

Ethoxylated Nonyl Phenols and Ethoxylated Fatty Alcohols–Ceric Ion Redox Systems for Aqueous Polymerization of Vinyl Monomers

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ABSTRACT: Ethoxylated nonyl phenols, ethoxylated fatty alcohols, and ceric ammonium nitrate redox systems were used for the polymerization of vinyl and acrylic monomers such as acrylonitrile, styrene, and acrylic acid. The initiating radical was formed on reducing organic compound which in turn initiated polymerization to give polymers containing chain ends of ethoxylated nonyl phenols and ethoxylated fatty alcohols that showed much higher water absorption. The effects of the concentration of Ce^{+4} salt, ethoxylated nonyl phenols, and monomers on both the yield and the molecular weight of corresponding polymers were studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 310–313, 2001

Key words: non-ionic surfactants; ceric salts; redox polymerization; polyacrylic acid; polyacrylonitrile

INTRODUCTION

Redox reaction systems of Ce^{+4} salts and reducing agents in aqueous solutions are well-known initiators for vinyl polymerization. Graft copolymers, block copolymers, and homopolymers are easily produced with this system. Compared with the other methods of polymerization, aqueous redox polymerization possesses a number of technical advantages. Because of their applicability at room temperature in water solution side reactions could be minimized. The polymerization mechanism involves complex formation between Ce^{+4} salt and reducing agent, followed by the generation of free radicals, which initiate the polymerization of vinyl monomers. The reducing agent for the preparation of graft and block copolymers were starch,¹ cellulose,² modified starch,³

methyl cellulose,⁴ and methyl hydroxy propyl cellulose.⁴ Block copolymers were prepared by using polyethylene glycols^{4,5} and ketonic resins⁶ as the reducing agent.

Organic reducing compounds⁷ including glucose,⁸ maltose,⁹ carboxylic acid,¹⁰ hydroxy acid,¹¹ amino acid,¹² ethylenediamine tetraacetic acid,^{13,14} nitrilotriacetic acid,¹⁵ nitrilotripropionic acid,¹⁵ iminodiacetic acid,¹⁵ amino tri(methylene phosphonic acid),¹⁶ diethylene triamine penta(methylene phosphonic acid),¹⁶ and 1-hydroxyethylidene-1,1-diphosphonic acid¹⁶ were used as reducing agent for redox polymerization of vinyl monomers. The polymers produced by Ce^{+4} /organic reducing compounds were suggested to have chain ends of the corresponding reducing compound moiety.¹⁶

In this work, acrylonitrile was polymerized with the redox system of Ce^{+4} salt and the commercial ethoxylated fatty alcohols and ethoxylated nonyl phenols, in order to produce polyacrylonitrile (PAN) containing ethoxylated fatty alco-

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hols and ethoxylated nonyl phenols chain ends, respectively.

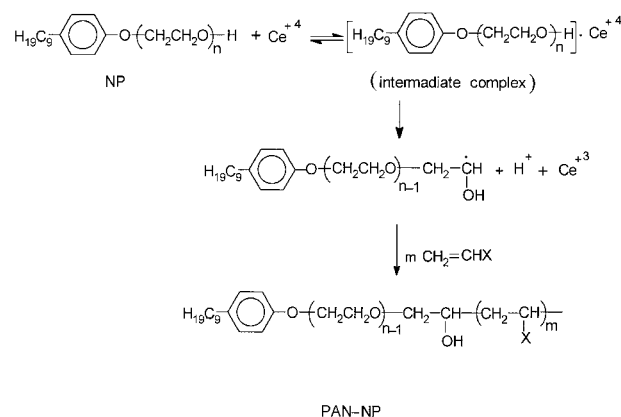
EXPERIMENTAL

Materials

Ceric ammonium nitrate was oven dried at 105°C for 1 h and stored in a desiccator. A calculated amount was dissolved in 1M HNO₃ solution to prepare 0.1M stock solution that was stored in a refrigerator. Ethoxylated nonyl phenols such as nonyl phenol 4 (NP4), nonyl phenol 6 (NP6), nonyl phenol 10 (NP 10), nonyl phenol 16 (NP16), nonyl phenol 30 (NP30), and ethoxylated fatty alcohols such as dehydol LS 7 (average hydroxyl value: 110–120), dehydol LT 7 (average hydroxyl value: 106–112), dehydol TA 11 (average hydroxyl value: 75–80), and dehydol TA 20 (average hydroxyl value: 49–53) were commercial grade and supplied by Henkel (Turkey). Acrylonitrile and acrylic acid were used as received. Styrene was freed from inhibitors by shaking with 10% NaOH solution.

Polymerization Procedure

The reducing compound was dissolved in water and a vinyl monomer such as acrylonitrile, acrylic acid, and styrene was added. The content of the flask was flushed with oxygen-free nitrogen. Ceric ammonium nitrate stock solution was then added drop-wise to the reaction mixture in about 20 min while stirring under nitrogen atmosphere at 20°C. In the case of the styrene monomer an emulsion was formed. Water-insoluble PAN precipitated during the polymerization. After about 45 min, the powdery PAN was filtered, washed several times with water, then with methanol, and finally dried under vacuum at 60°C. The PAN was purified by reprecipitation into water from its dimethylformamide solution. Polystyrene was formed both as an emulsion and as a precipitate. The solution was filtered and the emulsion filtrate was evaporated, then polystyrene was extracted with CH₂Cl₂. Polystyrene was purified by dissolving in 2-butanone and precipitating into methanol. The water-soluble polyacrylic acid and polyacrylamide were dissolved in water and their water solutions were poured into acetone to precipitate the polymers. They were then purified by dissolving in water and reprecipitating into acetone/methanol (2:1) mixture.



Scheme 1

In the absence of the reducing compound, no polymer was formed in 45 min at 20°C, by performing a similar experiment under comparable conditions using the vinyl monomer and Ce⁺⁴ salt in the absence of the reducing compounds.

Molecular Weight

Viscosities of PAN solutions in dimethylformamide were measured at 25°C using a Cannon-Fenske capillary viscometer and molecular weights were calculated from single-point values. The following equations were used^{17,18}:

$$[\eta] = \frac{\eta_{sp}/c}{1 + 0.28 \times \eta_{sp}};$$

$$[\eta] = 2.33 \times 10^{-4} \times \bar{M}w^{0.75}$$

RESULTS AND DISCUSSION

Mechanism for the Formation of Polymer

The mechanism of the polymerization of vinyl monomers by Ce⁺⁴ salt and an ethoxylated compound is represented in Scheme 1. Initiating radical is sequentially formed after the complex formation between Ce⁺⁴ and ethoxylated compound as suggested before. Tenfold reducing agent favors the complex formation with Ce⁺⁴.

The polymer obtained with the redox system of ethoxylated compounds and Ce⁺⁴ salt contained ethoxylated fatty alcohol or ethoxylated nonyl phenol chain ends because the radicals are formed on the reducing molecules. This was proven by ¹H-NMR. The purified PAN containing ethoxylated nonyl phenol chain ends showed

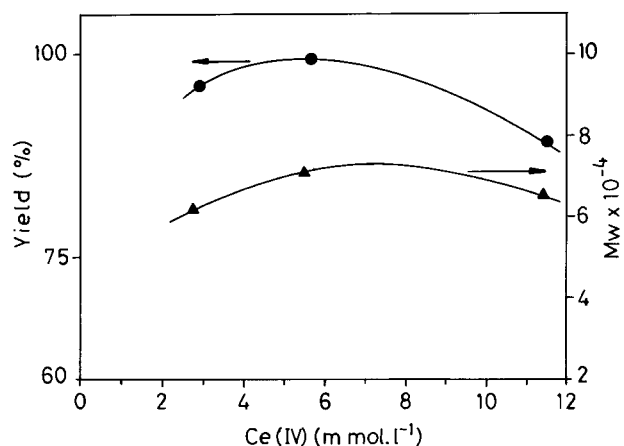


Figure 1 The effect of Ce^{+4} concentration on the polymerization yield and molecular weight. $[\text{AN}]$: $0.75 \text{ mol} \cdot \text{L}^{-1}$; $[\text{NP 16}]$: $20 \text{ g} \cdot \text{L}^{-1}$; T : 21°C ; t : 45 min.

small sharp peaks at between 7 and 7.5 ppm because of hydrogens of aromatic ring and small sharp peaks at between 0.5 and 2 ppm because of aliphatic hydrogens of nonyl group as well as a wide peak at about 2 ppm because of methylene protons and a wide peak at about 3 ppm because of methine protons of PAN.

The Effect of the Concentration of Ce^{+4} and the Reducing Compounds

The concentration of Ce^{+4} salt was varied between 3 and $12 \text{ mmol} \cdot \text{L}^{-1}$ keeping the other parameters of polymerization constant. An increase in the ceric ion concentration caused the polymerization yield to increase. The limiting conversion reached a maximum value when ceric

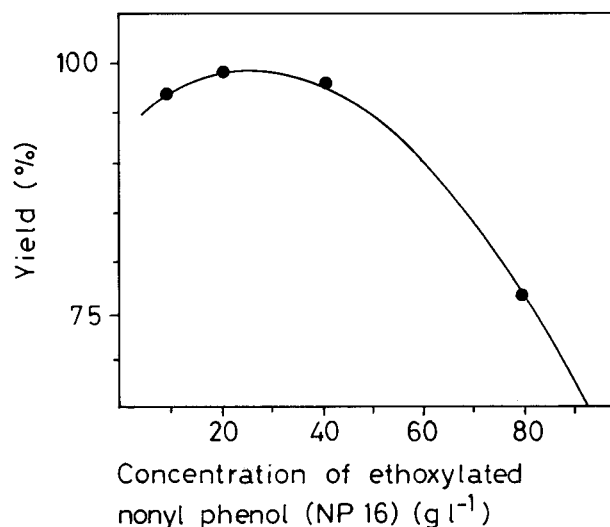


Figure 2 The effect of reducing agent concentration on the yield of polymerization. $[\text{AN}]$: $0.75 \text{ mol} \cdot \text{L}^{-1}$; $[\text{Ce}^{+4}]$: $5.7 \text{ mmol} \cdot \text{L}^{-1}$; T : 21°C ; t : 45 min.

ion concentration was about $5.7 \text{ mmol} \cdot \text{L}^{-1}$ (Fig. 1). Increasing the Ce^{+4} concentration above this value resulted in the yield of polymerization to become inversely proportional to Ce^{+4} concentration, probably because of linear termination by Ce^{+4} . Besides, increasing Ce^{+4} concentration is known to cause a significant increase in the rate of oxidative termination of primary radicals compared with the rate of initiation.¹⁶ Oxidative chain termination and linear termination by Ce^{+4} ions probably was significant at higher Ce^{+4} concentration ($>5.7 \text{ mmol} \cdot \text{L}^{-1}$) so both the molecular weight and the polymerization yield became inversely proportional to the Ce^{+4} concentration.

Table I The Effect of the Type Ethoxylated Nonyl Phenol (NP) and Ethoxylated Fatty Alcohol to the Polymerization Yield and Mol Weight of Polymers

	Reducing Compound	Monomer	Yield (%)	M_w
PAN-NP4	NP4	Acrylonitrile	86	60,000
PAN-NP6	NP6	Acrylonitrile	90	68,000
PAN-NP10	NP10	Acrylonitrile	93	76,000
PAN-NP16	NP16	Acrylonitrile	100	79,000
PAN-NP30	NP30	Acrylonitrile	95	79,000
PAA-NP30	NP30	Acrylic acid	100	—
PS-NP30	NP30	Styrene	80	—
PAN-LS7	Dehidol LS7	Acrylonitrile	95	91,500
PAN-LT7	Dehidol LT7	Acrylonitrile	93	90,000
PAN-TA11	Dehidol TA11	Acrylonitrile	91	80,000
PAN-TA20	Dehidol TA20	Acrylonitrile	94	94,000

$[\text{NP}]$: $20 \text{ g} \cdot \text{L}^{-1}$; $[\text{Ce}^{+4}]$: $5.7 \text{ mmol} \cdot \text{L}^{-1}$; $[\text{AN}]$: $0.75 \text{ mol} \cdot \text{L}^{-1}$; T : 21°C ; t : 45 min.

Table II Water Absorption of the Polyacrylonitriles Produced with Ethoxylated Nonyl Phenol-Ce⁺⁴ Redox Systems

Polymer	Water Absorption (%)
Polyacrylonitrile	0.1
Polyacrylonitrile-NP4	2.4
Polyacrylonitrile-NP30	6.2

The effect of reducing agent concentration on the yield of polymerization is shown in Figure 2. At low ceric ion concentration (5.7 mmol · L⁻¹), the polymerization yield reached to limiting value of 98% when ethoxylated nonyl phenol concentration was about 20 g/L. A further increase in ethoxylated nonyl phenol (NP16) caused degradative chain transfer reaction to become significant compared with bimolecular termination, so the yield decreased with increasing NP16 concentration above 20 g/L.

Performance of Ethoxylated Nonyl Phenol and Ethoxylated Fatty Alcohol

Both ethoxylated nonyl phenols and ethoxylated fatty alcohols were suitable organic reducing compounds in the redox pairs of Ce⁺⁴ and the reducing compounds for initiating the aqueous polymerizations of vinyl monomers such as acrylamide, acrylic acid, and styrene as well as acrylonitrile (Table I). The highest yield and molecular weight were obtained when NP16 was used as reducing agent. However, the polymerization yield seemed not to depend on the type of ethoxylated nonyl phenol and ethoxylated fatty alcohol.

Physical Properties of Polymers

PANs with ethoxylated nonyl phenol chain ends showed better water absorption than PAN (Table II). As expected, increasing the ethoxyl content of reducing agent increases the water absorption of the polymer produced.

CONCLUSION

Ethoxylated fatty alcohols and ethoxylated nonyl phenols-ceric ammonium nitrate redox pairs are effective initiators for aqueous polymerization of

acrylonitrile, acrylic acid, and styrene at ambient temperature to produce polymers with ethoxylated fatty alcohols and ethoxylated nonyl phenol chain ends, respectively. The water absorption of PANs produced with this method was significantly increased by the effect of their chain ends which were biodegradable non-ionic surfactants. These PANs may be used where high water absorption is desired. Besides, these PANs may also find some other application areas because of their biodegradable non-ionic surfactant chain ends such as in the floatation of ores.

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