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Vinyl Polymerization. 282. Vinyl Polymerization Initiated by Dimethylhydroxylamine-Titanous(III) Chloride Redox System

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ABSTRACT

The polymerization of vinyl monomers initiated by dimethylhydroxylamine hydrochloride (DHA)-titanous(III) chloride redox system has been studied in water under a nitrogen atmosphere. In the polymerization of methyl methyacrylate (MMA) initiated by the above system, the rate of polymerization has been found to be proportional to $[\mathrm{DHA}]^{0.5}$ for DHA concentrations of less than 2.06×10^{-3} mole/liter, whereas at higher concentrations the rate tends to fall rapidly. The rate has also been found to be proportional to $[\mathrm{Ti(III)}]^{0.58}$ and to $[\mathrm{MMA}]^{1.0}$. The maximum rate of polymerization has been observed at a 1:1 molar ratio of DHA to Ti(III). The polymerization proceeded via a radical mechanism. The overall activation energy was estimated as 5.5 kcal/mole. It has been suggested that the reduction of dimethylhydroxylamine by titanous(III) chloride yields the dimethylamino radical, which initiates vinyl polymerization. An examination of the initiating capacity of the initiator system for the polymerization of some vinyl monomers has also been made.

INTRODUCTION

In earlier work we have shown that dimethylamino radicals produced by thermolysis [1] and UV photolysis [2] of tetramethyltetrazene initiates the polymerization of vinyl monomers (e.g., acrylonitrile, methyl methacrylate, and styrene). Furthermore, it has been demonstrated that the thermal decomposition of tetramethyltetrazene is catalyzed by suitable electrophilic agents such as acetic anhydride [1], benzyl chroride [3], dimethyl maleate [4], bromoacetic acid [5], 1-halogeno-2,4-dinitrobenzene [6], and adenine [7].

Continuing our investigation of the vinyl polymerization initiated by the dimethylamino radical, it was of particular interest to examine whether the reactivity of dimethylamino radical is dependent of the method of its generation. On the other hand, some studies [8-11] of vinyl polymerization initiated by amino radicals generated from the hyroxylamine-titanous(III) chloride redox pair has been reported. In the present work the generation of dimethylamino radical was by the same procedure used for the amino radicals [11].

The present paper deals with a detailed study on the catalytic behavior of the dimethylhydroxylamine hydrochloride (DHA)-titanous(III) chloride redox system for vinyl polymerization.

EXPERIMENTAL

Reagents

Ceric sulfate, N-phenylanthranilic acid, and hydrochloric acid were special grade reagents of Wako Pure Chemical Industries, Ltd., and were used without further purification. Acrylonitrile

(AN), methyl methacrylate (MMA), vinyl acetate (VA), and styrene (St) were purified by standard methods and distilled twice under reduced pressure in an atmosphere of nitrogen. Water used as solvent was purified by passing it through Amberlite mixed bed ion exchange resin, followed by distillation in a nitrogen atmosphere. Dimethylhydroxylamine was prepared from methylmagnesium iodide, and ethyl nitrate by the method of Hepworth [12]. Titanous(III) chloride solution was prepared as follows: A mixture of 180 ml of 20% titanous(III) chloride solution of reagent grade and 100 ml of 12 N hydrochloric acid was refluxed under nitrogen for half an hour. The reaction mixture was allowed to come to room temperature. The titanium oxide formed was removed by filtration, and the filtrate was suitably diluted with water and was used as the catalyst of polymerization.

Estimation of Titanous(III) Chloride Concentration

Titanous(III) chloride concentration was estimated by titration against standard ceric sulfate solution, using N-phenyl-anthranilic acid as indicator.

Polymerization Procedures

A stream of purified nitrogen was passed through the solution containing a known volume of water and monomer in a clean stoppered flask for half an hour. A known volume of titanous(III) chloride solution was added. Polymerization was then started by adding a calculated amount of dimethylhydroxylamine hydrochloride(DHA) solution to the above solution which was kept in a thermostat maintained at a definite temperature. After a given time, polymerization was stopped by the additions of hydroquinone and an excess of methanol. The rate of conversion was calculated from the weight of the dry polymer obtained.

Viscosity Measurements

Viscosity of the poly(methyl methacrylate) was determined in the usual way in an Ubbelohde dilution viscometer at 30 ± 0.02°C, with benzene as solvent.

RESULTS

Kinetics of Polymerization

The polymerization of MMA initiated by the DHA-titanous(III) chloride system was investigated kinetically. The polymerization of MMA was carried out at 30°C by varying the DHA concentration with the concentration of titanous(III) chloride constant. As can be seen from Fig. 1, at concentrations of DHA below about 2.06 × 10^{-3} mole/liter, the rate of polymerization (R_p) was proportional to the 0.5 power of the DHA concentration, while at concentrations of DHA higher than about 2.06 × 10^{-3} mole/liter there was a sharp decrease in the rate with an increase in DHA concentration.

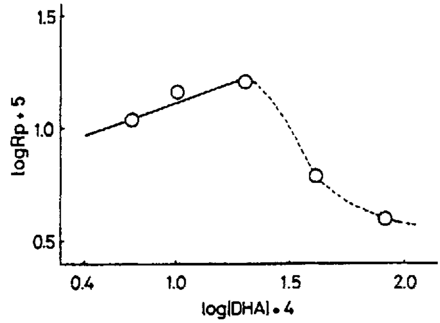

FIG. 1. Relationship between R_p and the DHA concentration in the polymerization of MMA in water at 30°C. [MMA] = 2.81 × 10^{-1} mole/liter. [Ti(III)] = 2.0 × 10^{-4} mole/liter.

A cause for the fall in the rate with increasing DHA concentration could be that DHA acts as an inhibitor. In order to check this point, the photopolymerization of MMA (2.8 moles/liter) initiated by tetramethyltetrazene (2.0 × 10^{-2} mole/liter) was performed in the presence of DHA (4 × 10^{-3} mole/liter) in a mixture of water and dioxane at 30°C for 4 hr, using a 100-W high-pressure mercury lamp [2]. And DHA was found to inhibit strongly the polymerization of MMA with tetramethyltetrazene, although the polymerization proceeded quite readily in the absence of DHA.

The polymerization was also carried out by varying the titanous(III) chloride concentration with the DHA concentration constant. As shown in Fig. 2, the rate was proportional to the 0.58 power of the concentration of titanous(III) chloride.

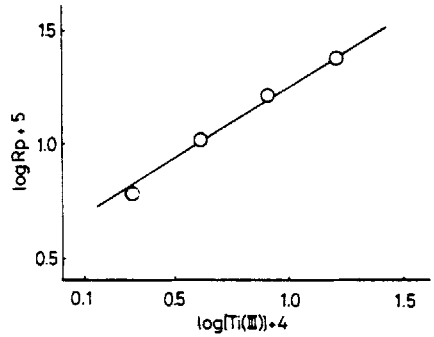

FIG. 2. Relationship between R_p and the concentration of titanous(III) chloride in the polymerization of MMA in water at 30°C. $[\mathrm{MMA}] = 2.81 \times 10^{-1}$ mole/liter. $[\mathrm{DHA}] = 4.12 \times 10^{-3}$ mole/liter.

At fixed concentrations of DHA and titanous(III) chloride, the polymerization was carried out by varying the monomer concentration. As seen in Fig. 3, the rate was directly proportional to the MMA concentration. Accordingly, at the lower concentration of DHA, the rate (R_p) can be expressed by

$$R_p = k[\mathrm{DHA}]^{0.5}[\mathrm{Ti(III)}]^{0.58}[\mathrm{MMA}]^{1.0} \tag{1}$$

On the other hand, the overall activation energy of the polymerization of MMA in water initiated by the DHA-titanous(III) chloride system was estimated as 5.5 kcal/mole from the Arrhenius plot of the rates of polymerization measured at 1, 10, 20, 30, and 40°C, as shown in Fig. 4.

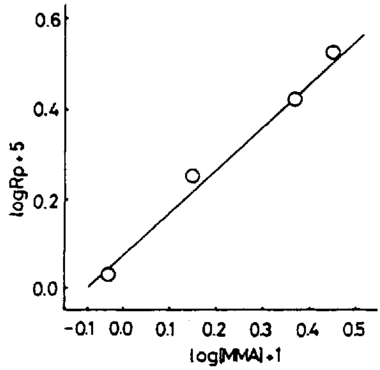

FIG. 3. Relationship between R_p and the monomer concentration in the polymerization of MMA in water at 30°C. [DHA] = 5.15×10^{-3} mole/liter. [Ti(III)] = 2.0×10^{-4} mole/liter.

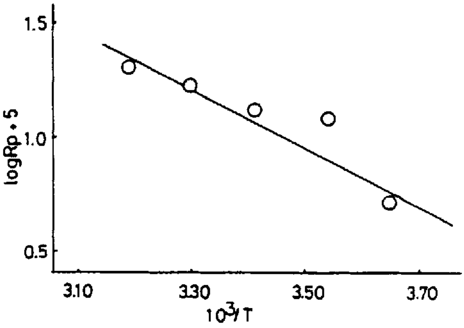

FIG. 4. Relationship between R_p and 1/T.

Effect of Oxygen on the Polymerization

All the experiments reported here were performed in oxygen-free closed systems. When oxygen was slowly bubbled into the system, however, polymerization did not start, as shown in Fig. 5. This indicates that oxygen is an inhibitor for the catalyst system, as it is for many other typical free-radical-initiated systems.

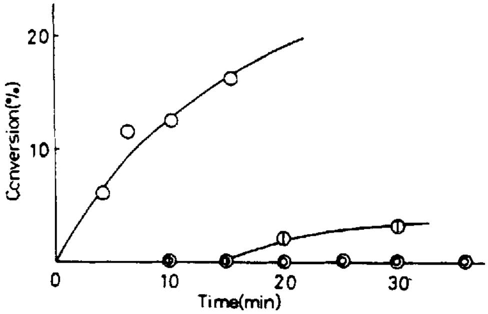

FIG. 5. Effect of oxygen on the polymerization of MMA initiated by the DHA-titanous(III) chloride system. [MMA] = 2.81×10^{-1} mole/liter [DHA] = 2.06×10^{-3} mole/liter. [Ti(III)] = 2.0×10^{-4} mole/liter. (○) Nitrogen was bubbled into the polymerization system for 30 min. (⦶) Neither nitrogen nor oxygen was bubbled into the polymerization system. (◎) Oxygen was bubbled into the polymerization system for 5 min.

Effect of DHA/Ti(III) Molar Ratio

The polymerization of MMA initiated by the DHA-titanous(III) chloride system was carried out at various DHA/Ti(III) molar ratios. Figure 6 shows the relation between the redox molar ratio and the rate of polymerization. As can be seen from Fig. 6, the maximum rate in the polymerization of MMA was obtained when the molar ratio of DHA to Ti(III) in the system was about unity.

Detection of Nitrogen in Polystyrene Initiated by the DHA-Titanous(III) Chloride

In order to obtain the information about the initiating radical for vinyl polymerization, the polymerization of St was carried out in water at 30°C for 1 hr, where [St], [DHA], and [Ti(III)] were 8.7×10^{-2}, 10×10^{-2} and 2.0×10^{-4} mole/liter, respectively. Elemental analysis of the resulting polymer showed the polymer to contain 0.28% nitrogen. However, no titanium metal was detected in the polymer.

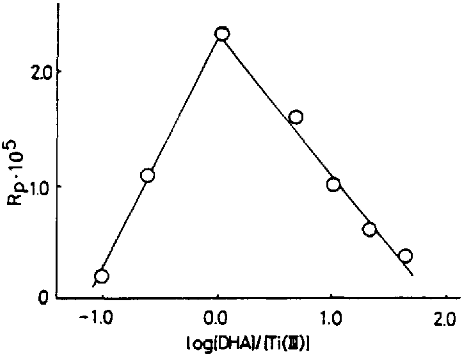

FIG. 6. Relationship between DHA/Ti(III) and the rate of polymerization (R_p).

Characterization of the Polymers Obtained

Figure 7 shows the reduced viscocities, η_{sp}/c, of the polymers obtained by the polymerization of MMA by varying the molar ratio of DHA to titanous(III) chloride.

The reduced viscocity undergoes a marked increase with dilution, as shown in Fig. 7. This observation is similar to those for polyelectrolytes such as the sodium salts of polymethacrylic acid in water and polyamide in formic acid [12]. In this work the solvent used for the viscocity measurement was not a polar solvent such as water and formic acid, but a nonpolar solvent, benzene. The latter solvent is considered to have no ability to dissociate the ion of the resulting polymer. Let us consider the reason. Since the polymerization was carried out in water, a small amount of water seemed to remain in the resulting polymer although the polymer was dried in vacuum. There is a possibility of the existence of water around the quaternary ammonium ion formed from the dimethylamino end group and the proton of hydrogen chloride. Thus the end group of the polymer could be dissociated by a trace of water. Accordingly, the resulting polymer shows the property of an polyelectrolyte.

The curves of Fig. 7 are representative of the results when the redox ratio of DHA to titanous(III) chloride are 20.6, 10.3, 5.2, and 2.6. As can be seen from Fig. 7, the larger the value of the redox ratio, the higher the reduced viscocity becomes.

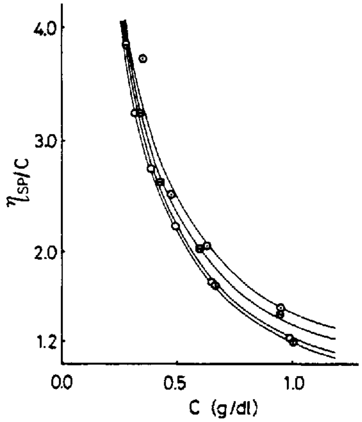

FIG. 7. Relationship between the reduced viscocities, η_{sp}/c, of the resulting polymers and their concentrations. [DHA] = 4.12 × 10^{-3} mole/liter. [MMA] = 2.81 × 10^{-1} mole/liter. (⊙) [Ti(III)] = 2.0 × 10^{-4} mole/liter. (⊖) [Ti(III)] = 4.0 × 10^{-4} mole/liter. (⦶) [Ti(III)] = 8.0 × 10^{-4} mole/liter. (○) [Ti(III)] = 16.0 × 10^{-4} mole/liter.

Catalytic Activity for Various Monomers

In order to examine the catalytic activity of the DHA-titanous(III) chloride system for vinyl polymerization, the polymerization of some vinyl monomers was carried out at 30°C. The other vinyl monomers further employed were AN, methyl acrylate (MA), VA, and St. The results are listed in Table 1. This system showed excellent activity for MA and VA, whereas little effect was observed for St.

DISCUSSION

It was found that DHA-titanous(III) chloride initiator system was effective for the addition polymerization of vinyl monomers. The value of 5.5 kcal/mole for the overall activation energy of the polymerization of MMA with the system was relatively lower than that for the ordinary redox systems. From the kinetics of the polymerization of MMA initiated by the DHA-titanous(III) chloride

TABLE 1. Polymerization of Various Vinyl Monomer Initiated by the DHA-Titanous(III) Chloride System in Water[a]

Monomer	[Monomer] (moles/liter)	$R_p \times 10^5$ (moles/liter sec)
AN	4.56	1.41
MA	3.34	19.00
VA	3.26	3.30
St	2.31	0.16
MMA	2.81	6.75

[a] [DHA] = 2.06×10^{-3} mole/liter [Ti(III)] = 2.0×10^{-4} mole/liter.

system and the inhibitory effect of molecular oxygen on the polymerization, it is obvious that the polymerization proceeds by a normal free-radical mechanism. The polystyrene initiated by the above system was found to contain nitrogen, presumably as the dimethylamino end group. Moreover, the polymerization rate increased with increasing concentration of titanous(III) chloride at constant DHA concentration. These results provide strong evidence for the existence of a transient dimethylamino radical in the initiating media. This consideration is in agreement with the conclusion of Abbisetti et al. [9] that the reaction of hydroxylamine with titanous(III) salts produces amino radicals which initiate vinyl polymerization. As already mentioned, the rate of polymerization increased with the DHA concentration, attained a maximum value at a DHA concentration of 2.06×10^{-3} mole/liter, and fell with an increase in the DHA concentration. It was observed that DHA behaved as an inhibiting agent as well as an initiating agent. Although the exact reaction mechanism is still uncertain, these findings may be explained as follows. With the increase in DHA concentration the rate of generation of dimethylamino radicals and its concentration increase. Accordingly, the rate of polymerization increases with DHA concentration. However, the dimethylamino radical derived from the redox pair undergoes more and more easily such side reaction as

$$(CH_3)_2N^{\cdot} + (CH_3)_2NOH \longrightarrow (CH_3)_2NH + (CH_3)_2NO^{\cdot} \qquad (2)$$

The radicals produced in Eq. (2) would be resonance-stabilized. This radical is considered to terminate polymerization. On the other hand, the maximum rate in polymerization was obtained at a 1:1 molar ratio of DHA to Ti(III). When an excess of titanous(III) chloride is treated with DHA, the following side reaction probably occurs [9, 14]:

$$(CH_3)_2N^{\cdot} + Ti(III) + H^+ \longrightarrow (CH_3)_2NH + Ti(IV) \qquad (3)$$

Furthermore, from the above-mentioned experimental results, the primary step of polymerization is recognized as a one-electron reduction of dimethylhydroxylamine by titanous(III) chloride:

$$(CH_3)_2HNOH^+ + Ti(III) \longrightarrow (CH_3)_2N^{\cdot} + H_2O + Ti(IV) \qquad (4)$$

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