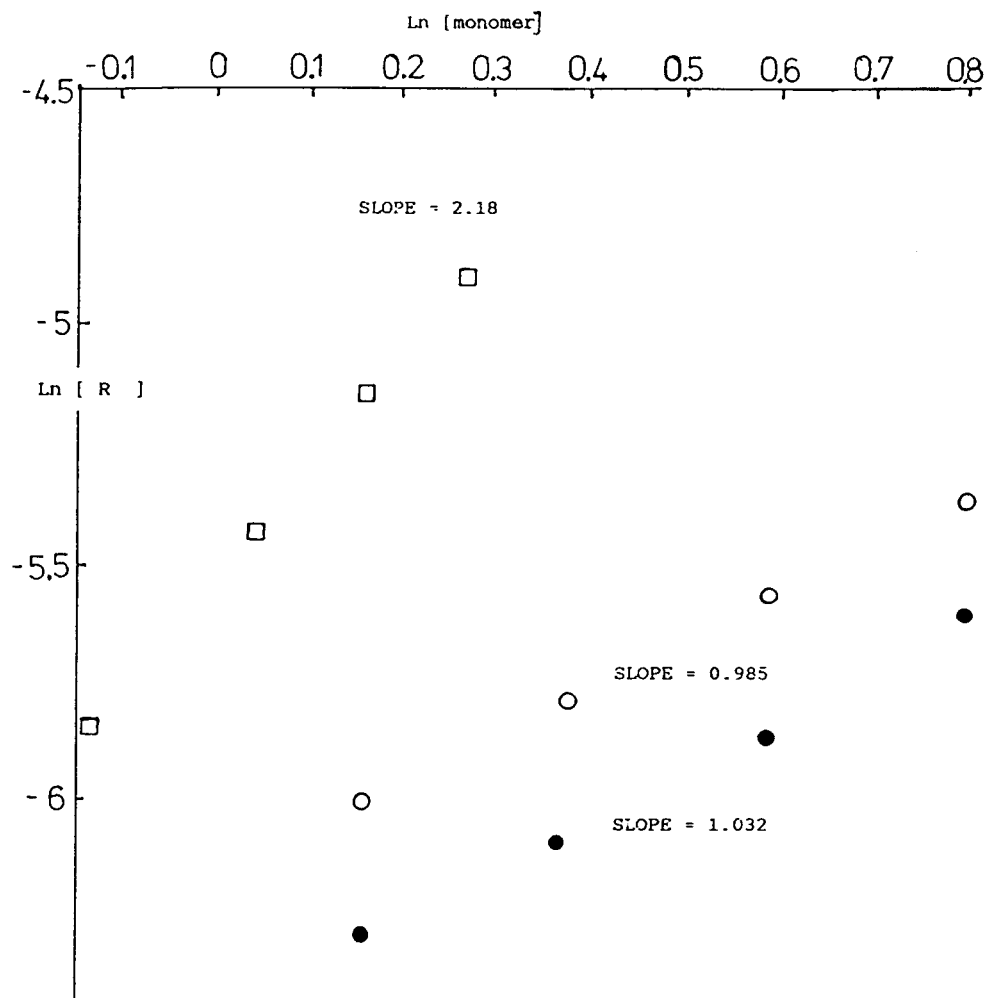
Figure 4 Isothermal solution polymerization of NVP at pH 7: variation of ln[R] with ln[NVP] with constant [initiator]: (○) [ACPA] = 3.25 mM at 45°C; (●) [AZBN] = 5.54 mM at 45°C; (□) [ABDH] = 7.02 mM at 40°C.

absence of any bimolecular termination of two propagating polymer radicals, the dependence of the polymerization rate is expected to be second order in [monomer] and zero order in [initiator]. This can happen with very active primary radicals that do not initiate but terminate and/or H-transfer, particularly with situations of low monomer concentrations. In this case, the monomer participates in the initiation step and one may assume that

$$2fk_i[I_0][M_0] = k_{t'}[\square\square\square\square\square\square\square\square\square*][I_0] \quad (7)$$

Here, the combination of eqs. (5) and (7) with the elimination of the steady state [macroradical] term gives

$$R_p = K''[M_0]^2 \quad (8)$$

where K'' is a constant.

Subsequently, with both mechanisms of termination operating, that is, termination by the primary radical as well as mutual termination of the polymer radicals, one expects the order with respect to the [monomer] to be between 1 and 2 and that with respect to the [initiator] to be less than $\frac{1}{2}$. Even though rare, an order near 2.5 with respect to the [monomer] has been observed and accounted for.[13]

For ABDH-initiated polymerizations, the order of [NVP] dependence of the polymerization rate is found to be in excess of 2 and unusually high. Such an increased dependence of the rate on the monomer may result from any of the steps leading

Table II Effect of [Initiator] on $[\eta]$ and M_v

Initiator[a]	$\otimes[\eta]$[b] in dL g^{-1}	$M_v \times 10^{-6}$ in g mol^{-1}
ACPA[c]		
0.3	2.87	1.4
0.5	2.78	1.2
0.7	2.10	0.92
0.9	2.14	0.95
AZBN[c]		
0.3	5.99	3.9
0.5	5.82	4.1
0.7	4.08	2.4
0.9	3.63	2.0
ABDH[d]		
0.3	2.62	1.2
0.5	1.72	0.70
0.6	1.62	0.64

[a] Percent by weight on monomer.
[b] $\otimes$, obtained from regression of η_{sp}/c against concentration plots at 30°C.
[c] From isothermal runs at 40°C.
[d] From isothermal runs at 45°C.

to initiation becoming rate-determining. Self-association or micellelike assembly of the initiator molecules or their H bonding would contribute to the slowness of the initiator decomposition. In fact, AZBN is not soluble in water, but goes into solution indirectly: It dissolves in NVP, which, upon dissolution of the latter in water, remains dispersed in the polymerization medium.

An order of dependence with respect to the [monomer] in excess of 1 but up to $\frac{3}{2}$ is interpreted in terms of the "cage theory" first proposed by Matheson[14]: This is a kinetic model that introduces the concept of the primary radical's obstructed addition-to-monomer. Thus, "paired-primary-radicals" have reduced mobility and the initiation has [monomer] dependence. The 1.5-order [NVP] with $\frac{1}{2}$-order [initiator] dependencies of the polymerization rate are preserved, provided always deactivation occurs by mutual termination of the macroradicals. A multitude of kinetic observations including those on methacrylic acid,[15] acrylic acid,[16] and acrylamide[17–20] are interpreted in terms of the cage model.

The observation of [NVP]$^{2.2}$ [ABDH]$^{1.1}$ dependence on the rate is uncommon but not exceptional in familiarity. For example, the polymerization rate of AZBN initiated (with $I_0 = 7.4$ mM) with NVP (with $M_0 = 1.25M$) at 74°C in dimethylformamide has been found to be dependent on [NVP]$^{2.1}$ [AZBN]$^{0.3-0.2}$.[21] In this case, a mechanistic account that fits the experimental observation

is one where the kinetics are dominated by primary radical termination and initiation has [NVP] dependence. In retrospect, a different study[22] on the polymerization behavior of NVP (with $M_0 = 2.2M$ and above) at 50°C used AZBN (with $I_0 = 4$ mM) but obtained decelerated conversions, albeit average chain lengths of the same order of magnitude to ours.

In the case of ABDH-containing polymerizations, our data is best rationalized with

- A [NVP] and [ABDH]-dependent initiation step and
- Additional fractional orders of 0.2 and 0.1 for monomer and initiator dependence, respectively, possibly linked to H-bonding effects[23] and dipole–dipole interactions.

Mechanistically, therefore, the following is considered:

$$2fk_{i'}[I_0][M_0] = k_{t'}[\square\square\square\square\square\square\square\square\square*][N] \quad (9)$$

Once again, the combination of eqs. (5) and (9) with the elimination of the steady-state [macroradical] term gives

$$R_p = \frac{K'''[M_0]^2[I_0]}{[N]} \quad (10)$$

where K''' is a constant.

With ABDH-initiated polymerizations, average chain lengths obtained are lower in comparison with those obtained with AZBN and ACPA (compare $[\eta]$ values and M_v's in Table II). It had previously been suggested[22] that degradative chain transfer to the initiator or monomer were factors for premature terminations involving NVP, without verification on the significance of such reactions. Here, however, the factor which is fundamental, relevant, and credible appears to be the relative proportion of primary radical flux for equivalent monomer concentration, given the absence of termination by primary radicals or other factors complicating chain-growth and chain-termination steps. The relative frequency of initiating events is far greater in ABDH-initiated runs: Based on their first-order thermolysis, it is calculated that the azo initiators at their respective temperatures of polymerization show a relative primary radical generation rates of 1 : 5 : 70 for ACPA : AZBN : ABDH, respectively.

CONCLUSIONS

In the polymerizations of NVP herein described, deactivation of macroradicals by a nonradical substrate appears to be the way termination occurs. In our experiments, this manner of deactivation is by no means interruptive and degradative to chain molecule growth.

In contrast with earlier findings on NVP polymerizations[12,22–24] and distinct from that of a recent account,[25] polyvinylpyrrolidones with gradually different molecular weights. (M_v's up to 4 $\times$ 10^6 g mol^{-1}) have been obtained with varying azo-initiator levels. The significantly lower molecular weights obtained with ABDH as an initiator is attributed to the higher primary radical flux available for initiation, in comparison with those from the other azo initiators.

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