

Copolymerization of Styrene with Fumaronitrile Initiated by L-Ascorbic Acid

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Synopsis

Copolymerization of styrene (ST) with fumaronitrile (FN) initiated by L-Ascorbic acid (L-Asc) was investigated in dioxane containing a small amount of methanol in the presence of atmospheric oxygen. L-Asc was found to initiate the alternating copolymerization of ST with FN at mild conditions. The copolymerization rate R_p was found to increase with increasing L-Asc concentration and was found to depend on $[L-Asc]^{0.6}[(ST) + (FN)]^{2.7}$. The overall energy of activation as calculated from Arrhenius plot was found to be $10.9 \text{ kcal/mol}^{-1}$ within the temperature range of 25–40°C.

INTRODUCTION

The copolymerization of ST with FN initiated by free radical initiator has been investigated by several authors.¹⁻³ Further experiments showed that FN copolymerizes easily with various aromatic monomers to give strictly alternating copolymers.^{4,5} It is well known that these monomers form charge transfer type complex which may effect the copolymerization behavior.⁶⁻⁹ On the other hand, L-Asc in combination with suitable oxidants proved to be an efficient redox initiator for various vinyl polymerizations.¹⁰⁻¹² It was shown previously in our laboratory that systems composed of maleic anhydride and L-Asc are very effective initiators of the free radical copolymerization of maleic anhydride with ST. Recently, it was found that L-Asc may act as a single electron donor toward the strong electron acceptor like maleic anhydride, producing strong initiating radicals. Thus, we can expect that the addition of such electron donors might initiate the copolymerization of FN with ST. It is the purpose of the present paper to examine the copolymerization of ST with FN initiated by L-Asc alone.

EXPERIMENTAL

Styrene was washed free of inhibitor with 5% NaOH solution, washed with water, distilled under vacuum, and stored at 0°C. Fumaronitrile was recrystallized twice from dry chloroform. L-Ascorbic acid was commercially available and used without further purification. Dioxane was refluxed over calcium hydride and distilled immediately before use. All other solvents used were purified by conventional methods.

Copolymerization was carried out in glass tubes, which were stored in the absence of external light. L-Asc was dissolved in methanol and diluted with

dioxane in a volumetric flask. The content of methanol was adjusted to 4 vol %. The required amounts of FN, ST, and L-Asc solution were charged into a glass tube, and set in a thermostatted water bath. This tube was wrapped with aluminum foil to protect it from external light, and placed in a thermostat to start polymerization. After a given time, the polymerization was stopped and its content was poured into a large amount of methanol to precipitate the copolymer. The copolymer was dried under vacuum to the constant weight. Conversions were calculated from the weight of the dried copolymer. Rates of copolymerization were obtained gravimetrically.

IR and NMR spectra were recorded by JASCO IR-S1 and Hitachi R-24B spectrophotometers, respectively.

RESULTS AND DISCUSSION

A small amount of methanol added to the copolymerization system results in homogeneous polymerization in the presence of the L-Asc. Dioxane was chosen as a diluent for all experiments, since it dissolves the monomer and the copolymer, and was miscible in methanol which solubilize the L-Asc. From the results of the analyses, the copolymer was found to be 1:1 alternating copolymer. The copolymerization of ST with FN can be initiated by L-Asc alone in dioxane containing a small amount of methanol at 25–50°C. However, in the absence of L-Asc the yields of copolymers obtained within a temperature range of 25–50°C is usually very low. As shown in Table I, it is clear that no polymer was obtained when either the L-Asc or the FN monomer was missing from the polymerization systems. It is reasonable to consider that the active complex for the initiation of the polymerization is the L-Asc-FN complex.

The copolymerization of ST with FN was carried out in the absence of atmospheric oxygen after thoroughly deaerating the reaction mixture because molecular oxygen generally tends to inhibit the polymerization reaction and induction period. It has been observed that the reaction between oxygen and L-Asc is autocatalytic, accelerated by oxygenated dehydroascorbic acid. It has been also reported that the ascorbic acid-oxidant redox system acts as an

TABLE I
Copolymerization of ST with FN at Various Conditions^a

Run	L-Asc (concn. $\times 10^{-4}$ mol/L)	Temp (°C)	Yield (%)
1	0	25	0
2	5.2	15	9.6
3 ^b	5.2	25	0
4	0	50	1.3
5	5.2	50	22.5
6 ^b	5.2	50	0
7	0	40	0
8	5.2	40	11.4
9 ^b	5.2	40	0

^a[ST] = [FN] = 2.6 mol/L, solvent = dioxane/methanol (96/4 vol %).

^bWithout FN.

TABLE II
Influence of Oxygen on Copolymerization of ST with FN^a

Run	Atmosphere	Time (h)	Yield (%)
1	Air	1	0
2	Nitrogen	1	1.4
3	Oxygen	1	0
4	Air	3	1.7
5	Nitrogen	3	4.0
6	Oxygen	3	0
7	Air	5	3.6
8	Nitrogen	5	9.6
9	Oxygen	5	0

^a[ST] = [FN] = 5.0 mmol/L, solvent = dioxane/methanol (96/4 vol %), temp = 25°C.

efficient initiator even in the presence of atmospheric oxygen.¹² It therefore appears that oxygen acts as a cocatalyst and helps to reduce rather than increase an induction period. The role of molecular oxygen in minimizing the induction period in such systems is of greater importance industrially. As can be seen from Table II, atmospheric oxygen (air) slightly inhibits the copolymerization of ST with FN and excess oxygen exhibit an inhibitory effects of the copolymerization. In further experiments, the copolymerization was carried out in the presence of atmospheric oxygen.

Table III shows the effect of adding a small amount of 1,1-diphenyl-2-picrylhydrazyl (DPPH) on the yield of copolymerization carried out at 40°C in the presence of L-Asc. In systems containing DPPH, a remarkable decrease of the copolymerization yield is observed. An increase of DPPH concentration results in a decrease of the copolymer yield. DPPH exhibit a remarkable inhibitory effect. It is very probable that the above reaction is radical in nature.

The effect of the temperature on the copolymerization rate is shown in Figure 1. The initial rate (taken from the slope of the conversion curves) increases with increasing copolymerization temperature. A variation in the induction period is noted with increasing polymerization temperature showing that the oxygen in the air is consumed by the L-Asc producing free radicals with a faster rate and have induction period decreases. The overall energy of activation as calculated from the Arrhenius plot (Fig. 2) has been found to

TABLE III
Effect of DPPH on the Copolymerization of ST with FN^a

Run	DPPH (concn. $\times 10^{-4}$ mol/L)	Yield (%)
1	0	11.4
2	0.3	10.1
3	0.8	8.8
4	1.0	8.0
5	1.3	7.1

^a[ST] = [FN] = 2.6 mol/L; [L-Asc] = 5.2×10^{-4} mol/L; temp = 40°C; solvent = dioxane/methanol (96/4 vol %); time = 5 h; atmosphere, air.

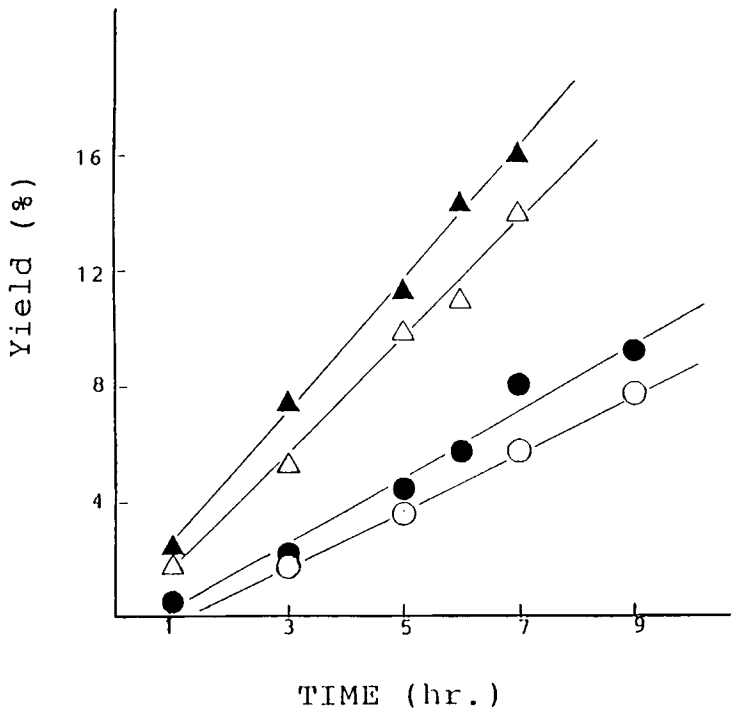


Fig. 1. Dependence of copolymerization rate (R_p) on temperature ($^{\circ}\text{C}$): (○) 25; (●) 30; (△) 35; (▲) 40 $^{\circ}\text{C}$. $[\text{ST}] = [\text{FN}] = 2.6 \text{ mol/L}$; $[\text{L-Asc}] = 5.2 \times 10^{-4} \text{ mol/L}$.

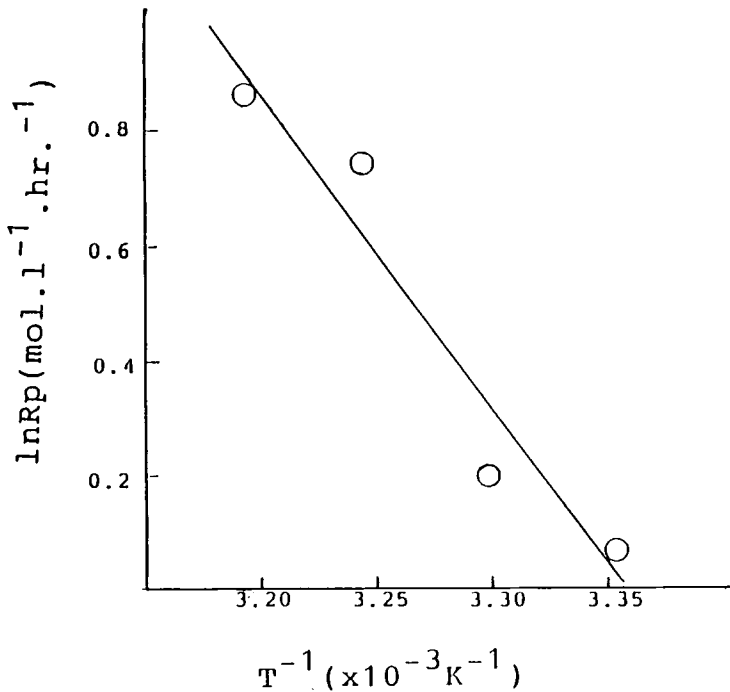


Fig. 2. Arrhenius plot for copolymerization of ST with FN initiated by L-Asc.

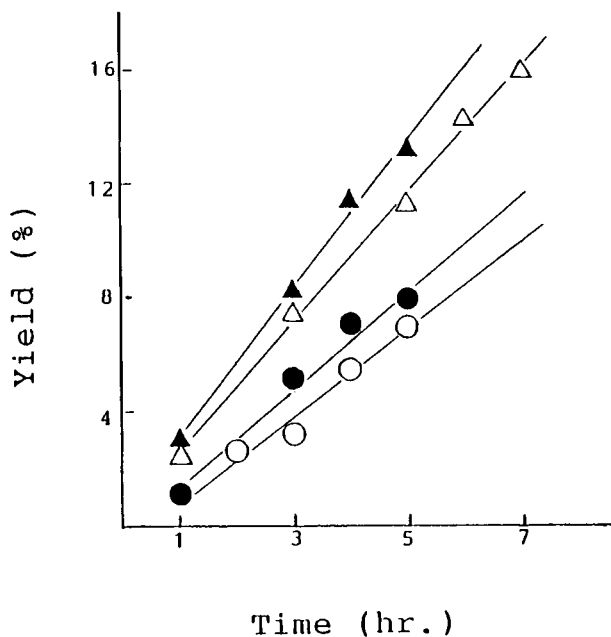


Fig. 3. Dependence of copolymerization rate (R_p) on L-Asc concentration: (○) 2.6×10^{-4} mol/L; (●) 3.9×10^{-4} mol/L; (△) 5.2×10^{-4} mol/L; (▲) 6.5×10^{-4} mol/L.

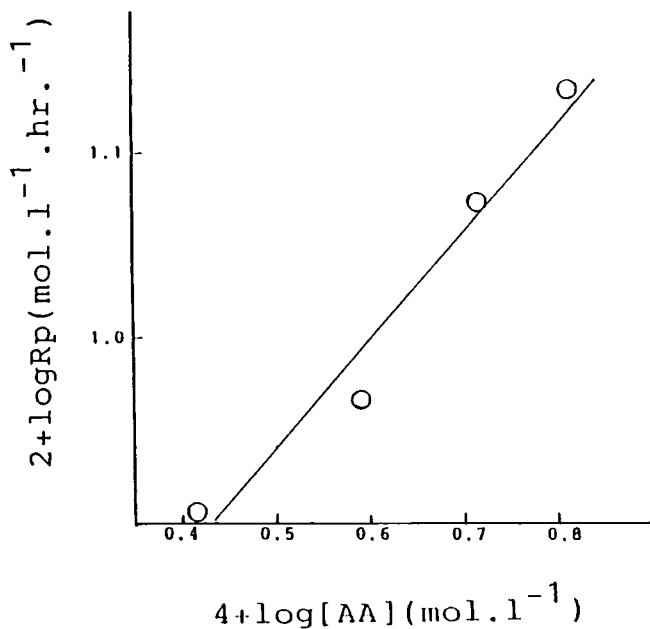


Fig. 4. Double logarithmic plot of copolymerization rate (R_p) vs. L-Asc concentration.

be 10.9 kcal/mol within the temperature range of 25–40°C. This value is in line with that obtained by using L-Asc–permanganate redox system for acrylamide polymerization. Shukra and Misra¹³ determined an activation energy of 9.8 kcal/mol in the aqueous polymerization of acrylamide initiated by the L-Asc–permanganate redox system.

The initial rate and induction period increase with increasing concentration of L-Asc in the range of $2.6\text{--}6.5 \times 10^{-4}$ mol/L at 40°C. This is shown in Figure 3. The order of the reaction with respect to L-Asc concentration can be obtained from the log–log plot of R_p vs. L-Asc concentration (Fig. 4). The slope of 0.6 for the linear plot indicates the normal half power dependence on L-Asc concentration, which means a mutual termination of the growing polymer chains. It is reasonable to consider a radical intermediate in the present polymerization system, as the rate of copolymerization is retarded by the addition of DPPH and the rate is nearly proportional to the square root of the concentration of the L-Asc. The induction period varies greatly with increasing the L-Asc concentration. We supposed that the initiation mechanism involves the formation of L-Asc and FN radicals and the starting reaction step between L-Asc and FN forms a complex, which breaks down liberating the initiating radicals.

A log–log plot of total monomer concentration vs. R_p shows that the copolymerization rate varies as the 2.7 power of total monomer concentration (Fig. 5). From Figure 5, it is clear that the rate of copolymerization increases with increasing total monomer concentration. The initial radical was produced by the charge transfer complex between L-Asc and FN monomer. It was shown previously in our laboratory that systems composed of maleic anhydride and L-Asc are very effective initiators of the free radical copolymerization of maleic anhydride with ST. Recently, it was found that thiol

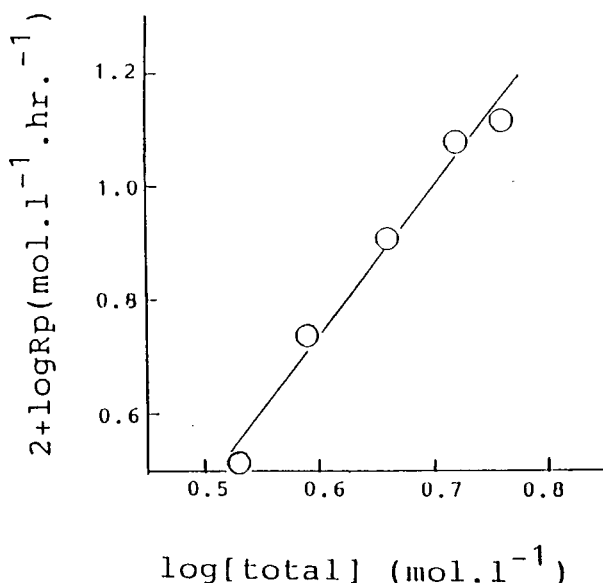


Fig. 5. Dependence of copolymerization rate (R_p) on total monomer concentration: [L-Asc] = 5.2×10^{-4} mol/L; temp = 40°C.

compounds may act as single electron donor toward strong electron acceptor like maleic anhydride, producing strong initiating radicals. It was suggested that the initiation radicals are produced via a homolytic cleavage of donor-acceptor complex formed between L-Asc and FN as an electron acceptor monomer.

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