

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Free Radical Polymerization in Aqueous Solution of Acrylic Acid Mediated by Nitroxides Originated from $\text{NaNO}_2$

E. Bortel<sup>a</sup>; A. Kochanowski<sup>a</sup>; S. Kudla<sup>b</sup>; E. Witek<sup>a</sup>

<sup>a</sup> Jagellonian University ul., Cracow, Poland <sup>b</sup> Institute of Heavy Organic Synthesis, ISO ul., Kedzierzyn-Kozle, Poland

**To cite this Article** Bortel, E. , Kochanowski, A. , Kudla, S. and Witek, E.(1998) 'Free Radical Polymerization in Aqueous Solution of Acrylic Acid Mediated by Nitroxides Originated from  $\text{NaNO}_2$ ', *Journal of Macromolecular Science, Part A*, 35: 2, 401 – 409

**To link to this Article:** DOI: 10.1080/10601329808001985

**URL:** <http://dx.doi.org/10.1080/10601329808001985>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## FREE RADICAL POLYMERIZATION IN AQUEOUS SOLUTION OF ACRYLIC ACID MEDIATED BY NITROXIDES ORIGINATED FROM $\text{NaNO}_2$

Edgar Bortel\*†, Andrzej Kochanowski,  
Stanislaw Kudla‡, and Ewa Witek

†Jagellonian University  
ul. Ingardena 3, PL 30-060  
Cracow, Poland

‡Institute of Heavy Organic Synthesis, ISO  
ul. Energetyków 9, PL 47-225  
Kedzierzyn-Kozle, Poland

### ABSTRACT

A series of investigations was carried out focusing on the confinement of the Trommsdorf (gel) effect in radical polymerization of acrylic acid, AA, in its Na-form. Sodium nitrite,  $\text{NaNO}_2$ , functioning at room temperature as an inhibitor for water-soluble monomers, proved to be an effective mediator in polymerizations carried out at  $t = 90^\circ\text{C}$ . As a result it was possible to polymerize AA at a high initial monomer concentration, i.e.  $[\text{M}]_0 = 40 \text{ g/dl}$ . Therefore, concentrated solutions of NaPAA in water were obtainable in a one-step process.

It was found that  $\text{NaNO}_2$  retards the onset of polymerization up to  $60^\circ\text{C}$  at which temperature only a small degree of conversion  $\alpha = 30\%$  was reached after 40 hours. On the other hand, without added  $\text{NaNO}_2$  a less concentrated monomer solution, having  $[\text{M}]_0 = 10 \text{ g/dl}$  was polymerized to  $\alpha = 96\%$  at  $60^\circ\text{C}$  after 40 minutes.

At  $90^\circ\text{C}$ , the polymerization of NaAA no longer appeared to be retarded by sodium nitrite, since in 40 g/dl solutions high degrees of conversion were obtainable within reasonable time periods, without any sign of autoacceleration. As  $\text{NaNO}_2$  generates nitroxides, it

seemed reasonable to analyze the progress of the mediated polymerizations as an approach to "livingness". In fact, some increase in  $\overline{M}_n$  over time of polymerization,  $\tau$ , was observed, but generally the criteria for a "living polymerization" remained unfulfilled. Relatively high coefficients of polydispersity

$$D = \frac{\overline{M}_w}{\overline{M}_n}$$
 ranging between 6.50 and 9.62 were found for all the  $\text{NaNO}_2$  mediated poly(acrylic acid)s. A value of the same order resulted for the non-mediated poly(acrylic acid).

## INTRODUCTION

Acrylic acid, AA, appears to be one of the chief constituents of water-soluble resins. Its current yield is estimated to account for ca. 2 mln t/year. Consequently, many papers have been published on AA polymers and continue to be published [1, 2, 3]. Despite extensive recent research carried out, the mechanism of polymerization remains not fully understood. The main obstacles may result from the strong tendency to form hydrogen bonds [4, 5] and from variable degrees of dissociation. Therefore, the tailoring of AA-polymers is difficult, especially when the polymerization is carried out in water, which appears to be the most desired solvent.

Principally, the control over molecular weight, low polydispersity, and desired end groups is obtainable by ionic polymerization of suitable monomers in systems wholly deprived of water. Nevertheless, in recent years reports were published about the achievement of "livingness" even in radical polymerizations [6, 7, 8, 9, 10]. These papers refer, however, to investigations carried out in non-aqueous media. In one case, a solvent-mixture comprising only 25 wt% of water and 75 wt% of poly(ethylene glycol)s was used in a mediated polymerization of sodium styrene sulfonate [13]. The principle in achieving "livingness" in radical systems is based on a reversible deactivation of the growing radicals. Such dormant deactivation can be achieved by the use of stable radicals as mediators, among which the 2,2,6,6-tetramethyl-piperidinyloxy free radical (designated as TEMPO [8]) appears to be the most often employed.

Major disadvantages of TEMPO result from its relatively high price which is not tolerable in large-scale processes, and from its insolubility in water. Water-soluble derivatives such as 4-hydroxy-TEMPO or 4-amino-TEMPO are even more expensive and less stable.

Besides an approach to "livingness", the use of the above cited mediators in radical systems provide further benefits resulting from the depression of the Trommsdorf (gel) effect [13]. Especially in case of AA, this effect confines the concentrations at which a polymerization can practically be carried out, to 10÷15 wt%. Most often, however, higher polymer concentrations are desired for real applications. Therefore, indirect procedures were used to get concentrated aqueous solutions of PAA. In one instance [14] a multi-step process has been developed which is now exploited commercially. Five equal volumes of AA solutions (10 wt%) are introduced successively into the reactor, whereby the attention is focused on not introducing the next portion until the last one has polymerized to a high degree of conversion. The end product is provided as a 40% aqueous solution of PAA in Na-form. The aim of the present work was to eliminate the Trommsdorf effect in AA polymerizations carried out in concentrated aqueous solutions with the result of substituting the multi-step procedure by a single-step process. When decomposing,  $\text{NaNO}_2$  generates two paramagnetic nitroxides NO and  $\text{NO}_2$ . Therefore, it was also attempted to find out whether there could be an approach to "livingness".

## EXPERIMENTAL

### Materials

Acrylic Acid, AA (Sojuzchim, former USSR), reagent grade, was distilled under reduced pressure in a stream of argon and checked for purity by its refractive index and  $^1\text{H}$  NMR spectrum. Ammonium persulfate (APS) (Merck), analytically pure, was used as received. Acetone (POCH, Poland), reagent grade, was dried with zeolite 4A and distilled. Water was twice redistilled. Sodium nitrite (Merck), analytically pure, was used as received.

### Measurements and Analysis

Number-average molecular weight,  $\overline{M}_n$ , and weight-average molecular weight,  $\overline{M}_w$ , were determined using a GPC-chromatograph Hewlett-Packard HP-1090M connected to a computer equipped with diode detector registering between 290–600 nm. Two columns 300x7.5 mm each, Polymer Laboratories, packed with Plaquagel-OH were used. In front of both the columns there was a third one, 50x7.5 mm, having the same packing. The mobile phase consisted of a 0.25 M  $\text{NaNO}_3$  + 0.01 M  $\text{NaH}_2\text{PO}_4$  solution in water, adjusted to pH 7. Temperature 40°C, wavelength 210  $\mu\text{m}$ , and dose loop 20  $\mu\text{L}$ . For calibration standards of poly(acrylic acid) (Polyscience) were used providing a 3rd order calibration curve.

### Procedure

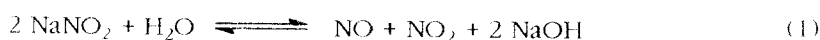
A 100 g weight of AA was introduced into a calibrated flask placed in an ice bath and neutralized to pH 7 (glass electrode) by saturated NaOH. Thereafter, 0.575 g of NaNO<sub>2</sub> were added, the content of the flask diluted to 250 cm<sup>3</sup> and flushed with a stream of argon. From the stock solution thus prepared, aliquots of 20 cm<sup>3</sup> (8 g AA) were taken and transferred into vials which subsequently were installed in a thermostated bath. The filled vials were thermostated at 60°C for 30 minutes, whereupon (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added into an amount of 0.253 g, thus matching the

$$\frac{n_i}{n_{[AA]_0}} = 0.01$$

molar ratio  $\frac{n_i}{n_{[AA]_0}}$ , where  $n_i$  denotes moles of initiator (APS) and  $n_{[AA]_0}$  moles of acrylic acid, respectively. The molar ratio of NaNO<sub>2</sub> vs (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was held constant at 1.5. The vials were sealed and warmed within 15 minutes to  $t = 90^\circ\text{C}$ . From that moment on, the preset time,  $\tau$ , of polymerization was measured. Thereafter, the vials were chilled, opened, and the contents precipitated into 7-fold volumes of acetone. Each sediment was brought quantitatively onto a filter, washed, and finally dried to constant weight for determination of the degree of polymerization  $\alpha$ .

## RESULTS AND DISCUSSION

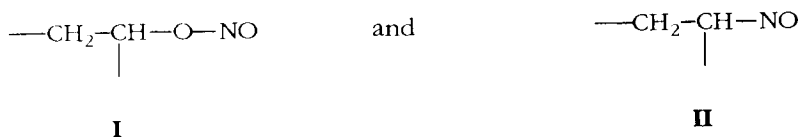
Sodium nitrite undergoes in aqueous media a reversible decomposition the equilibrium of which, illustrated by Equation 1, depends strongly on temperature:



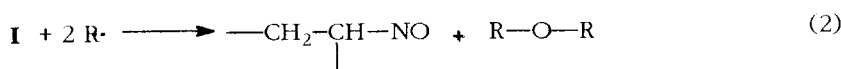
Nitric oxide is recommended elsewhere as a “volatile inhibitor” for acrylic monomers [2] and as a water-soluble inhibitor for acrylamide [15]. Generally, the role of an inhibitor is focused on retarding the onset of polymerization at room temperature. There are grounds to assume, however, that at higher temperatures some inhibitors will function differently.

Both the oxides residing on the right side of Equation 1 are paramagnetic. Nitric oxide has one odd electron in an antibonding  $\pi$  orbital. By electron shearing covalent species may result. Nitrogen dioxide, on the other hand, contains 17 electrons with one electron unpaired occupying either the nitrogen or oxygen atom, respectively. This is in agreement with the resonance structure of NO<sub>2</sub> having at least five canonical forms [16]. Consequently, two different types of species are expectedly to result from reactions between the two kinds of oxides and growing

radicals. One type may be represented by nitro-compounds **I**, and the other one by nitrite-compounds **II**, i.e.:



Further side-reactions involving nitrogroups cannot be ruled out and must be taken under consideration e.g.



It should be emphasized, that in aqueous solutions of NaAA, the sodium nitrite functions as an effective inhibitor up to 60°C only. Above that temperature, however, the results presented in Table 1 indicate a different behavior of NaNO<sub>2</sub> distinguishing it to be a mediator. In preliminary tests it was established that the molar ratio of mediator vs. initiator (I stands for (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was optimal

$$\frac{n_{\text{NaNO}_2}}{n_{\text{I}}} = 1.5.$$

This value was kept constant in all the polymerizations accomplished here. The designations of the polymers appear as NaAA<sub>t</sub>-NO-[M]<sub>0</sub> where NO indicates sodium nitrite used as mediator, [M]<sub>0</sub> denotes the initial monomer concentration, and t the temperature of polymerization. (The symbol 0 is used in the case where no mediator was used).

The non-mediated polymerization of acrylic acid (cf. PAA<sub>60-0-10</sub> in Table 1) initiated by (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> proceeds at 60°C very quickly and care should be taken to avoid autoacceleration in large-scale processes, although generally concentration [M]<sub>0</sub> = 10 g/dl is regarded to be a save in view of the gel effect.

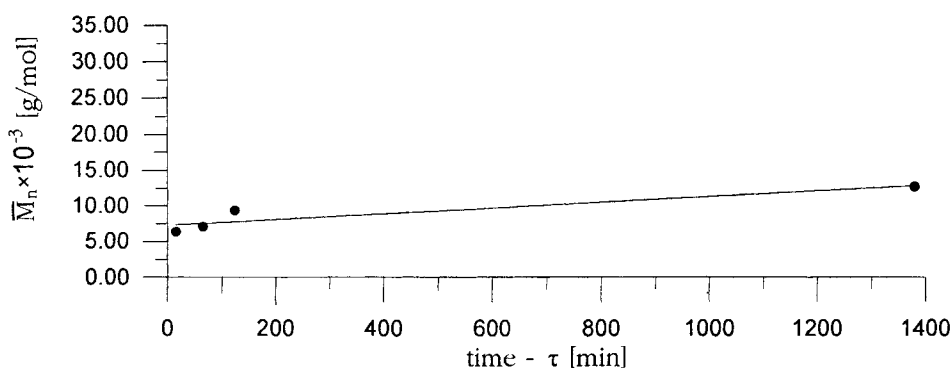
At 60°C, the decomposition of APS will continue over the entire polymerization time generating new radicals throughout. It assumed that in the presence of sodium nitrite the APS radicals and the growing radicals M<sub>n</sub><sup>•</sup> are capped by nitroxide, what generally may be depicted by the reaction:



TABLE 1. Degree of conversion ( $\alpha$ ); number-average molecular weight  $\bar{M}_n$ ; weight-average molecular weight  $\bar{M}_w$ ; coefficient of polydispersity  $D$  measured for the non-mediated poly(acrylic acid) PAA<sub>60</sub>-NO-10, and for NaNO<sub>2</sub> mediated polymers NaPAA<sub>60</sub>-NO-40, as well as NaPAA<sub>90</sub>-NO-40, after times of polymerization  $\tau$ , at temperatures  $t$ , using initial monomer concentration  $[M]_0$ .

Polymer	$t$ [°C]	$[M]_0$ [g/100 cm <sup>3</sup> ]	$\tau$ [min]	$\alpha$ [%]	$\bar{M}_n \times 10^{-3}$ [g/mol]	$\bar{M}_w \times 10^{-3}$ [g/mol]	$D = \frac{\bar{M}_w}{\bar{M}_n}$
<b>PAA<sub>60</sub>-0-10</b>	60	10	40	96	115.2	1130.2	9.81
<b>NaPAA<sub>60</sub>-NO-40</b>	60	40	24480	30	139.0	345.0	2.48
<b>NaPAA<sub>90</sub>-NO-40</b>	90	40	15	86.90	6.34	61.0	9.62
	90	40	65	80.90	7.03	65.6	9.33
	90	40	125	90.70	9.31	74.1	7.96
	90	40	1380	98.15	12.70	82.5	6.50

\*) 15 mins were required additionally to rise the temperature from 60°C to 90°C



**Figure 1.** Relation between number-average molecular weight  $\bar{M}_n$  and time of polymerization  $\tau$  for NaPAA<sub>90</sub>-NO-40.

In the case of NaAA the  $M_n^\bullet$  radical will be represented by  $\text{CH}_2=\dot{\text{C}}\text{H}-\text{COO}^\ominus$

The state of equilibrium in Equation 3 is important for acquiring living character. The criteria for this character are a linear increase of  $\bar{M}_n$  with conversion

$$D = \frac{M_w}{M_n}$$

$\alpha$  and a narrow coefficient of polydispersity. Two factors may play an important role in fulfilling both criteria. The first one is the time of duration of the active and dormant states, respectively, the second one refers to the equilibrium shift. For achieving true “livingness”, the equilibrium should not shift and the duration of both the states should be short and equal [17]. Data presented in Table 1 reveal that the system under consideration has no living character. At 60°C, the equilibrium lies (cf. NaPAA<sub>60</sub>-NO-40) almost exclusively on the dormant side. After two days, the degree of conversion was found to be  $\alpha = 30\%$  only.

An increase in temperature up to 90°C results in a rapid initial polymerization. After 15 minutes, (+ 15 minutes required to elevate the temperature from 60°C to 90°C) the degree of conversion reaches 87%. Further increase appears to be slow, and a complete loss of monomer, in practical terms ( $\alpha = 98.15\%$ ), is effected after 1380 minutes (i.e. ca. 23 hours). Therefore, the observed poor increase in  $\bar{M}_n$  with  $\alpha$  depicted in Figure 1 cannot be regarded as an approach to “livingness”. It is likely that in the case of the NaPAA<sub>90</sub>-NO-40 polymer, the APS radicals being generated in surplus at the very beginning of polymerization are at 90°C no longer capped effectively by the nitroxides. The result is a substantial shift of the equilibrium depicted by Equation 3 to the left side with longer duration of the active state. Consequently, due to statistical termination and transfer of the growing chains,



relative high coefficients of polydispersity are provided. The values ( $D = 9.62 \dots 6.50$  cf. Table 1) are of the same order as that of the conventional PAA<sub>60-0-10</sub> polymer having  $D = 9.81$ .

Nevertheless, the ability of sodium nitrite to control run-away reactions makes it possible to carry out polymerizations of acrylic acid in 40% aqueous solutions by employing the one-step process preferred for practical reasons.

More importantly, contrary to conventional inhibitors which must be removed just before polymerization, such a necessity does not exist in the case of NaNO<sub>2</sub> if the temperature of polymerization is set above 60°C. It must be taken into account, however, that a higher temperature decreases the molecular weight as is also shown in Table 1.

### ACKNOWLEDGMENT

The financial support by the State Committee for Scientific Research (Grant KBN 222/T09/09/95) is gratefully acknowledged.

### REFERENCES

- [1] W. M. Thomson and D. W. Wang, Acrylic Acid and Metacrylic Acid Polymers, *Encyclopedia of Polymer Science and Technology*, 2nd Ed., Vol. 1, H. F. Mark, N. M. Bikales, O. G. Overberger, and G. Menges, Eds., Wiley, New York 1985, p. 211.
- [2] R. A. M. Thomson, Acrylic and Metacrylic Acids, *Chemistry and Technology of Water Soluble Polymers*, C. A. Finch, Ed., Plenum Press, New York, 1985, p.53.
- [3] O. Nuyken and T. Völker, Acrylic Acid and Metacrylic Acid, *Handbook of Polymer Synthesis, Part A*, H. R Kricheldorf, Ed., Marcel Dekker, New York, 1992, p. 268.
- [4] A. Chapiro, *Eur. Polymer J.*, 9, 417 (1973).
- [5] A. Chapiro and J. Duliew, *Eur. Polymer J.*, 13, 563 (1977).
- [6] R. P. N. Veregin, M. K. Georges, P. M. Kazmaier, and G. K. Hamer, *Macromolecules*, 26, 2987 (1993).
- [7] M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, and G. K. Hamer, *Macromolecules*, 26, 2987 (1993).
- [8] D. Greszta, D. Mardare, and K. Matyjaszewski, *Macromolecules*, 27, 638 (1994).

- [9] D. Mardare and K. Matyjaszewski, *Macromolecules*, 27, 645 (1994).
- [10] M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, and G. K. Hamer, *Trends in Polymer Science*, 2, 66 (1995).
- [11] B. Koeshkerian, M. K. Georges, and D. Boils-Boissiev, *Makromol. Chem. Rapid Commun.*, 3, 225 (1982).
- [13] M. K. Georges, M. Saban, N. P. N. Veregin, G. K. Hamer, and P. M. Kazmaier, *Polymer Preprints*, 35(2),737 (1994).
- [14] S. Kudla, Doctor Thesis, Jagellonian University, Cracow, 1994.
- [15] S. R. Sandler and W. Karo, *Polymer Synthesis*, Vol.1, 2nd Ed. Academic Press, New York, 1994, p. 422.
- [16] P.J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry*, Longmans, London, 1962, p. 661, 671.
- [17] S. Penczek, *Polimery*, 40, 384 (1995).

Received February 5, 1997

Revision received October 1, 1997