Free Radical Kinetics of *N*-Methyl *N*-Vinyl Acetamide Polymerization at Low Conversions in Aqueous Media

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ABSTRACT: *N*-methyl *N*-vinyl acetamide (NMNVA) monomer was polymerized at low conversions and its free radical kinetics were detailed using capillary dilatometry. The polymerizations were conducted isothermally, at 40°C using 2,2′-azobis[2-(2-imidazo-lin-2-yl) propane dihydrochloride] (ABDH) as initiator. Monomer concentration and initiator concentration ranges were 1.10–$1.70 \ mol \cdot L^{-1}$ and 1–$4 \ mmol \cdot L^{-1}$, respectively. The aqueous polymerization media were kept at neutral pH. The rates of polymerization (R_p) and orders of reaction with respect to NMNVA and ABDH concentrations were evaluated and the kinetic expression was found to be ideal, with $R_p \propto$ $[NMNVA]^{1.07} [ABDH]^{0.61}$. The polymers obtained were characterized by their viscosity numbers and correlation of viscosity average molecular weights was made with the amount of ABDH initiator. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 337–341, 2001

Key words: azo initiators; *N*-methyl *N*-vinyl acetamide; solution polymerization; ideal free radical kinetics; dilatometry

INTRODUCTION

Specialty water soluble monomers help build in specific characteristics in hydrosoluble copolymers that are used in diversified industrial applications. Areas of use, be it copolymer adsorption on colloids as in steric stabilization and flocculation, viscosification, etc., rely on the physicochemical attributes of the so-designed polymer molecules. Segment interactions of the copolymer molecule involving the colloid surface properties as well as the dispersion medium properties (ionic strength, pH, temperature, etc.), and polymer coil properties, ultimately account for the performance of the polymer in its niche application. In flocculation for example, the achieved coil size

and the linearity of the polymer chain are directly implicated. The colloid particles that are flocculated by polymer bridging will usually not be closer together than some average interparticle distance, e.g., the distance of secondary minimum of 50–100 nm. This gap will not be reached by a low molecular weight polymer coil. In this respect, a polymer becomes more and more efficient as its molecular weight increases, because (1) polymers have distribution of sizes, and the higher the molecular weight, the greater the proportion of molecules that are able to close the gap, and (2) every polymer coil continually changes shape in solution and only occasionally adopts an extended conformation, the more frequently will the polymer be extended to greater than the interparticle distance that needs bridging. Thus, the skills with which monomers are converted to polymer with large size fraction and linearity will affect performance in flocculation.

The production of *N*-methyl, *N*-vinyl acetamide (NMNVA), $CH_2 = CH. N(CH_3) \cdot CO \cdot CH_3$ has first

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been reported in 1939.[1] Very few references have appeared on this monomer in the open literature.[2,3] A wide range of other azo-compounds are available, chosen for their controllable reactivities in polymerizations based on their thermal decomposition kinetics.[4] An idealized kinetic model[5] for free radical polymerizations expresses the rate of polymerization as:

$$R_p = \frac{k_p}{k_t^{1/2}} \cdot \{2f \cdot k_d\}^{1/2}[M_o][I_o]^{1/2} \qquad (1)$$

where k_d, k_p, and k_t are the initiator decomposition, propagation, and termination rate constants, respectively; f is the initiator efficiency factor (a constant for an initiator-monomer-solvent system), $[M_o]$ and $[I_o]$ are the initial monomer and initiator concentrations, respectively; a factor of 2 arises from generation of 2 mols of primary radicals from the decomposition of a mol of the initiator. $k_p/k_t^{1/2}$ is a characteristic ratio that is a measure of a given monomer's propensity for kinetic growth.

In real systems, often free radical polymerizations are far removed from this ideality. Chain transfer reactions with H-abstraction occur at the active site of a primary radical or a macroradical, potentially involving any species present in the system: initiator, solvent, monomer, polymer, etc. These may prematurely terminate a growing macroradical, limiting the kinetic chain growth. An authoritative account of the complexities that arise is beyond the scope of this work, but is well documented.[6]

Herein, some basic skills in attainment of high molecular weight polymer from NMVA are detailed and the polymerization behavior of this monomer is reported. Our experimental approach also exemplifies the rapid protocol that can be adopted in the correlation of polymerization variables with molecular structure of the polymers obtained.

EXPERIMENTAL

NMVA was obtained from Hoechst GmbH (Hoechst-Germany). It was purified by thorough deoxygenation at room temperature followed by fractional distillation under reduced nitrogen pressure (15 mmHg) and collection of middle fraction (bp = 44°C). The purified monomer was stored at 5–8°C (mp = 13.5°C). 2,2'-Azobis[2-(2-imidazolin-2-yl)
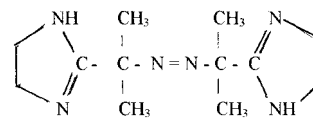
Scheme 1 Chemical formula of diazo compound used as initiator.

propane dihydrochloride] (ABDH) was used as supplied. The chemical formula of this azo initiator is given in Scheme 1. Deionized water had a specific conductance of $3.33 \times 10^{-5} \ \Omega^{-1}\text{cm}^{-1}$ at 30°C.

The basic design of the dilatometer is a simplification of that used by Voeks and Crane.[6] It is adopted recognizing the opposition to meniscus fall in following volume contractions in high pituity capillary media as of the onset of polymerization. A typical polymerization run is as follows: $1.10 \ \text{mol} \cdot \text{L}^{-1}$ of NMNVA and $2.00 \ \text{mmol} \cdot \text{L}^{-1}$ initiator (as total solution weight of 34.5000 g) 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 m³/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°C + 0.02°C. The precision capillary bore measured 2.80 mm + 0.01 mm. The height of the fluid level in the capillary was monitored using a cathetometer to the nearest 1/50 of a millimeter. Profiles of decreases in the capillary height with time and examples on the actual course of dilatometric runs are similar to those obtained in an earlier work.[7] An initial dilatometric conversion rate R_p is obtainable according to:

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

where Δt = time lapse from $t = 0$; Δh = change in the capillary height at Δth; and $[M_o]$ = initial concentration of the monomer.

Accurate determination of shrinkage factor $d[M_o]/\Delta h$ in mol/mm for a given capillary and the change in capillary height corresponding to full conversion ($\Delta h \infty$) enable the expression of monomer conversions in moles $\cdot \text{L}^{-1} \ \text{s}^{-1}$ and % conversions, respectively.

Capillary viscometry was conducted using Ubbelohde-suspended level instruments with 0.4-mm precision bore at T (°C) = 30.00 + 0.02. The conversion of intrinsic viscosity values to viscosity average
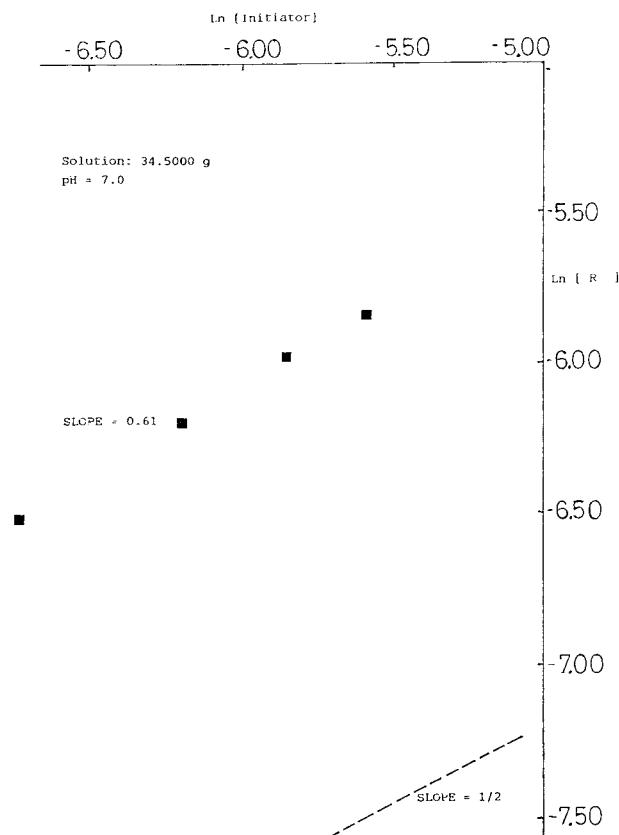
Figure 1 Isothermal solution polymerization of N-methyl N-vinyl acetamide at pH = 7: variation of ln [R] with ln [ABDH] and fixed [NMNVA] = 1.318 mol $\cdot$ l^{-1} at 40°C.

molecular weights were made using the relationship $[\eta]_{\text{H2O}}^{30} = 7.29 \times 10^{-5} M_v^{0.757}$.[3]

RESULTS AND DISCUSSION

The ideal model of free radical polymerization is simple in that the initiator decomposes giving free radical fragments (primary radicals), the monomer adds on to the radical, and the termination occurs by mutual deactivation between two macroradicals. Steady-state free radical concentrations are maintained in the course of this ideal reaction. Often one needs to validate agreement between experimental observations from 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:

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

where K is constant, and keeping any one of the second or third terms on the RHS of eq. (3) constant at a time; with the other follow the change in ln R_p. ln R_p versus ln $[M_o]$ plots at constant $[I_o]$ and ln R_p versus ln $[I_o]$ plots at constant $[M_o]$ are shown in Figures 1 and 2, respectively. At the NMNVA concentration of 1.10 mol $\cdot$ L^{-1}, azo-initiator concentrations were varied within the range 1 mmol $\cdot$ L^{-1} and 4 mmol $\cdot$ L^{-1} (Fig. 1).The dependence of polymerization rate with respect to [ABDH] is considered to be 1/2 order; that with respect to NMNVA, first order (see Fig. 2). This indicates kinetic growth to form polymer with predictable bimolecular termination of the macroradicals be it disproportionation or coupling mechanisms. A previous reference to free radical polymerization and copolymerization of this monomer used AIBN initiator[3] and provides data concerning low molecular weight polymers obtained from polymerizations in high concentrations of NMNVA in methanol, up to $\approx$10 mol $\cdot$ L^{-1}.

Unlike the case of N-vinyl pyrrolidone,[7] and those of a large number of other aqueous media polymerizations, the increments of 0.07 and 0.11 found above ideal orders with respect to [NMNVA] and [ABDH] appear marginal for attempting mech-
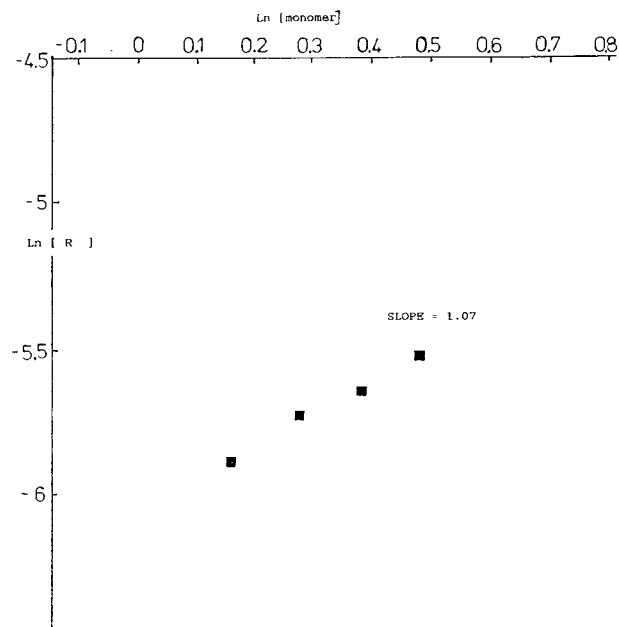
Figure 2 Isothermal solution polymerization of N-methyl N-vinyl acetamide at pH = 7: variation of ln [R] with ln [NMNVA] and fixed [ABDH] = 3.66 mM at 40°C.
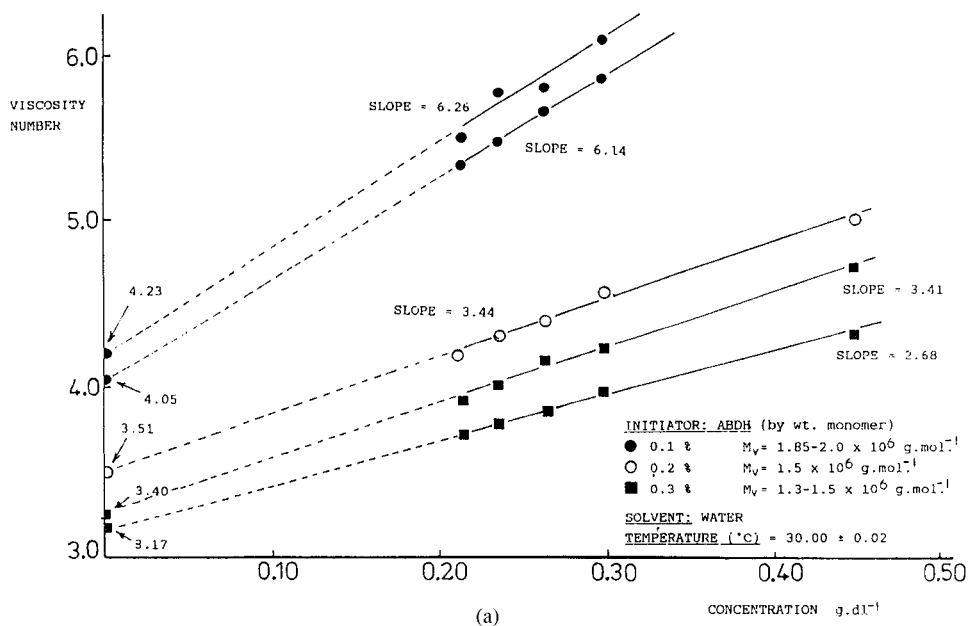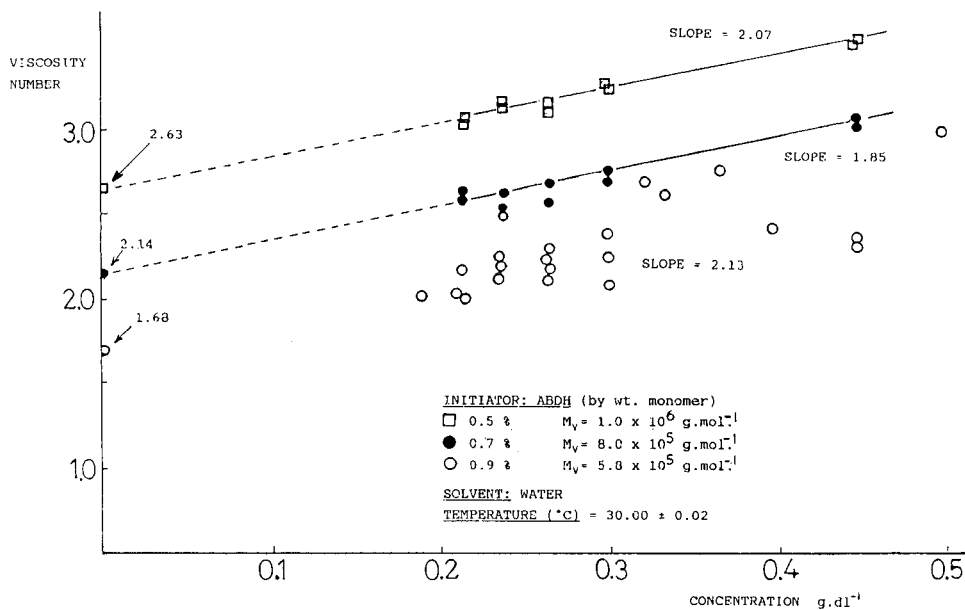
Figure 3 Effect of [ABDH] initiator on [η] and viscosity average molecular weight, M_v.

anistic rationalizations of the kinetic deviations. Such increments appear to result from the excessive rates of cleavage of ABDH initiator, even under the mild reaction temperature of 40°C[7]; I^Y initiator radical concentrations that are higher than those at the onset would account for the higher than 1/2-order dependence on [initiator]. As the first-order dependence in [NMNVA] is preserved, one cannot account for the deviation in terms of terminations other than mutual ones between macroradicals. Figure 3(a,b) shows the variation of viscosity number with poly(N-methyl, N-vinyl acetamide) concentration. Intrinsic viscosity values are from the regression of η_{sp}/c against polymer concentration obtained from viscometry. It is evident that this water soluble polymer can be produced with gradually increasing molecular weights up to $M_v = 2 \times 10^6$ g·mol^{-1}.

CONCLUSIONS

In the polymerizations of NMNVA herein described, termination occurs by mutual deactivation of macroradicals. This work affirms the potential use of poly(*N*-methyl, *N*-vinyl acetamides) with gradually different molecular weights in the applications of hydrosoluble flocculants and hydrophobic colloid treatments.

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