Effect of Plant Gums on Thermal Polymerization of Acrylonitrile

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ABSTRACT: The effect of some plant gums on the polymerization of acrylonitrile (AN) using ceric ammonium nitrate (CAN) as an initiator in the presence of air (containing 21% oxygen) was studied. The induction period and percent conversion were determined. The induction period in the presence of gum was comparatively lower than that under a N_2 atmosphere. The rate of polymerization has a 1.5-power dependence on the monomer concentration and the rate is sufficiently high at moderate temperature. The rate also increased with an increasing initiator concentration and reaches a maximum value of 93% at 0.72×10^{-2} mol L^{-1} of CAN. The activation energy was found to be 6.4 kcal mol^{-1}. Both the molecular weight and density of the polyacrylonitrile (PAN) prepared in the presence of gum were higher than those of PAN prepared in the absence of the gum. The PAN produced in the presence of the gum was thermostable than that prepared in its absence. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3596–3600, 2002

Keywords: plant gums; acrylonitrile; thermal polymerization; ceric ammonium nitrate

INTRODUCTION

The aqueous photopolymerization of vinyl monomers is usually carried out in an inert medium in the presence of redox initiators.[1–2] In vinyl polymerization, the role of oxygen as a retarder or inhibitor is well known. Most polymerization reactions are, thus, commonly carried out in an inert atmosphere to avoid the problem of retardation by atmospheric oxygen. It is known that some plant gums or extracts contain pyrogallol derivatives,[3] which may cause the formation of free-radical generation and the scavenging of oxygen. Evans and Uri[4] were the first to show that irradiation of an aqueous solution containing metal complexes (ion-pair complexes), such as $Fe^{3+}X^{-}$, with high energy could initiate aqueous polymerization of acrylonitirle, methacrylonitrile, styrene, etc. Photopolymerization was studied by Kuriacose and Markhan's[5] who polymerized an unstirred aqueous suspension of methyl methacrylate (MMA) and acrylonitrile (AN) containing zinc oxide by irradiation with ultraviolet rays. Evans et al.[6] polymerized MMA and AN using hydroxylamine in the presence of metal ions such as Ti^{+3}, Cr^{+2}, and V^{+2}. Oster[7] reported that dyes such as fluorescein, eosin, phloxin, and rose bengal in the presence of a reducing agent (e.g., ascorbic acid, phe-nylhydrazine hydrochloride, hydrazine sulfate, hydroxylamine, thiourea) were good sensitizers in the photoactivated aqueous polymerization of AN in the presence of oxygen. They suggested a mechanism involving a redox cycle in which the dye was first reduced by a reducing agent, followed by oxidation of the reduced dye with the oxygen:

$$\text{Dye} + \text{reducing agent} \rightarrow \text{dye } H_2 \rightarrow \text{dye } H + OH$$
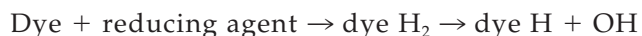
Shepp et al.[8] showed that thionine, methylene, and proflavin produced aqueous polymerization of AN at pH 8.4. Although ceric ammonium nitrate (CAN) forms an efficient redox initiating system[9–15] under an inert atmosphere, its use as a redox component in an oxygen atmosphere has been hardly reported. In the present study, CAN was used as an initiator for aqueous thermal polymerization of AN in the presence of some plant gums under atmospheric oxygen.

EXPERIMENTAL

Materials

AN (SD Fine Chemicals, Mumbai, India), CAN; (Merck, Mumbai, India), acetone (SD), and dimethylformamide (DMF; BDH, Mumbai, India) were purified according to the usual procedures.[16] HNO_3 (BDH) was analytical grade and used without further purification. Raw plant gums were collected from stems of local plants and dried in a vacuum at 40°C. A number of gums were used in the polymerization experiments.
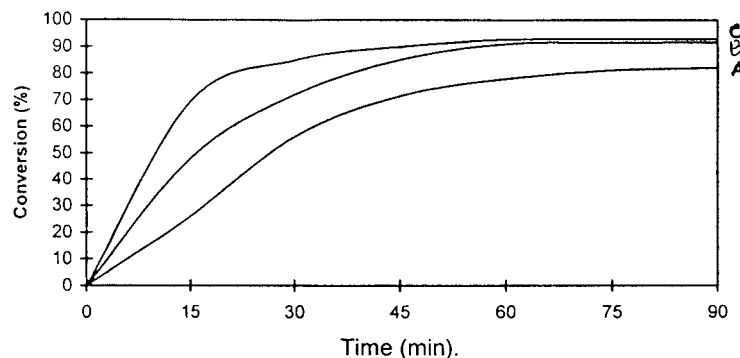
Figure 1 Conversion–time curves of AN polymerization in aqueous medium: [CAN] = 0.72×10^{-2} mol L; [gum] = 0.2% (w/w); [AN] varies: (A) 0.2, (B) 0.38, and (C) 0.76 mol L.

These include *M. Latifolia (Mahwa), P. guajava (Guava), E. Melanophloia, F. Muell (Eucalyptus),* and *Moringa olefera (Sajina). M. olefera* has been found to give the highest rate of polymerization among the different types of gum used. All the experiments reported herein were carried out using *M. olefera* as the gum. The acetone extract of the gum obtained through Soxhlet extraction was dried under a vacuum. This dry powder of the extracted gum was used for all polymerization experiments. The structure of the acetone-extracted gum is shown below:
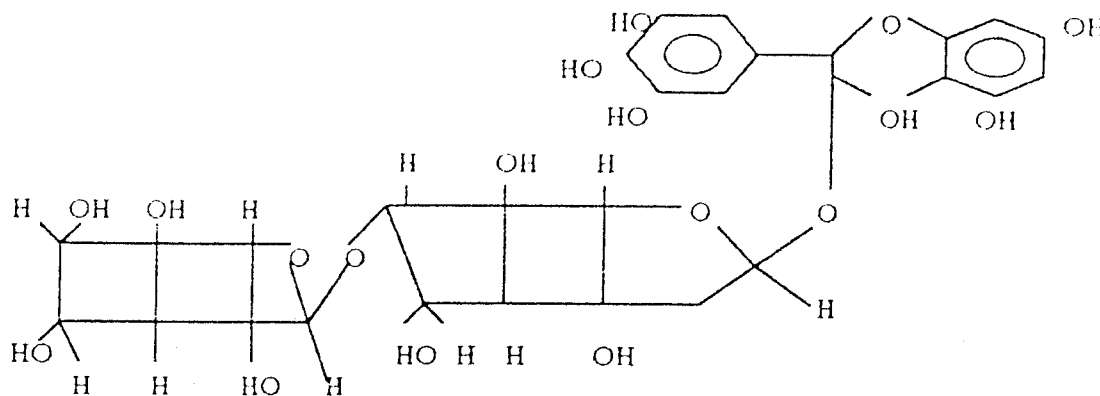
Leucodelphinidin-3-O-β-D-galactoyranosyl(1–4)-O-β-D-glucopyroside.

Polymerization

A measured amount of AN from a stock solution was placed in 100-mL conical flasks and diluted with water to 48 mL and the gum was added to it. A 2-mL CAN solution of a specified concentration was then injected into the flask. The flasks were placed in a constant temperature water bath. The induction periods for the polymerizations were noted by observing the appearance of the first white turbidity. After requisite time intervals, the polymer was precipitated by the addition of Na_2SO_4 and then filtered in a sintered bed crucible. The precipitate was washed thoroughly with hot water and then dried under a vacuum until constant weight. The yield was calculated gravimetrically.

RESULTS AND DISCUSSION

The polymerization of AN by the CAN initiating system in the presence of gum depends on the concentration of the monomer. The time–conversion curve for thermal polymerization of AN in the presence of gum is shown in Figure 1. The initial rate of polymerization and limiting conversion are found to increase with increase in the concentration of the monomer in the range of 0.1–1.0 mol L^{-1}. The rate of polymerization is found to have a 1.5-power dependence on the monomer concentration. It may be quite possible that the higher monomer exponent in the case of initiation is due to the complex nature of the initiation reaction involving monomer molecules as participating reactants to generate free radicals.

It was observed that the induction period was drastically reduced to only few seconds in the presence of gum compared to those in absence of the gum, either in air or in nitrogen. Both the rate of polymerization and the limiting conversion are comparatively low when polymerization is carried out in an inert atmosphere (Fig. 2). This shows that the gum not only acts
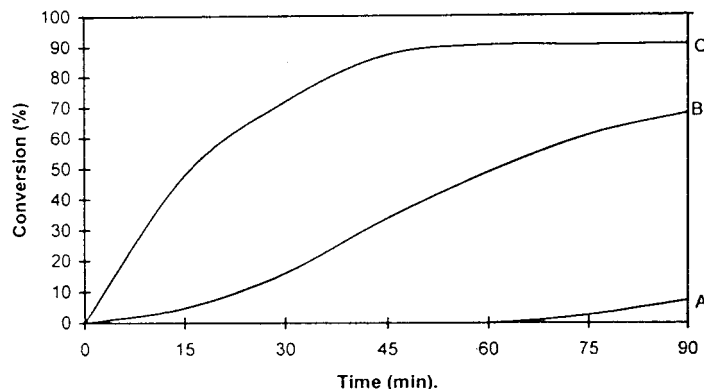
Figure 2 Conversion of AN polymerization with time. [AN] = 0.38 mol L^{-1}; [CAN] = 0.72 × 10^{-2} mol L^{-1}; [gum] = 0.2% (w/w). (A) Without gum in airy atmosphere; (B) with gum in nitrogen atmosphere; (C) with gum in airy atmosphere.

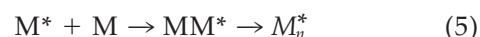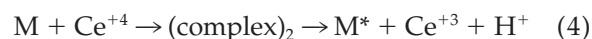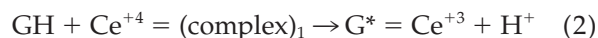as an oxygen scavenger but also as an accelerator for decomposition of the initiator.

In presence of air, oxygen reacts with radicals, which leads to a retardation of the free-radical chain polymerization. The retardation is usually explained by the scavenging of the radicals to form a radical species having much lower reactivity towards the monomer molecules [eq. (1)]:

$$R' + O_2 \rightarrow ROO' \qquad (1)$$

where R' denotes a radical species derived from a monomer, a polymer, or an initiator-derived radical.[17]

A mechanism may be postulated by assuming a prior complex formation between the gum (GH) and the ceric ion. The complex then decomposes to generate the macroradical (G), which then reacts with the monomer to produce monomer free radicals for chain propagation:

$$GH + Ce^{+4} = (complex)_1 \rightarrow G^* = Ce^{+3} + H^+ \quad (2)$$

$$G^* + M \rightarrow GM^* + M \rightarrow GMM^* \qquad (3)$$

$$M + Ce^{+4} \rightarrow (complex)_2 \rightarrow M^* + Ce^{+3} + H^+ \quad (4)$$

$$M^* + M \rightarrow MM^* \rightarrow M_n^* \qquad (5)$$

The effect of the gum concentration of the polymer yield is plotted in Figure 3. It is found that the rate of polymerization increases to a certain concentration of the gum and thereafter decreases, showing a retardation effect at a higher concentration of the gum.
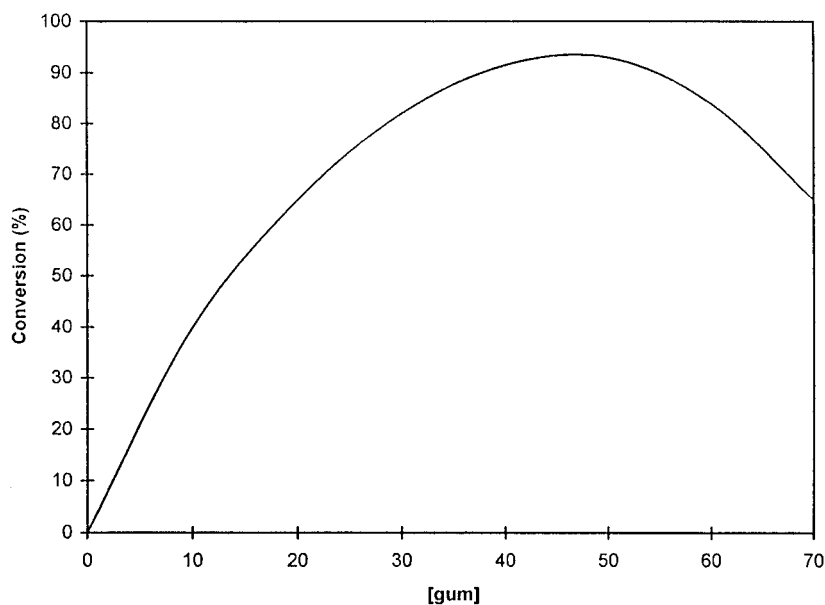

Figure 3 Effect of the gum on polymerization for varying concentrations of gum at fixed [AN] = mol L^{-1}; [CAN] = 0.72 × 10^{-2} mol L^{-1}.

TABLE I
**Effects of [H⁺] and Temperature on Aqueous Photopolymerization of AN**

Concentrations of HNO_3 (mol L^{-1}) $\times 10^{-2}$	Temperature (°C)	Conversion (%)
0	27	0
0.7	27	6.6
1.0	27	8.9
1.4	27	78.6
1.4	35	88.7
1.4	45	91.9
1.4	48	54.8
5.6	27	89.6
5.6	35	91.2
5.6	45	92.1
5.6	48	76.1
7.0	27	90.2
7.0	35	91.8
7.0	45	92.3
7.0	48	69.1
8.5	27	89.5
8.5	35	92.7
8.5	45	93.2
8.5	48	74.3
9.6	27	91.7
9.6	35	92.2
9.6	45	92.5
9.6	48	74.7
10.5	27	63.5
10.5	35	69.1
10.5	45	58.8
10.5	48	52.7

[AN] = 0.38 mol L^{-1}; [CAN] = 0.76 $\times 10^{-2}$ mol L^{-1}; [gum] = 0.2% (w/w); total volume = 50 cc; time = 60 min.

When the temperature of the reaction medium is increased, both the initial rate of polymerization and the limiting conversion increase to 45°C and then decrease (Table I). The observed increase in the rate with increase in the temperature is due to the enhanced rate of formation of free radicals. On increasing the temperature further, some side reactions appear to occur.

This is evident from the development of the color of the polymerization medium, leading, finally, to a brown-colored precipitate. This side reaction may cause an increase in the rate of primary radical termination, thereby decreasing both the initial rate and limiting conversion. The overall energy of activation as calculated from the Arrhenious plot (not shown) was found to 6.4 kcal mol^{-1}.

The CAN initiating system is quite sensitive to [H⁺]. The effect of the H⁺ ion on the course of polymerization was studied by the addition of nitric acid in the range of 1.4×10^{-2} to 1.5×10^{-2} mol L^{-1}. It was observed that when the [H⁺] was kept below 1.4×10^{-2} mol L^{-1} polymerization does not occur. This is explained by the fact that the ceric ion in water is believed to react in the following manner:

$$Ce^{+4} + H_2O = Ce(OH)_3^{+3} \qquad (6)$$

$$Ce(OH)_3^{+2} = [Ce—O—Ce]^{+6} + H_2O \qquad (7)$$
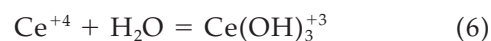
Thus, the ceric ion exists as Ce^{+4}, $Ce(OH)_3^{+3}$, and $[Ce—O—Ce]^{+6}$ water solutions. The observed zero nitric acid concentration indicates the inability of $[Ce—O—Ce]^{+6}$ to form a complex with the monomer. The increase observed is well explained as a function of [H⁺]. With increasing nitric acid concentration in the range of $1.4–8.4 \times 10^{-2}$ mol L^{-1}, the equilibria (6) and (7) moderately shift toward formation of Ce^{+4} and $Ce(OH)_3^{+3}$ at the cost of $[Ce—O—Ce]^{+6}$, thereby facilitating the radical generation steps. But on increasing [H⁺] beyond 8.4×10^{-2} mol L^{-1}, the rate of formation of Ce^{+4} and $[Ce(OH)_3^{+3}]$ increases. This is evident from the clear and orange-colored solution formation. These species at higher concentration affect the polymerization efficiency adversely by termination of the growing propagated chain.
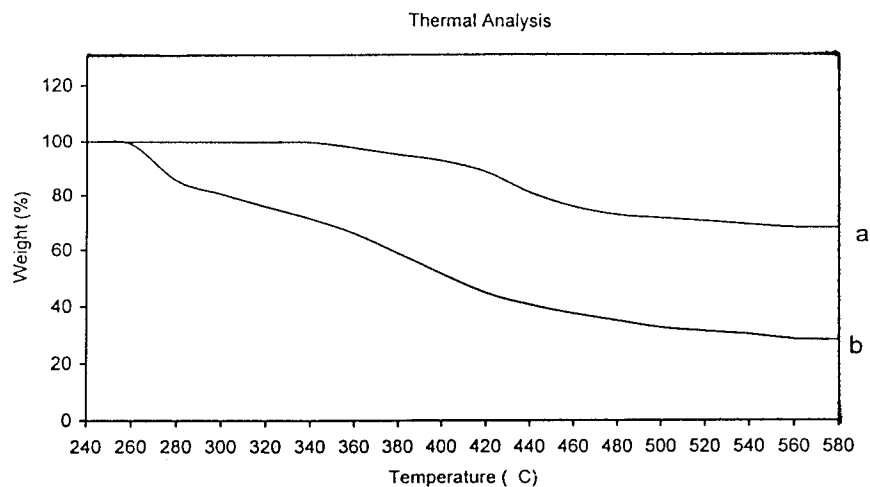

Figure 4 TGA curves (heating rate 10°C/min in air) of PAN prepared (a) with and (b) without gum.

TABLE II
Thermal Analysis of PAN Prepared in Presence of the Gum

Gum (% w/w)	Initial decomposition temperature (°C)	10% wt loss at °C	30% wt loss at °C	Char residue (%) at 600 °C	Peak decomposition temperature (°C)
0	260	268	347	27.88	260
0.2	380	423	522	67.4	380

[AN] = 0.38 mol L^{-1}; [CAN] = 0.76 × 10^{-2} mol L^{-1}; [gum] = 0.2% (w/w); total volume = 50 cc; time = 60 min.

Viscosity-average molecular weight

Viscosity measurements of *polyacrylonitrile* (PAN) solutions in DMF were carried out at 30°C using an Ubbelohde suspended level viscometer and the viscosity-average molecular weight was calculated using the equaton[18]

$$[\eta] = K \overline{M_v^\alpha}$$

where $[\eta]$ and M_n, respectively, are the limiting viscosity number and the viscosity-average molecular weight and K and α are constants for a particular polymer–solvent system at a given temperature. It is found that the viscosity–average molecular weight of PAN prepared in the presence of the gum lies in the region of 1.1×10^5 to 1.8×10^5 and increases with increasing monomer concentrations.

Density

The density of the powder PAN polymers prepared under different concentrations of the gum and monomer were measured and compared to that of polymer prepared without the gum. The density values were 1.06 and 1.36 g/cc for the PAN polymer prepared without the gum and with the gum, respectively, for a given set of polymer samples. The increase in the density of the PAN polymer when prepared with the gum may be due to the degree of regularity of the structural units and the degree of orientation of the macrochains and crystallinity. This observation is in agreement with that of Maiti and Bag[19] for polymerization of AN under an applied magnetic field.

Thermal behavior

The thermal degradation of PAN is a complex process. At least three distinct thermal processes compete with one another in the thermal degradation of PAN: (i) initial cyclization by cyanide group polymerization; (ii) cyclization followed by ammonia evolution, and (iii) chain scission and decomposition with production of H, HCN, the monomer, and other fragments.

The thermal behavior of PAN polymers prepared with and without the gum was studied by thermogravimetric (TG) and differential thermal analysis (DTA) (Fig. 4). The results of the thermal analysis are summarized in Table II. At a particular temperature,

the percent weight loss of PAN prepared with the gum in air is less than that of PAN prepared without the gum in a N$_2$ atmosphere. The char residue at 600°C is also higher for PAN prepared with the gum. The DTA peak temperature for decomposition is higher for PAN prepared with the gum than that of the PAN prepared without the gum. Therefore, PAN obtained with the gum is more thermostable than that obtained without the gum. The more thermostable PAN polymer obtained with the gum is perhaps due to its higher molecular weight, stereoregularity, and crystallinity.[19]

The exotherm peak temperature depends on the molecular weight of PAN.[20] The PAN prepared with the gum having a higher molecular weight decomposes at higher temperature. The char residue is due more to the higher molecular weight and enhanced microregularity of the chain. It was reported that the stereo regularity of the PAN molecule forms cyclization of the chain, leading to a higher char residue. However, this observation by DTA is similar to that observed in the DSC analysis.

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