Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Renders, G. , Broze, G. , Jérôme, R. and Teyssié, Ph.(1981) 'Acrylonitrile Polymerization by Ceric Ion-Primary Alcohol Redox Systems in Aqueous Nitric Acid', Journal of Macromolecular Science, Part A, 16: 8, 1399 — 1412
To link to this Article: DOI: 10.1080/00222338108063244
URL: http://dx.doi.org/10.1080/00222338108063244

J. MACROMOL. SCI.–CHEM., A16(8), pp. 1399-1412 (1981)

Acrylonitrile Polymerization by Ceric Ion-Primary Alcohol Redox Systems in Aqueous Nitric Acid

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ABSTRACT

The polymerization of acrylonitrile (AN) initiated by Ce^{IV}-primary alcohol redox systems has been studied in aqueous nitric acid under nitrogen in the temperature range 0 to 45°C. Taft's correlation can be applied to fit the kinetic results relative to a series of differently substituted primary alcohols. The polymerization is initiated by primary radicals formed in water from the dismutation of the Ce^{IV}-alcohol complex. This process has a high activation energy (21 kcal/mol) and gives rise to an induction period at temperatures lower than 40°C. PAN chains containing the alcohol residue are terminated predominantly on metal ions. The alcohol enhances the AN solubility in water and accordingly influences the polymerization kinetics. Variations in temperature and concentration of both components of the redox system allow control of the polymerization rate and of the molecular weight of the resulting PAN.

INTRODUCTION

Redox systems are largely used as initiators in radical and more especially in emulsion polymerization [1, 2]. They have the prime advantage of operating at reasonable rates at very moderate temperatures (approximately 0-50°C). Furthermore, they offer an efficient way to attach a functional group at the end(s) of the polymer chains formed. When such reducing substrates as alcohols (ethanol [3], propane-1,2-diol [4], glycol [5], cyclohexanol [6]), amines (di- or triethylamine [7], ethanolamines [8]), or reducing acids (thiomalic [9], ascorbic [10], malonic [11] acids) are added together with Ce(IV), V(v), Co(III), and Mn(III) salts in the presence of acrylic or styrenic monomers, polymerization takes place and yields chains containing the substrate.

The kinetic and mechanistic aspects of these polymerizations have been analyzed, but the conclusions of these studies have often been in disagreement. This situation is related to the complexity of redox processes involving both an organic substrate and an inorganic salt. Complexes are formed but their nature and their relative concentrations are affected by any change in the experimental conditions [5]. The radical production as well as the polymerization rate are accordingly dependent on the choice of the experimental parameters. Furthermore, the monomer can be completely soluble (i.e., acrylamide) or not (i.e., acrylonitrile) in the reaction medium. For all these reasons, kinetic results are often valid only for the particular conditions defined in each work.

Acrylonitrile (AN) polymerization initiated by redox systems in aqueous media has been thoroughly considered [4-6, 10, 12-16]. Surprisingly, the mechanistic schemes proposed do not take into account the heterophase character of the reaction medium due to the partial insolubility of AN. This peculiar characteristic is considered in this work, wherein the AN polymerization is initiated by cerium ammonium nitrate/alcohol redox systems in aqueous nitric acid. A series of differently substituted primary alcohols was selected to analyze the effect of these substituents on the relative reactivity in redox polymerizations. Temperature and concentration of both alcohol and cerium salt are evaluated as molecular weight-controlling parameters.

EXPERIMENTAL PART

Materials

Acrylonitrile (Aldrich) was freed from inhibitor and distilled under nitrogen. The reagents (ceric ammonium nitrate, nitric acid, and alcohols) were Aldrich products used without further purification. Water was doubly distilled over alkaline permanganate.

Polymerization

Forty milliliters of water and 10 mL of 10^{-1} mol/L HNO_3 aqueous solution were added into a 100-mL flask equipped with a thermocouple. The mixture was deaerated by passing nitrogen for about 15 min. Five milliliters of AN were added under N_2 and the flask thermostated at the appropriate temperature. The calculated amounts of cerium salt and alcohol were also added under N_2, and the reaction flask immediately set in an isolating box, the thermal loss of which was very low, and standardized between 0 and 45° C. The temperature variation was recorded and corrected for thermal losses.

The polymer formed was poured into a large excess of acetone, filtered off, washed, and dried to constant weight. The viscosity of its dilute solutions in dimethylformamide was measured at 25° C by use of the Desreux-Bischoff dilution viscometer [17]. The viscometric relationships $[\eta] = 57.4 \times 10^{-5} M^{0.73}$ was used to calculate the mean viscometric molecular weight [18].

RESULTS

Kinetic Study

The kinetics of the AN polymerization was determined by recording the temperature variation in adiabatic conditions. Figure 1 is a representative curve recorded at room temperature. An induction time is observed; it corresponds approximately to the onset of turbidity in the reaction medium. The slope at the inflection point of the temperature-time curve, or $(\Delta T/dt)_{max}$, was used to represent the polymerization rate (R_p in °C/min).

The AN is polymerized at room temperature by the Ce^{IV}/ethanol redox initiator. In a first series of polymerizations, the ethanol concentration is modified whereas all the other parameters are kept constant: $[H^+] = 1.8 \times 10^{-3}$ mol/L, $[Ce^{IV}] = 3 \times 10^{-2}$ mol/L, and $[AN] = 1.5$ mol/L. The AN concentrations are systematically calculated by assuming a complete solubility of AN in water. Table 1 and Fig. 2 summarize the kinetic results and agree with an apparent 0.5 order with respect to the alcohol at concentrations lower than 0.35 mol/L. At higher concentrations the polymerization rate is independent of the amount of alcohol.

In a second series of polymerizations, the cerium salt concentration is modified at a constant concentration of ethanol (10^{-1} mol/L), H^+ (1.8×10^{-3} mol/L), and AN (1.5 mol/L). R_p values are reported in Table 1 and Fig. 3. It is only beyond a cerium salt concentration of about 10^{-2} mol/L that the polymerization rate is significant and practically independent on this reagent.

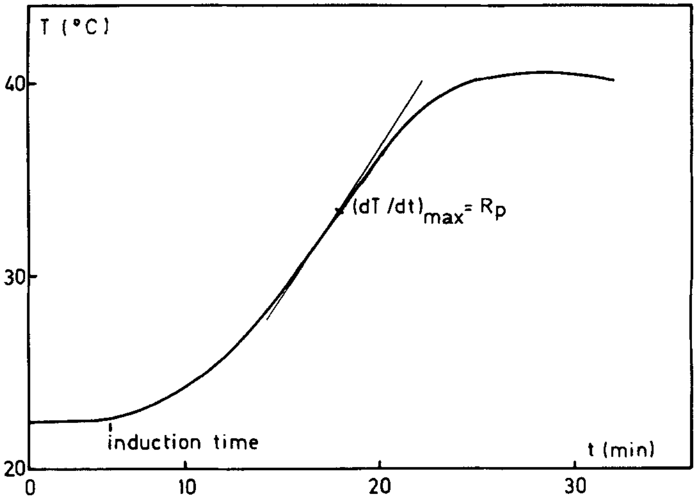

FIG. 1. Temperature versus time curve. Experimental conditions: $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[Ce^{IV}] = 0.03$ mol/L, $[C_2H_5OH] = 0.1$ mol/L. Initial temperature: 22°C.

TABLE 1. Effect of Cerium Salt and Alcohol Concentrations on the AN Polymerization Rate (R_p)[a]

Effect of Ce^{IV} concentration[b]		Effect of ethanol concentration[c]	
$[Ce^{IV}]$ mol/L ($\times 10^3$)	Rp (°C/min)	$[C_2H_5OH]$ mol/L	Rp (°C/min)
7.5	0.10	0.05	1.20
15	1.20	0.10	1.25
30	1.25	0.20	1.80
60	1.50	0.35	2.20
		0.50	2.30
		1.00	2.30

[a] $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, initial temperature = 22°C.

[b] $[C_2H_5OH] = 0.1$ mol/L.

[c] $[Ce^{IV}] = 0.03$ mol/L.

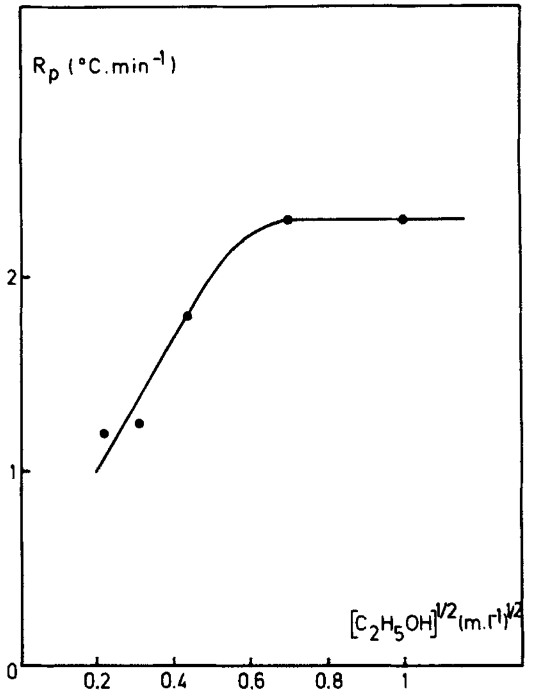

FIG. 2. AN polymerization rate versus square root of ethanol concentration. $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[Ce^{IV}] = 0.03$ mol/L. Initial temperature: 22°C.

Both the induction time and the polymerization rate depend on the temperature. The results mentioned in Table 2 are obtained for $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[Ce^{IV}] = 3 \times 10^{-2}$ mol/L, and [alcohol] = 10^{-1} mol/L. The higher the temperature, and the shorter the induction time; the latter is longer than 1 d at 0°C, but vanishes completely at 46°C. The polymerization yield is quantitative only from 20°C and above.

The Arrhenius equation, applied to the induction time and the polymerization rate as shown by Fig. 4, yields an activation energy of 21 kcal/mol for the induction process, whereas the one for polymerization is 4 times lower (5.5 kcal/mol). As proposed in the literature [5, 7, 19-22], the induction can be related to the disproportionation of the reversible Ce^{IV}/alcohol complex [C] (Eq. 1) in a rate-determining step:

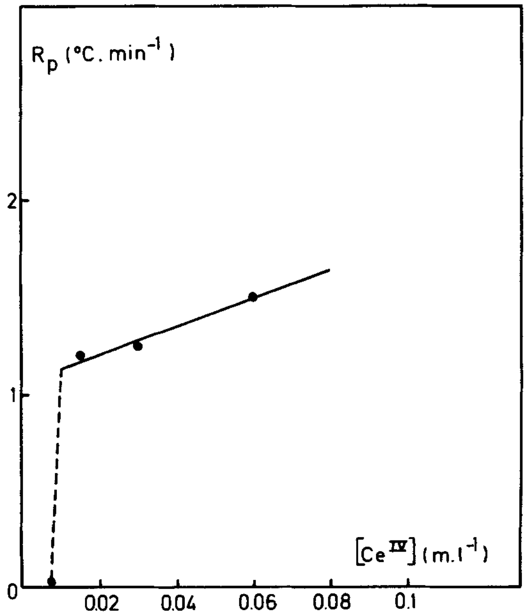

FIG. 3. AN polymerization rate versus Ce^{IV} concentration. $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[C_2H_5OH] = 0.1$ mol/L. Initial temperature: 22°C.

TABLE 2. Dependence of the Induction Time and the Polymerization Rate on the Temperature[a]

Initial temperature (°C)	Induction time (min)	Polymerization rate (°C/min)
0	b	b
9	960	d
16	16	d
22	6	1.25
32	2.4	1.70
39	1.2	2.00
46	c	3.00

[a] $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[C_2H_5OH] = 0.1$ mol/L, $[Ce^{IV}] = 0.03$ mol/L.

[b] Longer than 1 d.

[c] Too short to be measured accurately.

[d] Too slow to be determined accurately.

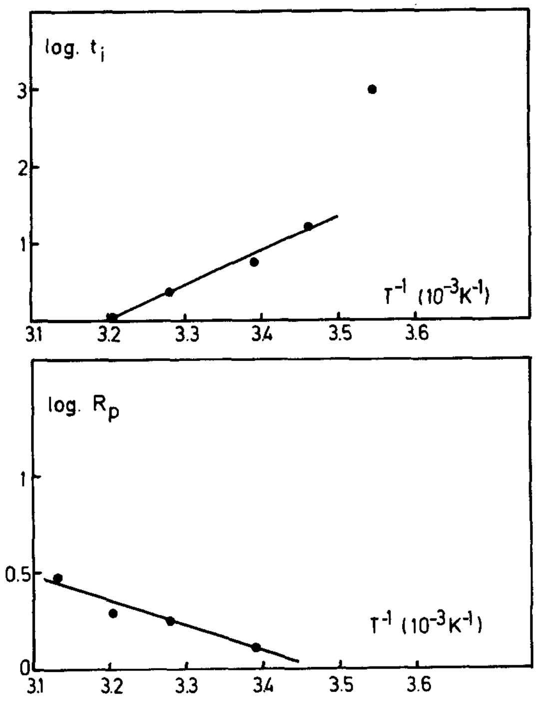

FIG. 4. Arrhenius plot relative to the induction time (t_i) and the polymerization rate (R_p). [H^+] = 1.8 × 10^{-3} mol/L, [AN] = 1.5 mol/L, [Ce^{IV}] = 0.03 mol/L, [C_2H_5OH] = 0.1 mol/L.

$$Ce^{IV} + R{-}CH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow{k_d} R{-}\dot{C}H{-}OH + Ce^{III} + H^+ \quad (1)$$

Effect of the Substitution of the Alcohol

To further clarify the mechanism of the AN polymerization by the Ce^{IV}-primary alcohol redox system in aqueous nitric acid, a series of differently substituted primary alcohols has been considered. Table 3 summarizes the kinetic results together with the characteristics of the RCH_2OH alcohols used [23] (σ^* is the polar substituent constant and E_S is the steric substituent constant for R).

Figure 5 shows Taft's correlations [24] obtained from the experimental results. By applying the least-squares method, it is determined that

TABLE 3. Effect of the Substitution of the Primary Alcohol ($-CH_2OH$) on the Polymerization Rate[a]

Alcohol	Polar constant, σ^*	Steric constant, E_S	Log R_p	Log $\frac{R_p}{(R_p)_{C_2H_5OH}}$
CH_3-CH_2OH	0.00	0.00	0.09	0.00
$C_2H_5-O-CH_2-CH_2OH$	0.52	-0.19	0.00	-0.09
$BrCH_2-CH_2OH$	1.00	-0.27	-0.30	-0.39
$C_2H_5-O-CO-CH_2OH$	1.65	-0.00	-0.22	-0.31
F_3C-CH_2OH	2.80	-2.00	-1.10	-1.19

[a] $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, $[Ce^{IV}] = 0.03$ mol/L, [alcohol] = 0.1 mol/L, initial temperature = 22° C.

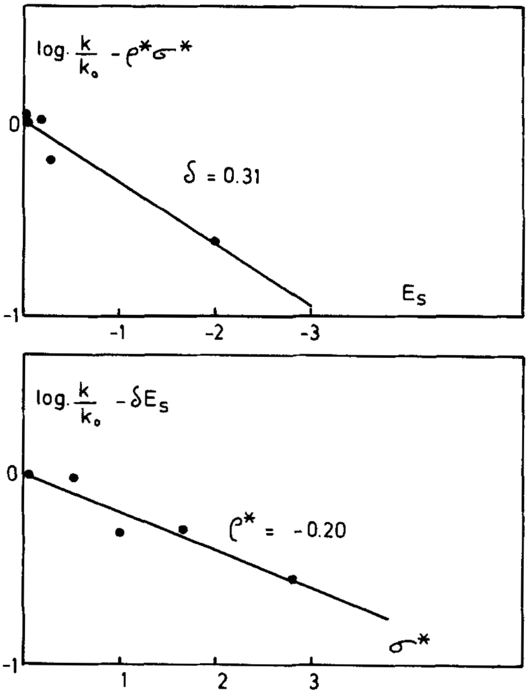

FIG. 5. Determination of the Taft's polar (ρ^*) and steric (δ) parameters.

$$\log \frac{R_p}{(R_p)_{C_2H_5OH}} = -0.2\sigma^* + 0.3E_S \qquad (2)$$

As the coefficient of σ^* ($\rho^* = -0.2$) is close to zero, the mechanism must be essentially radical. Furthermore, it is very lightly sensitive to steric effects as proved by the low value of the coefficient of E_S (δ, steric susceptibility constant, = 0.3).

Control of the Molecular Weight

It is important in practice to master the production of PAN with controlled molecular weight. In that respect, the influence of such experimental parameters as temperature and concentration of both cerium salt and alcohol has been analyzed; n-butanol has been used in this study.

Table 4 and Fig. 6 show that the viscometric average molecular weight ($\overline{M}_v$) decreases as the cerium salt concentration increases. Similarly, increasing amounts of alcohol are responsible for decreasing molecular weights which tend, however, to a lowest limiting value (Table 4, Fig. 7).

As the induction process, i.e. the radicals formation (Eq. 1), has a largely higher activated energy than the polymerization itself, an increase of temperature should decrease the molecular weight. The experimental results agree with this expectation (Table 4).

End-Group Analysis

To confirm the incorporation of the substrate at the end of the PAN chains, i.e., their hydroxyl end-functionalization, the AN has been polymerized in the presence of 1,3-bis(dimethylamino)-2-propanol. The concentrations used are the following: $[H^+] = 1.8 \times 10^{-3}$ mol/L, $[AN] = 1.5$ mol/L, $[Ce^{IV}] = 3 \times 10^{-2}$ mol/L, and $[\text{alcohol}] = 10^{-1}$ mol/L.

After recovery and purification of the PAN formed, the dimethylamino groups have been titrated by p-toluenesulfonic acid in DMF. Assuming one bis(dimethylamino) group per PAN chain, a number-average molecular weight ($\overline{M}_n$) of 59,000 is calculated whereas the mean viscometric molecular weight rises to 94,000; the $\overline{M}_v/\overline{M}_n$ ratio is accordingly 1.6, i.e., a reasonable value for a radical polymerization.

TABLE 4. Effect of the Ce^{IV} and Alcohol Concentrations and the Temperature on the PAN Molecular Weight ($\overline{M}_v$)[a]

Effect of $[Ce^{IV}]$[b]		Effect of [n-butanol][c]		Effect of temperature[d]	
$[Ce^{IV}]$ mol/L ($\times 10^{-3}$)	$\overline{M}_v$ ($\times 10^{-3}$)	[Butanol] mol/L	$\overline{M}_v$ ($\times 10^{-3}$)	T (°C)[e]	$\overline{M}_v$ ($\times 10^{-3}$)
7	Gel	0.04	Gel	22	8
15	90	0.10	Gel	32	7
30	37	0.20	80	42	6
55	8	0.40	37		
		1.00	32		

[a] $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L.
[b] [Butanol] = 0.4 mol/L, initial temperature = 22° C.
[c] $[Ce^{IV}] = 3.0 \times 10^{-2}$ mol/L, initial temperature = 22° C.
[d] $[Ce^{IV}] = 5.5 \times 10^{-2}$ mol/L, [n-butanol] = 0.4 mol/L.
[e] Initial temperature.

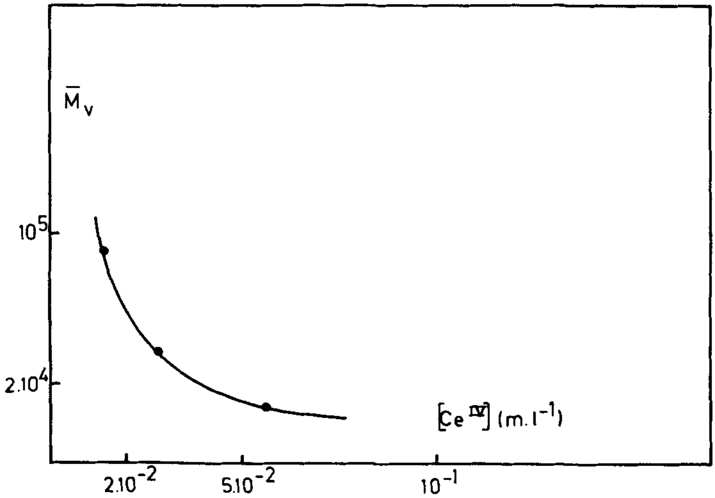

FIG. 6. Viscosimetric average molecular weight ($\overline{M}_v$) versus Ce^{IV} concentration. $[H^+] = 1.8 \times 10^{-3}$ mol/L, [AN] = 1.5 mol/L, [n-butanol] = 0.4 mol/L. Initial temperature: 22° C.

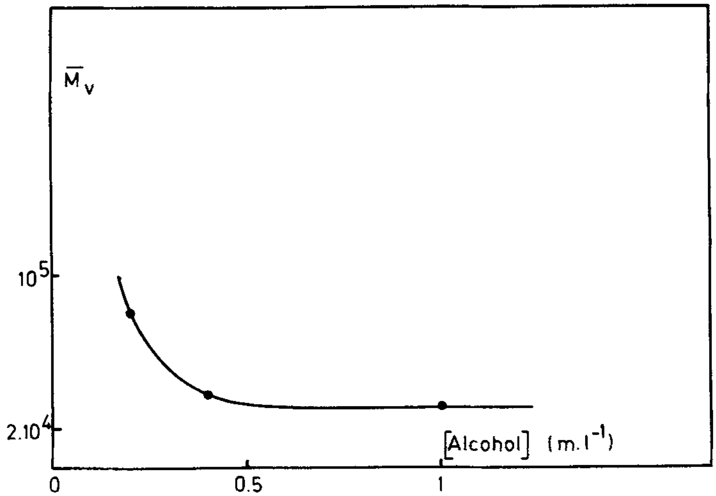

FIG. 7. Viscosimetric average molecular weight ($\overline{M}_v$) versus n-butanol concentration. [H^+] = 1.8×10^{-3} mol/L, [AN] = 1.5 mol/L, [Ce^{IV}] = 0.03 mol/L. Initial temperature: 22°C.

DISCUSSION

The experimental results, especially Taft's correlations, agree with the radical nature of AN polymerization initiated by the Ce^{IV}-alcohol redox system in aqueous nitric acid.

The induction observed can be related to the Ce^{IV} alcohol complexation and the subsequent disproportionation of this complex. This process has a high activation energy (21 kcal/mol) and accordingly requires a minimum cerium salt concentration (10^{-2} mol/L) to be effective at room temperature (Table 1).

To explain the influence of the alcohol on the kinetics of the AN polymerization, it is important to note the incidence of the alcohol addition on the physical state of the reaction medium. In all experiments, 5 mL of AN are added to 50 mL of acidified water and a heterophase system is obtained due to the partial solubility of AN in water. The addition of alcohol enhances AN solubility which is complete at alcohol concentrations around 0.35 mol/L. Increasing alcohol concentration is therefore responsible for increasing the effective concentration of AN in water until complete solubility is reached. A parallel increase of R_p is accordingly observed as long as the alcohol concentration is lower than 0.35 mol/L (Table 1, Fig. 2).

The limited influence of the cerium salt concentration on R_p has already been reported [19], and it probably results from the simultaneous effect of the cerium salt concentration on the initiation (R_i) and the termination (R_t) rate. The termination of the growing PAN chains can proceed through recombination and/or oxidation of the macroradical:

$$(\mathrm{PAN})^{\bullet} + \mathrm{Ce}^{\mathrm{IV}} \longrightarrow \mathrm{PAN} + \mathrm{Ce}^{\mathrm{III}} + \mathrm{H}^{+} \tag{3}$$

As the cerium salt concentration increases, the complex formation and the radical production (Eq. 1) are favored and R_i is accordingly increased. Simultaneously, the linear termination (Eq. 3), if effective, is also enhanced and R_t must increase. The very low dependence of R_p on $[\mathrm{Ce}^{\mathrm{IV}}]$ could be explained by the approximative balance of the variation of R_i and R_t with $[\mathrm{Ce}^{\mathrm{IV}}]$.

The preference for linear termination is often mentioned in the literature [3, 4, 7, 9, 18, 25], but is also confirmed by the experimental end-functionalization of the PAN formed. Furthermore, Dainton et al. [25] have calculated the activation energy of propagation (4.1 kcal/mol), linear termination (2.3 kcal/mol), and recombination (5.4 kcal/mol) for AN polymerization in water. The low activation energy reported in this work for the polymerization (5.5 kcal/mol) agrees best with a linear termination.

The PAN molecular weight is influenced by alcohol (n-butanol) concentrations lower than 0.4 mol/L. Beyond this value the molecular weight is slightly modified. The cerium salt concentration is efficient in controlling the PAN chain length even in the range of the lowest molecular weights.

As already explained, an increasing concentration of the cerium salt gives rise to an increase of the radicals formed (Eq. 1). As the total amount of AN is kept constant, the mean length of the PAN chains must accordingly decrease (Table 4 and Fig. 6). The same event is expected to occur when the alcohol concentration is increased. The alcohol, however, has been systematically used in excess with respect to the cerium salt; as this excess becomes larger and larger, the complexation equilibrium (Eq. 1) is less and less displaced toward radical formation, and the PAN molecular weight tends to a limiting value (Table 4, Fig. 7).

In conclusion, the alcohol used in the initiating redox system enhances the solubility of AN in water and accordingly influences the polymerization rate. The amount of alcohol necessary to dissolve AN completely in water is in so large an excess with respect to $\mathrm{Ce}^{\mathrm{IV}}$ that any further addition of alcohol has no more influence on the kinetics of polymerization. Taft's correlation confirms the radical nature of this AN polymerization, which can be controlled (R_p and $\overline{M}_v$) particularly by modifying temperature and cerium salt and alcohol concentrations.

ACKNOWLEDGMENT

The authors are indebted to the "Services de la Programmation de la Politique Scientifique" (Brussels) for support and fellowships (to G.B.).

REFERENCES

[1] G. Odian, Principles of Polymerization, McGraw-Hill, New York, 1970, p. 189.

[2] R. Buvet, J. Neel, and P. Sigwalt, Chimie Macromoléculaire I, Hermann, Paris, 1970, p. 90.

[3] K. Kaeriyama, Polymer, 10, 11 (1969).

[4] M. Mohanty, B. Pradhan, and M. C. Mohanta, Eur. Polym. J., 15, 743 (1979).

[5] A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, J. Polym. Sci., C, 2, 403 (1963).

[6] R. K. Samal, M. C. Nayak, and P. L. Nayak, J. Macromol. Sci.–Chem., A12, 815 (1978).

[7] D. Pramanick, Colloid Polym. Sci., 257, 41 (1979).

[8] H. Kinshi and M. Nishio, J. Chem. Ind., Tokyo, 67, 1476 (1964).

[9] G. S. Misra and G. P. Dubey, Polym. Bull., 1, 671 (1979).

[10] P. L. Nayak, R. K. Samal, M. C. Nayak, and A. K. Dhal, J. Macromol. Sci.–Chem., A13, 261 (1979).

[11] S. V. Subramanian and M. Santappa, J. Polym. Sci., A1, 6, 493 (1968).

[12] S. S. Hariharan and M. Maruthamuthu, Makromol. Chem., 180, 2031, 2175, 2513 (1979).

[13] N. C. Pati, S. Lenka, P. L. Nayak, and T. R. Mohanty, J. Polym. Sci., Polym. Chem. Ed., 16, 343 (1978).

[14] A. Rout, S. P. Rout, N. Mallick, and B. C. Singh, Ibid., 16, 391 (1978).

[15] P. L. Nayak, R. K. Samal, and M. C. Nayak, J. Macromol. Sci.–Chem., A12, 827 (1978).

[16] A. K. Roy, S. Pattnaik, R. K. Samal, and P. L. Nayak, Ibid., A12, 1241 (1978).

[17] V. Desreux and J. Bisschoff, Bull. Soc. Chim. Belg., 59, 93 (1950).

[18] J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley, New York, 1975.

[19] G. Mino, S. Kaizerman, and E. Rasmussen, J. Polym. Sci., 38, 393 (1959).

[20] F. R. Duke and R. F. Bremer, J. Am. Chem. Soc., 73, 5179 (1951).

[21] M. Ardon, J. Chem. Soc., p. 1811 (1957).

[22] S. K. Saba and A. K. Chaudhuri, J. Indian Chem. Soc., 42, 735 (1965).

[23] M. S. Newman, Steric Effects in Organic Chemistry, Wiley, New York, 1956, Chap. 13.

[24] N. B. Chapman and J. Shorter, Advances in Linear Free Energy Relationships, Plenum, New York, 1972, Chap. 2.

[25] F. S. Dainton, P. H. Seaman, D. G. L. James, and R. S. Eaton, J. Polym. Sci., 34, 209 (1959).

Accepted by editor October 31, 1980
Received for publication November 8, 1980