CHEMISTRY LETTERS, pp. 1385-1388, 1982. © The Chemical Society of Japan 1982

POLYMERIZATION OF METHYL METHACRYLATE IN THE WATER-DIOXANE SYSTEM CONTAINING PEROXIDE AND WATER-SOLUBLE POLYMER

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The polymerization of methyl methacrylate in the water-dioxane system containing peroxide and water-soluble polymer(PST) with amino groups was investigated. It was found that the polymerization proceeds smoothly at 60°C in the presence of both hydroperoxide and PST. The generation of radicals from the interaction between hydroperoxide and PST was observed by the ESR spectrum using spin trapping method.

The polymerization of vinyl monomers by various polymer-metal complexes has been reported by many investigators.$^{1)}$ We also found that the polymerization of methyl methacrylate(MMA) proceeds smoothly at 60°C in an aqueous solution of 1,4-dioxane(dioxane) not only in the presence of water-soluble polymer(PST)—metal complexes but also in the presence of PST only. PST was prepared by the amination of chloromethylated polystyrene with triethylenetetramine and purified by a dialysis against water. Later, we found that the radicals for the polymerization of MMA was generated from dioxane hydroperoxide. However, even in the presence of dioxane hydroperoxide, the polymerization of MMA did not proceed in the absence of PST. This report is concerned with the polymerization of MMA in the water—dioxane system containing peroxide and PST.

The content of peroxide in organic solvents was determined by iodometry.$^{2)}$ Table 1 shows the amination conditions of chloromethylated polystyrene and the characterization of PST obtained.

The polymerization was carried out as follows: 1 cm^3 of MMA was added into the

Table 1 Amination of chloromethylated polystyrene

Chloromethylated PS[a)] $\bar{P}_n$[b)]	(g)	Dioxane (cm^3)	TTA[c)] (cm^3)	Temp. (°C)	Time (min)	Amination (%)
460	0.5	125	40	60	25	45.1

a) Polystyrene b) Degree of polymerization c) Triethylenetetramine

water—dioxane system in the test tube containing peroxide and PST. After bubbling nitrogen into the solution, the content of the tube was frozen and then the tube was degassed and sealed under reduced pressure. The polymerization was carried out at 60°C under shaking. The polymer obtained was precipitated by pouring the content of the tube into a large amount of methanol, separated by centrifugation, and dried in vacuo.

The polymerization of MMA was carried out in the water—dioxane(10 vol%) system containing both various amounts of hydroperoxide and of PST. The results are shown in Fig.1. Figure 1 shows that the polymerization rate of MMA increased with an increase in the content of hydroperoxide and the polymerization proceeds most rapidly at a suitable concentration of PST. In the absence of hydroperoxide, the polymerization did not proceed at all. Thus it was found that the polymerization of MMA proceeds smoothly at 60°C in the presence of a very small amount of hydroperoxide. However, in the absence of PST, this polymerization scarcely proceeded even at 60°C for 24 h. Moreover, this polymerization scarcely proceeded in the presence of both hydroperoxide and triethylenetetramine. These results also suggest that both hydroperoxide and PST were necessary for this polymerization.

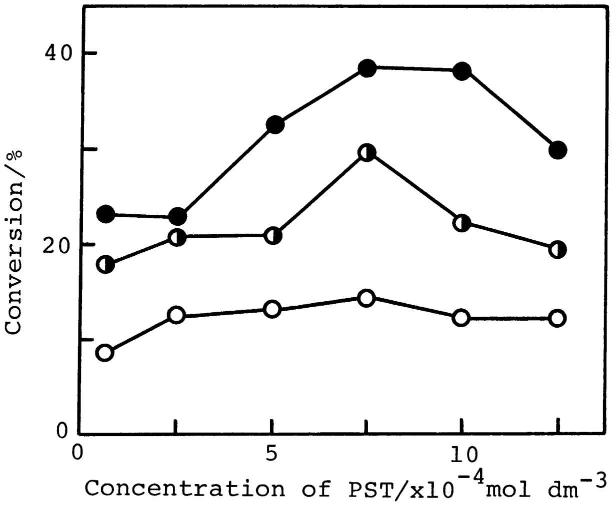

Fig.1 Polymerization of MMA in the water—dioxane(10 vol%) system containing a various amounts of hydroperoxide and of PST. Polymerization: 60°C, 1.5 h. [Added active oxygen] (wt/vol % to MMA); ○ :3x10^{-4}, ◑ :5x10^{-4}, ● :7x10^{-4}

The polymerization of MMA was carried out in the water—dioxane system containing various kinds of peroxide and PST. The results are shown in Fig.2. The activity of peroxide for the polymerization of MMA decreased in the following order: dioxane hydroperoxide > tetrahydrofuran hydroperoxide > hydrogen peroxide $\approx$ 0. The reason why the activity of dioxane hydroperoxide for the polymerization of MMA is highest is not obviously at present. Figure 2 also shows that the polymerization activity decreased with an increase in the dioxane content in the polymerization system. The results suggest that dioxane as solvent for MMA is not always necessary for this polymerization.

In order to ascertain the generation of radicals, the ESR spectrum of the water—dioxane(10 vol%) system containing both hydroperoxide and PST was observed by spin trapping method. The spectrum(Fig.3) shows

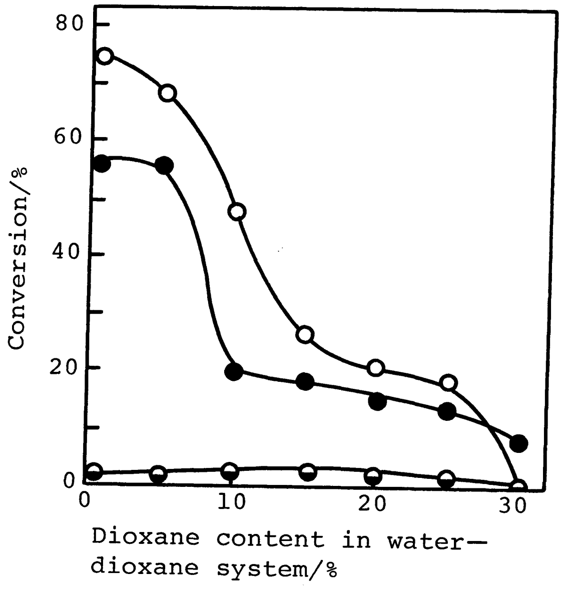

Fig.2 Effect of the kind of peroxide on the polymerization of MMA. [PST]=5×10^{-4}mol dm^{-3},[Added active oxygen]=1.2×10^{-3}wt/vol % to MMA, Polymerization: 60°C, 1 h. Peroxide; ○ :Dioxane hydroperoxide, ● :Tetrahydrofuran hydroperoxide, ◒ :hydrogen peroxide.

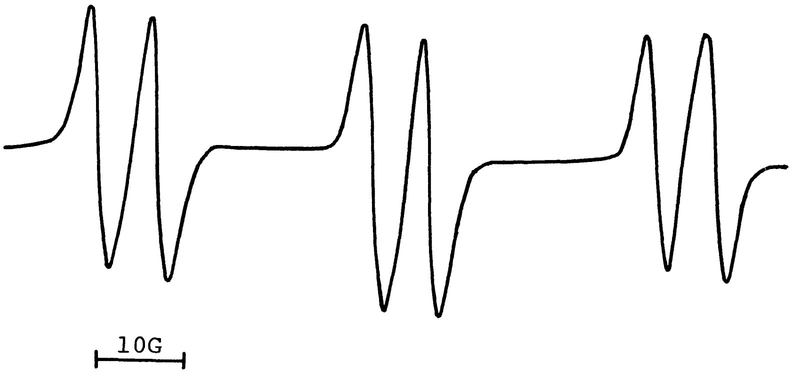

Fig.3 Observed ESR spectrum of the water— dioxane system containing dioxane hydroperoxide and PST. [PST]=3×10^{-2}mol dm^{-3}, [Added active oxygen]=5.3×10^{-3} wt/vol %. Anealing: 60°C, 30 min, Measurement: 30°C. Spin trapping agent: Phenyl-N-tert-butyl nitron.

that the radicals were generated in the system containing hydroperoxide and PST. However, the generation of radicals could not be recognized from the ESR spectrum of the similar system containing hydroperoxide and no PST.

This preliminary experiments indicate that the polymerization of MMA was initiated with the radicals generated by the interaction between hydroperoxide and PST. The details of the polymerization mechanism and the properties of the polymers obtained are currently under investigation.

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(Received May 14, 1982)