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NOTE

COPOLYMERIZATION OF STYRENE WITH MALEIC ANHYDRIDE INITIATED BY L-ASCORBIC ACID

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INTRODUCTION

It is well known that maleic anhydride (MAH) behaves as an electron acceptor and forms charge-transfer complexes with donor monomers such as styrene (ST) [1, 2], divinyl ether [3], and some of other olefins [4-6]. The charge-transfer polymerization of ST with MAH has been extensively studied [1, 7-11]. On the other hand, *L*-ascorbic acid (L-Asc) in combination with a suitable oxidants proved to be an efficient redox initiator for various vinyl polymerizations. Misra et al. [12] showed that the reduction of peroxides by ascorbic acid follows a chain mechanism with ascorbate and other free radicals as intermediates. Thus, we can expect that such an electron donor might initiate the copolymerization of MAH with ST.

EXPERIMENTAL

ST was washed free of inhibitor with 5% aqueous NaOH, washed with water, distilled under vacuum, and stored at 0°C. Maleic anhydride was recrystallized twice from dry chloroform. Commercial L-Asc was used without further purification. Dioxane was refluxed over calcium hydride and distilled immediately before use. All other solvents were purified by conventional methods.

Copolymerization was carried out in glass tubes in the dark. The required amounts of a dioxane solution of MAH and ST were charged into a tube. Then aqueous L-Asc solution was added. The water content was adjusted to 4 vol%. The tube was wrapped with aluminum foil to protect it from light and placed in a thermostat. After the desired time the tube contents were poured into a large amount of diethyl ether to precipitate the copolymer, which was then dried under vacuum to constant weight. Conversions and rates were calculated from the weight of the dried copolymer.

Ultraviolet absorption spectra of dioxane solutions were obtained on a Shimadzu UV-210A spectrophotometer with a 1-cm cell. IR and NMR spectra were recorded with a JASCO IR-S1 and a Hitachi R-24B spectrophotometer, respectively.

RESULTS AND DISCUSSION

The copolymerization of ST with MAH can be initiated by L-Asc alone in dioxane containing 4 vol% water at 25-50°C. However, in the absence of L-Asc, the yields of copolymer obtained at 25-50°C are usually very low. A small amount of water or methanol added to the copolymerization system allows homogeneous copolymerization in the presence of L-Asc. Dioxane was used for all experiments since it dissolves the monomer and the copolymer and is miscible with water and methanol. The solvolysis of the MAH unit in the copolymer by water or methanol was examined by NMR and IR analysis, which showed that the product was a 1:1 alternating copolymer not solvolyzed under the experimental conditions.

A preliminary experiment showed that the copolymerization proceeds very fast and is not very reproducible in the absence of atmospheric oxygen even at 25°C and with a low concentration of L-Asc. Atmospheric oxygen exhibit an inhibitory effects (Table 1). It has been observed that the reaction between oxygen and L-Asc is autocatalytic, accelerated by oxygenated dehydro-L-Asc, and that the L-Asc-oxidant redox system acts as an efficient initiator even in the presence of atmospheric oxygen [13]. In order to improve reproducibility the copolymerization was carried out in the presence of atmospheric oxygen.

Low concentrations of diphenylpicrylhydrazyl (DPPH) caused a marked decrease in the yield (Table 2). This inhibitory effect of DPPH suggests that this is a free radical copolymerization.

As shown in Table 3, no polymer was obtained when either the L-Asc or the MAH monomer was absent. It is reasonable to conclude that the L-Asc-MAH complex is the active initiator.

TABLE 1. Influence of Oxygen[a]

Run	[L-Asc], mmol/L	Atmosphere	Time, h	Yield, %
1	0.043	Nitrogen	4	14.7
2	0.043	Oxygen	4	0
3	0.43	Nitrogen	3	64.7
4	0.43	Oxygen	3	10.2

[a] [ST] = [MAH] = 2 67 mol/L; solvent, dioxane/water (96/4 v/v); temperature, 25°C.

TABLE 2. Effect of Diphenylpicrylhydrazyl[a]

Run	[DPPH], mmol/L	Yield, %
1	0	10.3
2	0.11	9.2
3	0.17	5.9
4	0.22	Trace

[a] [ST] = [MAH] = 1.67 mmol/L; [L-Asc] = 1.3 mmol/L; temperature, 40°C; solvent, dioxand/water (96/4 v/v); time, 3h; atmosphere, air.

TABLE 3. Effect of Absence of L-Asc and MAH[a]

Run	[L-Asc], mmol/L	[MAH], mmol/L	Temperature, °C	Time, h	Yield, %
1	0	1.67	25	4	0
2	1.3	1.67	25	4	8.5
3	0	1.67	40	3	0
4	1.3	1.67	40	3	10.3
5	0	0	40	4	0
6	2.7	0	40	4	0

[a] [ST] = 1.67 mol/L; solvent, dioxane/water (96/4 v/v).

TABLE 4. Effect of Water and Methanol[a]

Run	Solvent	Time, h	Yield, %
1	Dioxane/water[b]	0.5	29.6
2	"	1	62.8
3	"	3	90.6
4	Dioxane/methanol[b]	0.5	0
5	"	1	2.7
6	"	3	27.7

[a] [ST] = [MAH] = 2.67 mol/L; [L-Asc] = 5.4 mmol/L; temperature, 25°C; atmosphere, air.

[b] 90/10 v/v.

Table 4 illustrates the effect of adding 10% of a solvent that solubilizes L-Asc. Water causes a marked increase in the yield, while methanol shows a lower activity as a solubilizing solvent.

The initial copolymerization rate (taken from the slope of the conversion curves in Fig. 1) increases with increasing temperature. The induction period (15 min at 40°C and 50 min at 25°C) decreases with increasing temperature, showing that the rate of consumption oxygen by the free radicals increases with the temperature. The overall energy of activation from the Arrhenius plot of the rates from Fig. 1 is 4.1 kcal/mol, i.e., lower than the value of 9.8 kcal/mol obtained by Shukla et al. [14] for the aqueous polymerization of acrylamide initiated by the L-Asc-permanganate redox system.

The initial rate and induction period increase with increasing L-Asc concentration (Fig. 2). The log-log plot of R_p versus L-Asc concentration (Fig. 3) has a slope of 0.6, and thus indicates the normal half-power dependence on the L-Asc concentration expected for mutual termination of the growing polymer chains. This also points to a radical intermediate in the present system.

The reason for the rather variable induction period is unknown. We suppose that the initiation mechanism involves formation of a complex between L-Asc and MAH, which breaks down to liberate the initiating radicals.

Figure 4 shows that the rate of copolymerization increases with increasing total monomer concentration. The slope of the log-log plot in Fig. 5 indicates that the rate varies as the 2.7 power of the total monomer con-

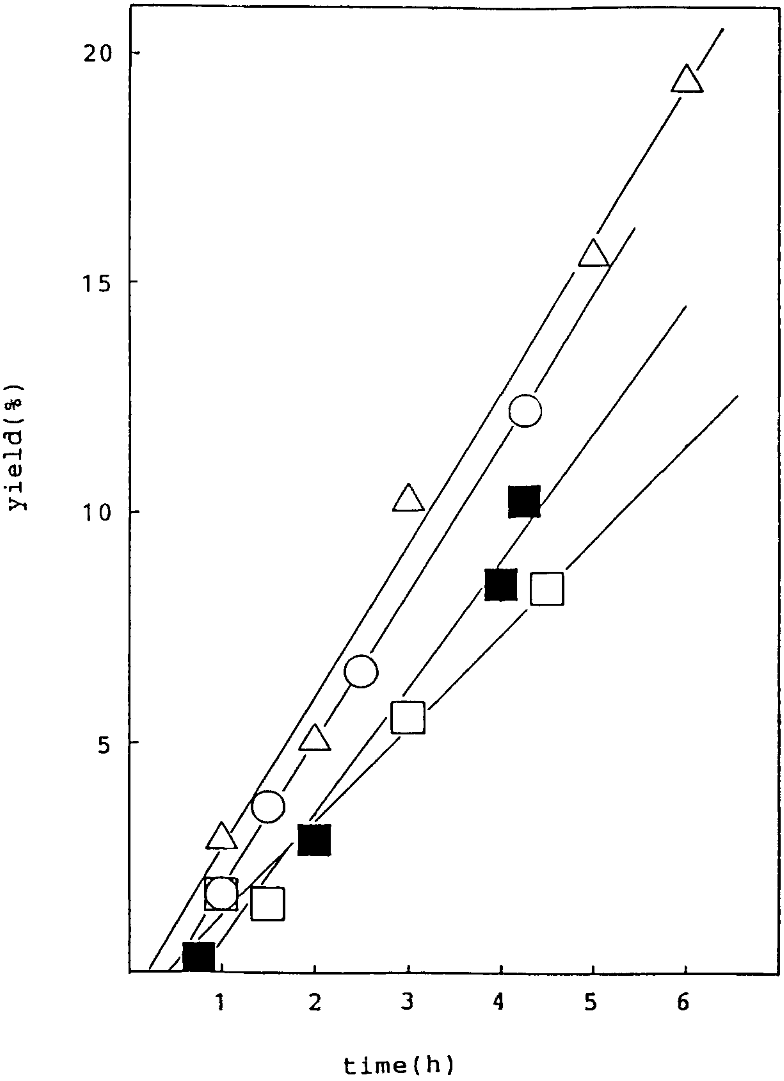

FIG. 1. Dependence of copolymerization rate on temperature. [ST] = [MAH] = 1.67 mol/L; [L-Asc] = 1.3 mmol/L; solvent, dioxane/water (96/4 v/v); atmosphere, air. Temperature: □ 20°C, ■ 25°C, ○ 30°C, △ 40°C.

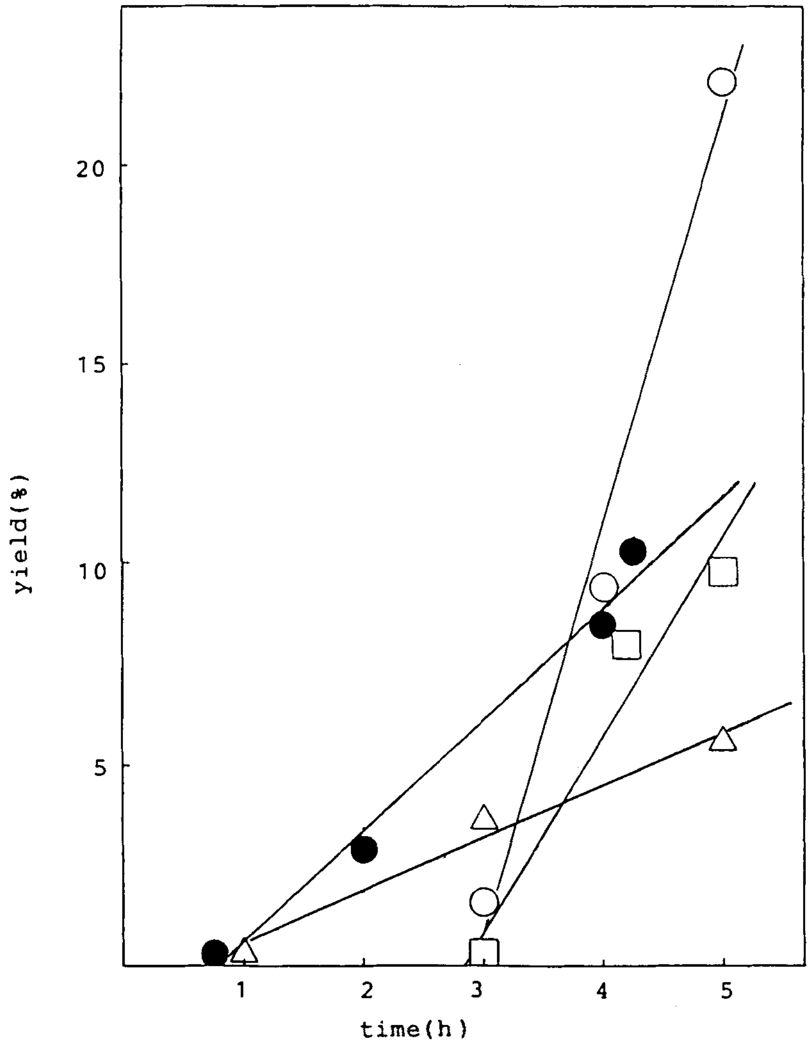

FIG. 2. Dependence of copolymerization rate on concentration of L-Asc. [ST] = [MAH] = 1.67 mol/L; temperature 25°C; atmosphere, air; solvent, dioxane/water (69/4 v/v). [L-Asc] (mmol/L): △ 0.77, ● 1.3, □ 6.7, ○ 13.

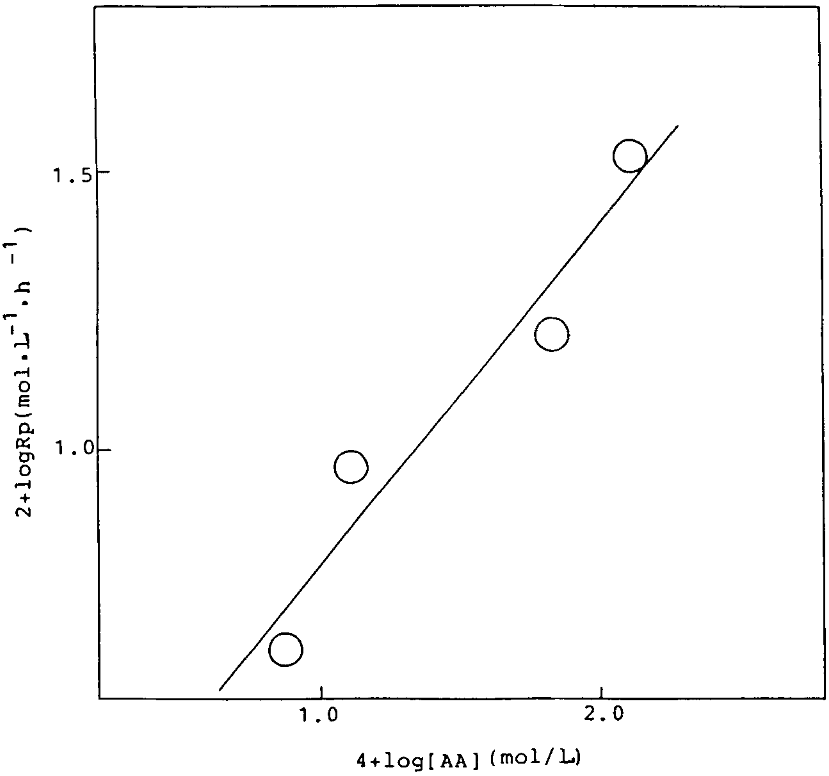

FIG. 3. Double logarithmic plot of copolymerization rate vs concentration of L-Asc.

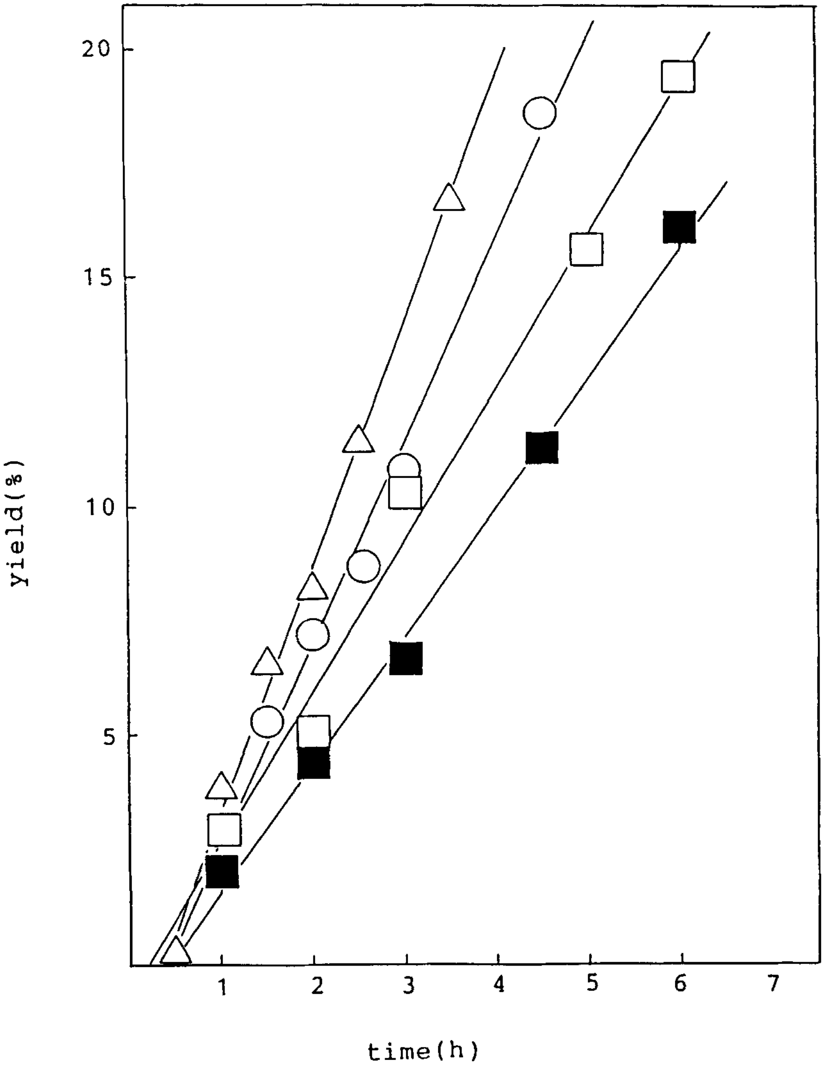

FIG. 4. Dependence of copolymerization rate on total monomer concentration. [ST] = [MAH] = 1.67 mol/L; temperature, 40°C; atmosphere, air; solvent, dioxane/water (69/4 v/v). Total monomer concentration, [MAH] + [ST] (mmol/L): ■ 3 0, □ 3.3, ○ 4.0, △ 4.3.

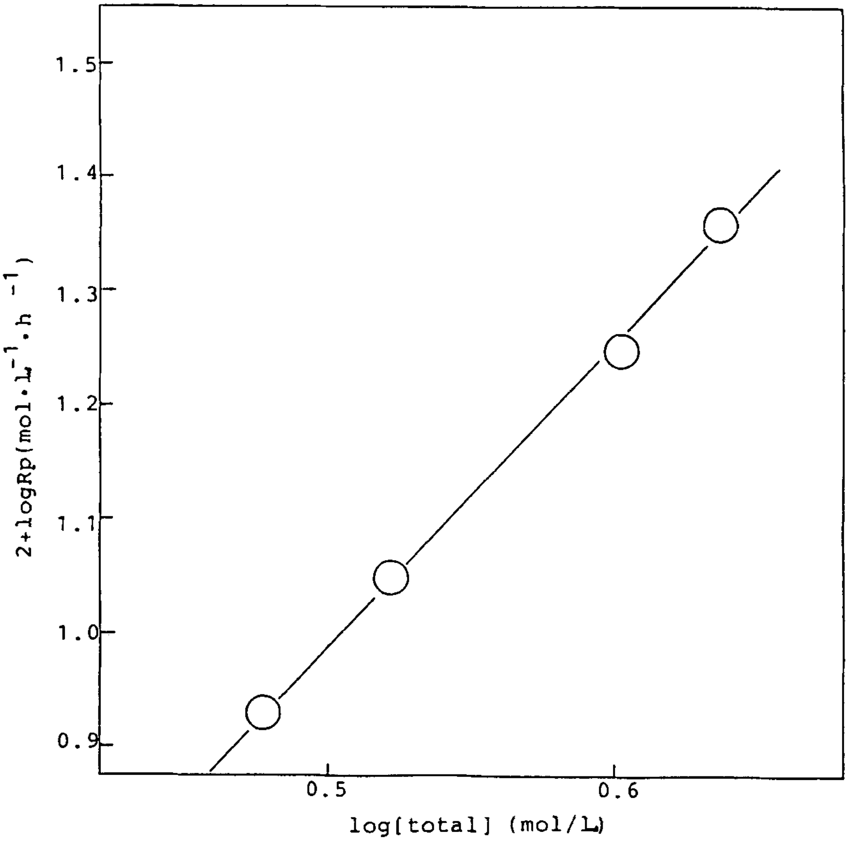

FIG. 5. Double logarithmic plot of copolymerization rate vs total monomer concentration.

centration, which we interpret as follows. The initial radical is produced by a charge-transfer complex between L-Asc and MAH monomer. We have shown previously that MAH with thiol compounds is a very effective initiator of free-radical copolymerization of MAH with ST. Recently, it was found that thiol compounds may act as single-electron donors toward a strong electron acceptor like MAH, producing strong initiating radicals. It is suggested that the initiation radicals are produced via homolytic cleavage of the donor-acceptor complex formed between L-Asc and MAH.

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