

# Kinetics and Mechanism of the $K_2CrO_4$ – $NaAsO_2$ Redox-Initiated Aqueous Polymerization of Acrylonitrile

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**ABSTRACT:** The kinetics and mechanism of acrylonitrile polymerization initiated by a redox pair [potassium chromate ( $K_2CrO_4$ ) and sodium arsenite ( $NaAsO_2$ )] were studied. The overall rate of polymerization was proportional to  $\sqrt{[K_2CrO_4] \times [NaAsO_2]}$ , and the energy of activation was approximately 10.5 kJ/mol. Polyacrylonitrile was recovered as a coagulum in the medium. The formation of polyacrylonitrile was confirmed with Fourier transform infrared and  $^1H$ -NMR analyses. Scanning electron microscopy analysis of the polymer revealed the formation of aggregates of poly-

mer particles (3–67 nm). Thermogravimetric studies indicated 50% weight loss at 400°C, and dynamic thermal analysis scan studies revealed an exothermic peak at 507°C due to massive oxidative thermal degradation of the polyacrylonitrile backbone. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 276–280, 2005

**Key words:** redox polymerization; acrylonitrile; activation energy

## INTRODUCTION

A vast literature<sup>1–8</sup> on the aqueous polymerization of conventional vinyl monomers by a variety of redox initiator systems exists. Some recent work has used interesting redox combinations, such as  $Mn^{3+}$  and poly(ethylene glycol)<sup>9</sup> or lactic acid,<sup>10,11</sup> for the polymerization of vinyl monomers. Ammonium persulfate and potassium persulfate based systems were have used been for the dispersion polymerization of acrylamide and the microemulsion polymerization of methyl methacrylate and *n*-butyl acrylate monomers,<sup>12,13</sup> respectively. Redox polymerization studies involving  $Cr^{+6}$  as an oxidant are very few. Of the various reducing agents examined by us for use in combination with  $Cr^{+6}$ , including  $Na_2S_2O_3$ ,  $FeSO_4$ , and  $SnCl_2$ ,  $Na_2AsO_2$  was found to be very efficient for acrylonitrile (AN) polymerization in an aqueous medium. In this article, we highlight the kinetic and mechanistic aspects of the polymerization of AN by the potassium chromate ( $K_2CrO_4$ )–sodium arsenite ( $NaAsO_2$ ) redox pair.

An additional reason for choosing  $Cr^{+6}$  as an oxidant was our observation that the aqueous polymerizations of some specialty monomers such as pyrrole (PY) and aniline (ANI) could be induced by this oxi-

dant. These polymers, polypyrrole (PPY) and polyaniline (PANI), are well known for their conductivity. Accordingly, we felt that a fairly wide range existed for the preparation of binary polymer composites of vinyl polymers with PPY or PANI in the same redox system, which would exhibit characteristically high conductivity values.

## EXPERIMENTAL

### Materials

AN (Aldrich, Milwaukee, WI) was freed from inhibitors by successive washings with a dilute sodium carbonate solution, dilute sulfuric acid, and distilled water. It was kept overnight over calcium chloride and distilled in an all glass apparatus. The fraction boiling at 77–78°C was collected and stored carefully.  $K_2CrO_4$  (Riedel, Germany) and  $NaAsO_2$  (Riedel) were used as the oxidant and reductant, respectively. All other solvents were analytical-grade and were freshly distilled before they were used.

### Polymerization of AN with the $K_2CrO_4$ – $NaAsO_2$ redox system

In a Pyrex flask, a definite amount ( $1.8$ – $3.0 \times 10^{-3}$  mol) of  $K_2CrO_4$  was dissolved in 30 mL of distilled water, to which 0.02 mol of AN was injected. The system was kept under stirring at the ambient temperature under an  $N_2$  atmosphere for 10 min, and thereafter, a definite amount ( $3.8 \times 10^{-4}$  to  $2.3 \times 10^{-3}$  mol) of  $NaAsO_2$  was dissolved into this solution. The in-

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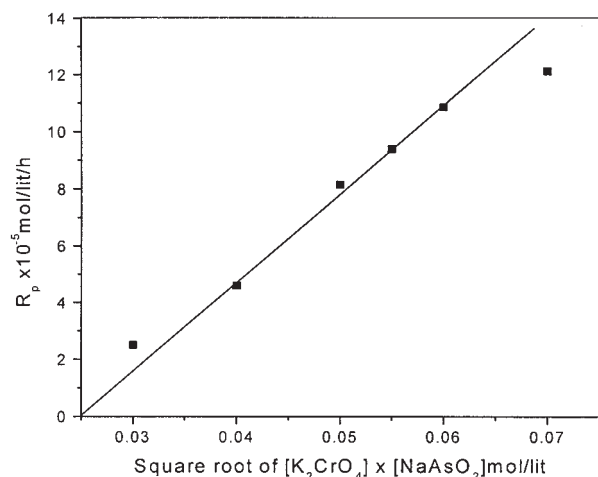
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duction periods were within 3–5 min, and the polymerization was allowed to continue for 2–6 h. Afterward, the white polymer was centrifuged, washed in succession with distilled water, methanol, and acetone, and finally dried *in vacuo* for 12 h. The conversions were estimated gravimetrically. The rate of polymerization ( $R_p$ ) was calculated from the slope of the conversion–time plots.

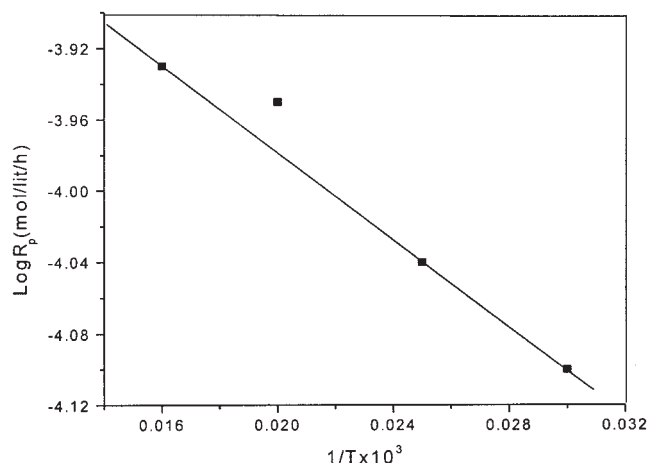
For the evaluation of the activation energy, the polymerizations were conducted at 30, 40, 50, and 60°C with fixed initial feed compositions ( $[AN] = 0.75$  mol/L,  $[K_2CrO_4] = 0.06$  mol/L,  $[NaAsO_2] = 0.05$  mol/L).

### Characterization and property evaluation of the polyacrylonitrile (PAN) homopolymer

End-group analysis for the presence of arsenic in the polymer was performed spectrophotometrically with the silver diethyl dithiocarbamate (SDDC) method detailed by Vogel.<sup>14</sup> The intrinsic viscosity ( $[\eta]$ ) of the PAN homopolymer was determined with an Ostwald viscometer in a dimethylformamide solution at 25°C, and the molecular weight was calculated with the Ueberreiter–Springer equation:  $[\eta] = 16.6 \times 10^{-5} \times M^{0.81}$ .<sup>15,16</sup> The Fourier transform infrared (FTIR) spectra of the PAN homopolymer were taken on a Jasco (Essex, United Kingdom) 410 instrument in pressed KBr pellets. <sup>1</sup>H-NMR spectra were obtained in DMSO at room temperature with a Bruker (Germany) instrument at 300 MHz. The surface morphologies of the polymers were studied with scanning electron microscopy (SEM) micrographs (S415A, Hitachi). Thermogravimetric analyses were performed on a Shimadzu (Kyoto, Japan) DT-40 instrument.



**Figure 1** Dependence of  $R_p$  on the square root of the product of  $[K_2CrO_4]$  and  $[NaAsO_2]$  ( $[AN] = 0.75$  mol/L).



**Figure 2** Dependence of  $R_p$  on the reaction temperature ( $[AN] = 0.75$  mol/L,  $[K_2CrO_4] = 0.06$  mol/L,  $[NaAsO_2] = 0.05$  mol/L).

## RESULTS AND DISCUSSION

### General features of the polymerization of AN

The aqueous polymerization of AN could not be induced by  $Cr^{6+}$  or  $AsO_2^-$  alone under ambient and higher temperature conditions. Polymerization occurred only when both constituents were present in the reaction mixture.

With the recipe used in this study, the polymerizations were pretty fast, and after an induction period of 3–5 min, the appearance of a milky white suspension of PAN was noted. At the end of the polymerization time, the suspension coagulated in the medium, which was centrifuged, and the conversion percentage was determined gravimetrically. The PAN homopolymer thus collected was characterized with FTIR spectroscopy. The molecular weight of the polymer, determined viscometrically, was  $7.9 \times 10^4$ .

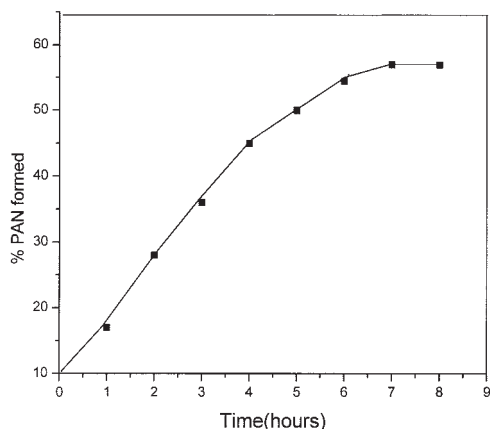
Figure 1 shows that the initial  $R_p$  varied linearly with the square root of the product of  $[K_2CrO_4]$  and  $[NaAsO_2]$ . Figure 2 shows the Arrhenius plot for the polymerization, and the overall energy of activation was determined to be approximately 10.5 kJ/mol. Figure 3 shows that the percentage of PAN that formed increased progressively to a limiting value with the time of the polymerization at a fixed initial feed composition of the polymerization.

### Spectroscopic analysis of the prepared polymer

The formation of PAN in this system was endorsed by spectroscopic analyses.

### FTIR characteristics

The FTIR scan (Fig. 4) of the prepared polymer revealed the manifestation of peaks at 2939 (C—H

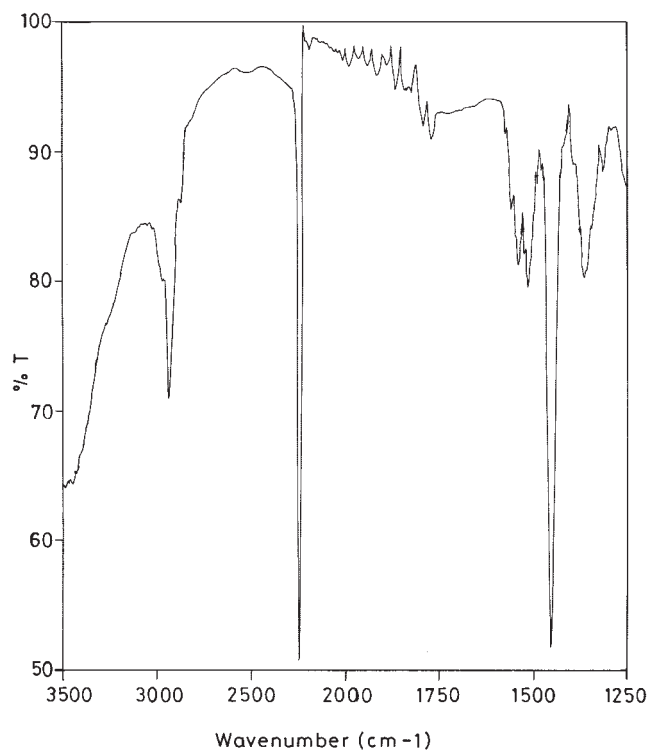


**Figure 3** Dependence of the percentage of the formed polymer on the reaction time ( $[\text{AN}] = 0.75 \text{ mol/L}$ ,  $[\text{K}_2\text{CrO}_4] = 0.06 \text{ mol/L}$ ,  $[\text{NaAsO}_2] = 0.05 \text{ mol/L}$ ).

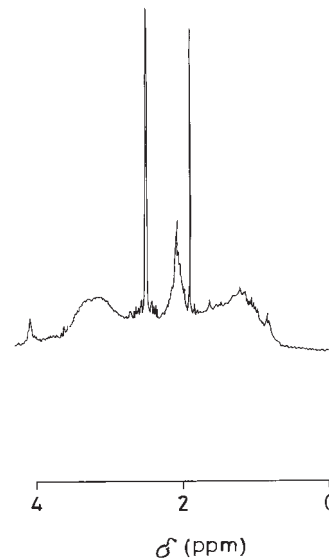
stretching),  $2250 \text{ cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretching), and  $1454 \text{ cm}^{-1}$  ( $\text{C}-\text{H}$  bending), which matched with the reported FTIR spectra for PAN.<sup>17-19</sup>

### $^1\text{H-NMR}$ analysis

The  $^1\text{H-NMR}$  spectrum (Fig. 5) for the prepared polymer showed two prominent peaks<sup>9</sup> at 2.5 ( $\alpha$ -hydrogen with respect to CN) and 1.9 ppm ( $\text{CH}_2$ ).



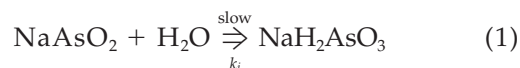
**Figure 4** FTIR spectrum of the PAN homopolymer.



**Figure 5**  $^1\text{H-NMR}$  spectrum of the PAN homopolymer.

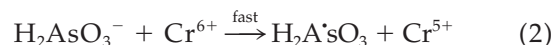
### Mechanism of the polymerization

The aqueous polymerization of AN could not be induced by  $\text{Cr}^{6+}$  or  $\text{AsO}_2^-$  alone under ambient or higher temperature conditions. Polymerization occurred only when both constituents were present in the reaction mixture. According to Smedley and Kinniburgh,<sup>20</sup> when  $\text{NaAsO}_2$  was dissolved in water, the reaction occurred, as shown in eq. (1), in the pH range of 8-9. It is well established<sup>21</sup> that the anion  $\text{H}_2\text{AsO}_3^-$  possesses a pyramidal structure with one lone pair on the As atom:

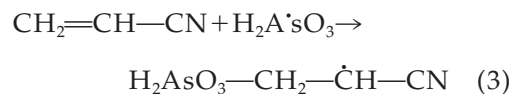


where  $k_i$  is the rate constant.

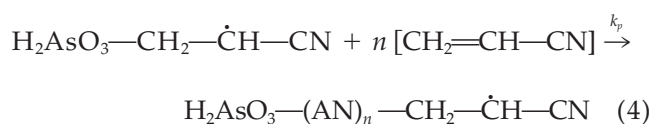
On the addition of  $\text{Cr}^{6+}$ , reduction activation<sup>22</sup> via the oxidizing metal ion  $\text{Cr}^{6+}$  and the reducing  $\text{H}_2\text{AsO}_3^-$  ion leads to a single electron-transfer reaction,<sup>22</sup> as shown in eq. (2), with the free radical on the As atom:



Thus, the AN polymerization can proceed as follows. For initiation



For propagation



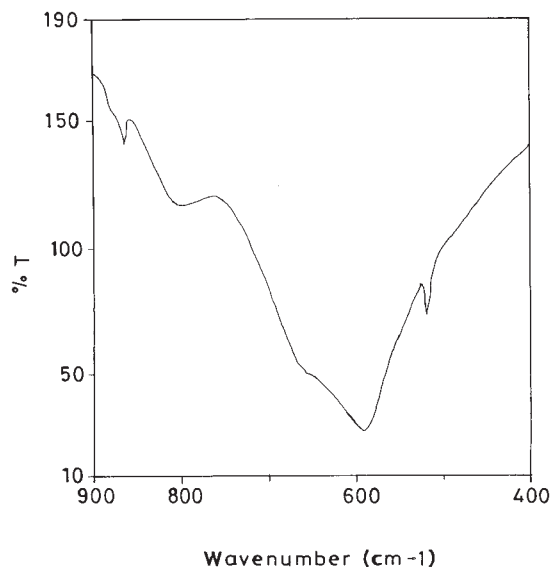
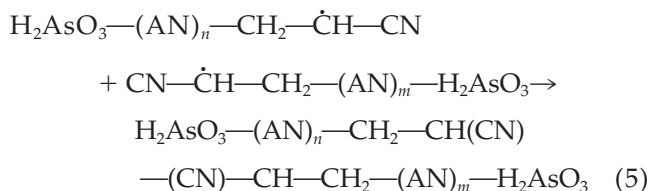


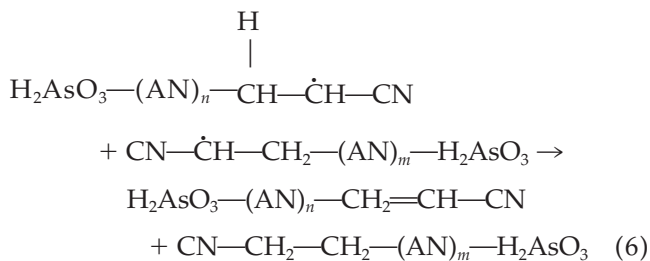
Figure 6 FTIR spectrum for the confirmation of As in the PAN homopolymer.

where  $k_p$  is the rate constant.

Termination can involve either coupling



or disproportionation



#### Evidence for the presence of As in the polymer and the nature of the bond between $\text{H}_2\text{AsO}_3$ and the polymer

##### End-group analysis

Using 1 g of the polymer with the SDDC method, we obtained  $2 \times 10^{-3}$  g of arsenic. These data corresponded to 2 mol of arsenic/mol of the polymer. This was consistent with chain termination by a coupling reaction [eq. (5)].

##### FTIR analysis

The formation of the As—C bond, as expected from the initiation scheme, was endorsed by the appearance of two peaks at 536 and at 580  $\text{cm}^{-1}$  in the FTIR scan for the polymer in the 400–900- $\text{cm}^{-1}$  range (Fig. 6). As established by Borisov et al.,<sup>23</sup> these corresponded to symmetric stretching (570–563  $\text{cm}^{-1}$ ) and asymmetric stretching (540  $\text{cm}^{-1}$ ) for the As—C single bond. Another peak manifesting at 860  $\text{cm}^{-1}$  was due to As—O stretching, as reported by Goldberg and Johnston.<sup>24</sup>

##### Kinetics of polymerization

On the basis of the aforementioned mechanism, the following expression for  $R_p$  may be derived for steady-state conditions:

$$R_i = 2k_i[\text{H}_2\text{AsO}_3^-][\text{Cr}^{6+}] \quad (7)$$

$$R_p = k_p[\text{CH}_2=\text{CH}-\text{CN}][\text{H}_2\text{AsO}_3-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CN}]_n \quad (8)$$

$$R_i = 2K_i[\text{H}_2\text{AsO}_3-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CN}]_n^2 \quad (9)$$

where  $R_i$  is the rate and  $k_i$  is the rate constant.

$R_i$  is equal to  $R_t$  under steady-state conditions:

$$\begin{aligned} & [\text{H}_2\text{AsO}_3-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CN}]_n^2 = k_i/k_t[\text{H}_2\text{AsO}_3^-][\text{Cr}^{6+}] \\ & [\text{H}_2\text{AsO}_3-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CN}]_n \\ & = \text{Constant} \sqrt{[\text{H}_2\text{AsO}_3^-][\text{Cr}^{6+}]} \\ & = \text{Constant} \sqrt{[\text{AsO}_2^-][\text{Cr}^{6+}]} \quad (10) \end{aligned}$$

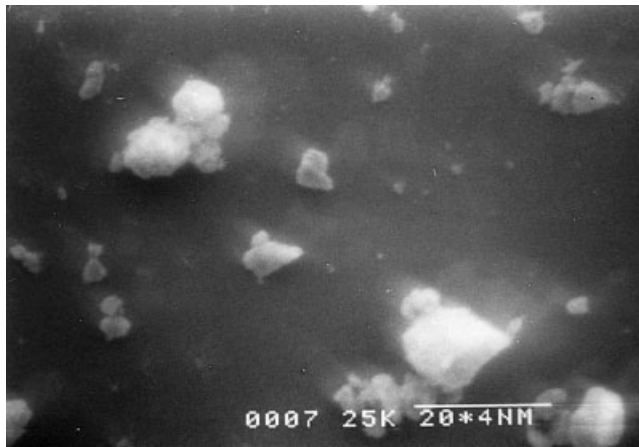


Figure 7 SEM photograph of the PAN homopolymer.

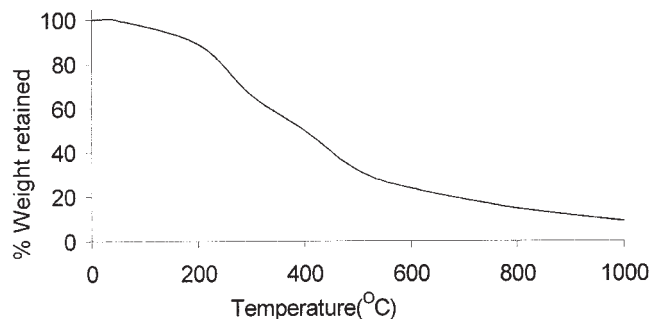


Figure 8 TGA of the PAN homopolymer.

According to eq. (1), the  $\text{H}_2\text{AsO}_3^-$  concentration is proportional to the  $\text{AsO}_2^-$  concentration. Therefore, combining eqs. (8) and (10), we obtain

$$R_p = \text{Constant}[\text{CH}_2=\text{CH}-\text{CN}] (\sqrt{[\text{AsO}_2^-][\text{Cr}^{6+}]}) \quad (11)$$

This equation is consistent with the kinetic pattern in Figure 1.

### Some properties of PAN obtained in this system

#### SEM analysis

The morphology of the PAN homopolymer, as studied by SEM analysis (Fig. 7), was essentially indicative of the formation of small (3–15 nm) and large lumps (20–67 nm) with no definite pattern.

#### Thermogravimetric stability

Figure 8 shows a thermogram of the PAN homopolymer. The polymer lost approximately 10% of its weight at 200°C, and this was mostly due to a loss of volatile impurities, as no exothermic hump was found in this region by the differential thermal analysis (DTA) scan. A 50% weight loss of the polymer occurred at 400°C, and 90% occurred at 1000°C.

The DTA scan for the PAN homopolymer revealed a sharp exothermic peak at 507°C corresponding to the region of maximum weight loss (300–600°C). In this region, PAN suffered massive oxidative degradation.

#### Conductivity characteristics

The direct-current conductivity of the PAN homopolymer prepared in this system was approximately  $10^{-11}$  S/cm. However, the addition of PY and ANI to the AN/ $\text{K}_2\text{CrO}_4$ – $\text{NaAsO}_2$  system in the presence of  $\text{Cr}^{+6}$  in a 2N HCl medium produced PPY–PAN and PANI–PAN binary composite systems, which displayed much improved conductivity (ca.  $10^{-3}$  and  $10^{-4}$  S/cm, respectively). These studies will be reported in detail elsewhere.

## CONCLUSIONS

The  $\text{K}_2\text{CrO}_4$ – $\text{NaAsO}_2$  redox pair initiated the aqueous polymerization of AN.  $R_p$  was proportional to  $\sqrt{[\text{K}_2\text{CrO}_4] \times [\text{NaAsO}_2]}$ , and an appropriate mechanism was proposed. Preliminary studies revealed that  $\text{CrO}_4^{2-}$  could initiate the polymerization of ANI or PY in an aqueous medium, and this feature had a wide range for preparing binary PANI–PAN and PPY–PAN composites with conductivity of approximately  $10^{-3}$  and  $10^{-4}$  S/cm, respectively. These values were much better than that of the PAN homopolymer ( $10^{-11}$  S/cm).

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