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Metal-Containing Initiator Systems. VII. The Polymerization of Vinyl Monomers by N-Bromosuccinimide in the Presence of Reduced Nickel*

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SUMMARY

A study of the polymerization of some vinyl monomers by the system of N-bromosuccinimide (NBS) and reduced nickel was made at 60°C. It was found that this system shows excellent activity for methyl methacrylate, weak activity for styrene, and no effect for vinyl acetate polymerizations. From the results of the polymerization kinetics, the copolymerization experiment, and the effect of radical inhibitors, it was proved that polymerization by this initiator system proceeds via a radical intermediate. The initiation is considered to be induced by a succinimide radical that is produced. The mechanism for initiation is presented and discussed.

INTRODUCTION

It is well known that the nitrogen—bromine bond in N-bromosuccinimide (NBS), which is a typical brominating agent, decomposes into free radicals when exposed to light. In 1960, Dannley and Esayian [1] found that NBS can initiate the radical polymerization of methyl methacrylate at 100°C but that it inhibits the styrene

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polymerization. These results were explained on the basis of the stability and the reactivity of the produced succinimide radical and bromine atom toward the monomer used.

Recently, we found that some organic halides having the chemical bonds of C-X, O-X, N-X, S-X, and Si-X, where X is halogen atoms, can serve as effective polymerization initiators of vinyl monomers in the presence of some activated metals such as hydrogenation catalysts [2, 3]. In a previous paper [3] it was stated that the system of NBS and reduced nickel could also induce the radical polymerization of styrene and methyl methacrylate at 60°C.

The present paper describes the kinetic results on the polymerization of styrene, methyl methacrylate, and vinyl acetate by NBS in the presence or absence of reduced nickel at 60°C.

EXPERIMENTAL

Materials

The reduced nickel used was commercially obtainable hydrogenation catalyst (Nikki Chemical Co.), which was composed of 50% Ni atom on kieserite. Before use, this catalyst was activated by heating it at about 200°C in a stream of hydrogen for 1 hr.

Commercial NBS was used after recrystallization from benzene. Styrene, methyl methacrylate, and vinyl acetate were purified by ordinary methods and distilled under reduced pressure before use. The other reagents were purified by ordinary methods.

Polymerization Procedure

Required amounts of NBS and monomer were placed into a hard glass tube containing a given amount of activated reduced nickel. After its contents were degassed, the tube was sealed off under vacuum.

Dark polymerizations and copolymerizations were carried out in ethyl acetate solution in this tube with shaking in a thermostat maintained at 60°C. After polymerization, the contents of the tube were poured into a large amount of methanol, which contained concentrated hydrochloric acid, in order to precipitate the polymer and to dissolve the residual metal initiator. The resulting polymer was then purified by reprecipitating two or three times from the system of benzene and methanol. The conversion was calculated from the weight of the dried polymer obtained.

Analysis of the Polymer

The intrinsic viscosities, $[\eta]$, of the resulting polymethyl methacrylates were measured in benzene at 30°C. Infrared spectra of

the polymers were determined using a Hitachi IR-G infrared spectrometer.

The composition of the copolymers of methyl methacrylate with styrene was determined from the results of elementary carbon analysis.

RESULTS AND DISCUSSION

Polymerizations by NBS Alone

The results of the polymerization of styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAC) by NBS alone in the presence or absence of sunlight are shown in Table 1.

Table 1. Polymerizations by NBS: [NBS] = 0.03 mole/liter. [M] = 50 vol. % in Ethyl Acetate

Monomer	Polymerization conditions			Yield %	[η] ^a dl/g
	Sunlight	Temp., °C	Time, hr		
MMA	Present	ca. 30	6	49.9	0.36
	Absent	ca. 30	240	0.03	2.8
	Absent	60	3	0	—
	Absent	60 ^b	3	12.4	3.6 (7600)
St	Present	ca. 30	5	0.1	—
	Absent	60	12	0	—
	Absent	60 ^b	12	3.7	(1450)
VAC	Absent	60	12	0	—
	Absent	60 ^b	12	0	—

^aValues in parentheses indicate the degree of polymerization.

^bPolymerized in the presence of reduced nickel ([Ni] = 4.3×10^{-2} g-atom/liter).

From Table 1, it was observed that NBS could initiate the rapid polymerization of MMA in the presence of sunlight to give a quite low molecular weight polymer, but it did not induce St and VAC polymerizations. In the absence of sunlight, NBS did not show any activity for initiation of any of these monomers at 60°C.

However, the binary system of NBS and reduced nickel was found to show an excellent activity for MMA and a weak activity for St polymerizations, but no effect for VAC polymerization at 60°C. These selectivities of initiation against monomers used were in agreement with the results reported by Dannley and Esayian [1] and might be explained by the differences in stability of the succinimide radical produced from NBS and its reactivity toward the monomers or their growing radicals.

The infrared spectrum of the low molecular weight poly (MMA) obtained by NBS in the presence of sunlight was in agreement with that of ordinary radical polymer, except for the existence of an absorption band at 680 cm^{-1} due to the carbon-bromine bond. The existence of the bromine atom in this polymer was also confirmed by bromine analysis. However, the infrared spectrum of the high molecular weight poly (MMA) obtained by NBS-reduced nickel was identical to that of ordinary radical polymer.

Figure 1 shows the infrared spectra of the resulting poly (St). As seen in this figure, the polymer obtained by NBS in the presence

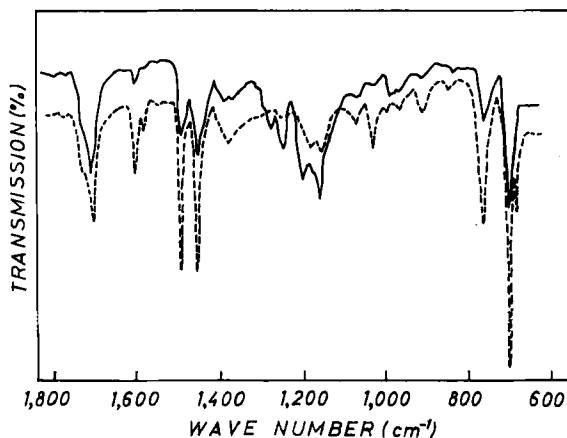


Fig. 1. Infrared spectra of the resulting polystyrenes obtained by NBS alone in the presence of sunlight (-----) and obtained by NBS-reduced nickel in the absence of light (—).

of sunlight showed absorption bands at 680 cm^{-1} due to the carbon-bromine bond and at 1710 cm^{-1} due to the carbonyl group. On the other hand, the polymer obtained in the presence of reduced nickel without sunlight showed only an absorption band at 1710 cm^{-1} . Accordingly, this result might suggest that the polymerization was initiated by the succinimide radical.

Kinetic Studies of the MMA Polymerization by NBS and Reduced Nickel

Figure 2 shows the time-conversion relations in the polymerization of MMA by the system of NBS and reduced nickel in ethyl acetate at the temperature range of 30–80°C. From this figure, the straight line relationships were obtained at every temperature.

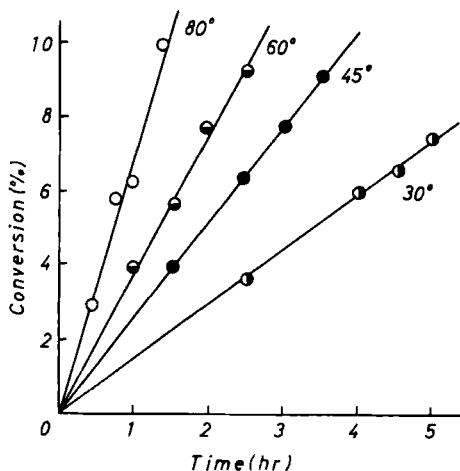


Fig. 2. Time-conversion relations for the polymerization of MMA at 30–80°C: $[MMA] = 4.68$ moles/liter, $[NBS] = 5.6 \times 10^{-2}$ moles/liter, $[Ni] = 4.3 \times 10^{-2}$ g-atom/liter in ethyl acetate.

The rates of polymerization (R_p), which were determined from Fig. 2, were plotted against the reciprocal polymerization temperatures as shown in Fig. 3. From the slope of the resulting straight line, the apparent activation energy for overall polymerization by this initiator system was calculated to be 6.3 kcal/mole. Accordingly, the activation energy for initiation was then obtained as 3.8 kcal/mole by using the reported rate constants [4] for propagation and termination. This value was quite small as compared with that of ordinary radical initiator, indicating that the initiating radical may be produced through a redox interaction between NBS and reduced nickel.

Figure 4 shows the relationship between R_p and the concentration of reduced nickel at constant concentrations of both MMA and NBS. As seen in Fig. 4, R_p was proportional to the square root concentration of reduced nickel used.

A similar relationship between R_p and the concentration of NBS was observed in its concentration range, lower than 5×10^{-3} mole/liter, as is shown in Fig. 5. At a higher concentration of NBS than

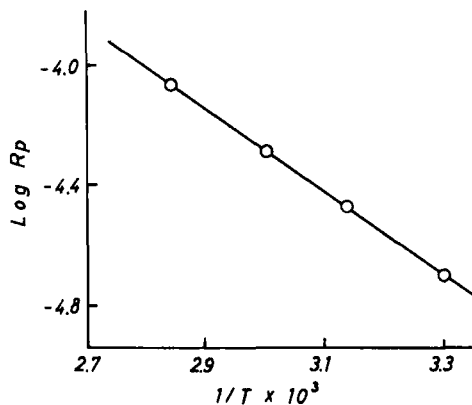


Fig. 3. Relationship between $\log R_p$ and the reciprocal polymerization temperature.

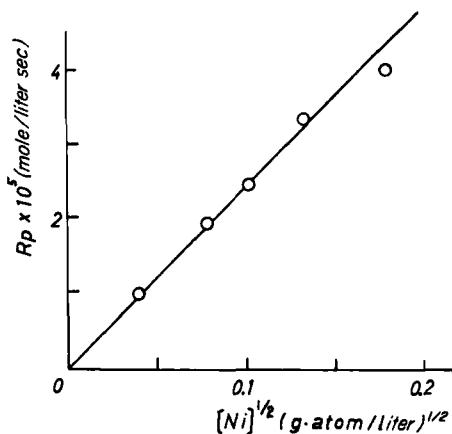


Fig. 4. Relationship between R_p and the concentration of reduced nickel: $[MMA] = 4.68$ moles/liter, $[NBS] = 2.8 \times 10^{-2}$ moles/liter in ethyl acetate at 60°C .

this, the rate seemed to remain constant, independent of its concentration, as was discussed in a previous paper [5] for the system of carbon tetrachloride and reduced nickel. Accordingly, it might be thought that this polymerization proceeded with a radical mechanism, and the initiating radical was produced via a complex formation between NBS and reduced nickel, as was pointed out by Olivé and Olivé [6] and Iwatsuki et al. [7] in the initiation by activated metals and carbon tetrachloride.

Figure 6 shows the plot of the R_p against the monomer concentration. It was obvious that R_p was directly proportional to the monomer concentration, and this result might suggest that the monomer did not participate in initiating radical production.

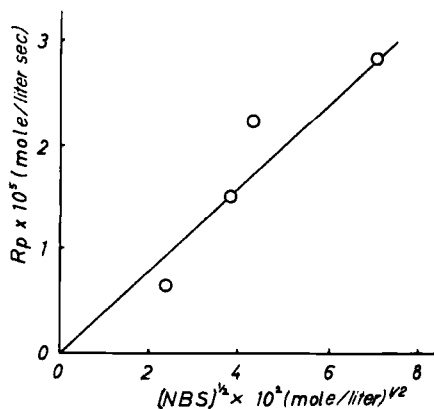


Fig. 5. Relationship between R_p and the concentration of NBS: $[MMA] = 4.68$ moles/liter, $[Ni] = 4.3 \times 10^{-2}$ g-atom/liter in ethyl acetate at $60^\circ C$.

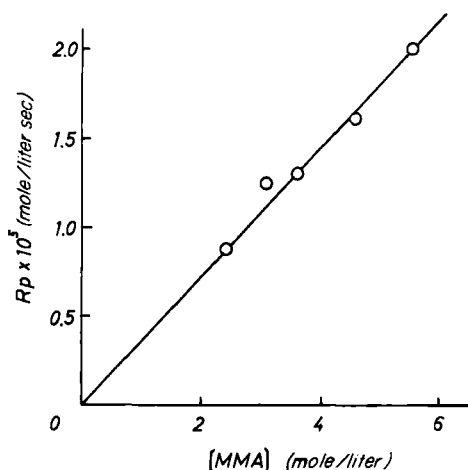


Fig. 6. Relationship between R_p and the MMA concentration: $[Ni] = 4.3 \times 10^{-2}$ g-atom/liter, $[NBS] = 1.4 \times 10^{-3}$ moles/liter in ethyl acetate at $60^\circ C$.

Copolymerization of MMA and St by NBS-Reduced Nickel

To clarify further whether the polymerization by this system proceeds via a radical mechanism, the copolymerization of MMA(M_2) with St(M_1) was investigated. From the results obtained, the copolymer composition curve was drawn as is seen in Fig. 7. The resulting curve was found to coincide with that obtained by ordinary radical initiator. Accordingly, it was concluded that the copolymerization proceeded through a radical intermediate.

Effect of Radical Inhibitor

Table 2 shows the results of the polymerization of MMA by the system of NBS and reduced nickel in the presence of some radical inhibitors.

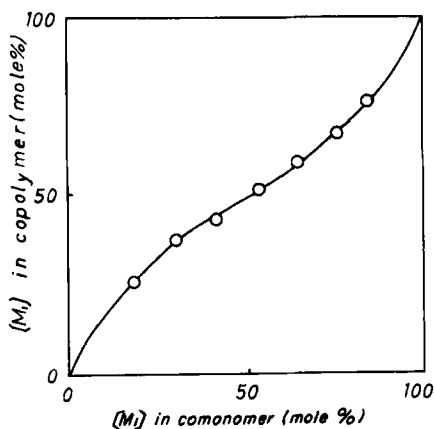


Fig. 7. Copolymer composition curve for the copolymerization of MMA (M_2) and St (M_1): $[\text{Ni}] = 1.14 \times 10^{-1}$ g-atom/liter, $[\text{NBS}] = 1.9 \times 10^{-2}$ moles/liter in ethyl acetate at 60°C .

Table 2. Effect of Radical Inhibitors on the Polymerization of MMA by NBS-Reduced Nickel at 60°C for 6 Hr: $[\text{M}] = 4.68$ moles/liter, $[\text{NBS}] = 0.03$ mole/liter, $[\text{Ni}] = 4.3 \times 10^{-2}$ g-atom/liter in Ethyl Acetate

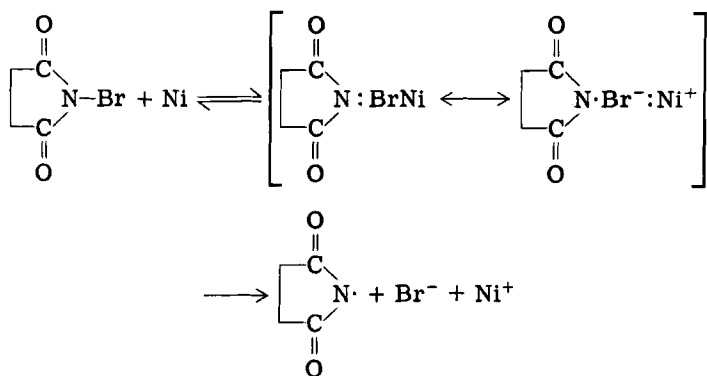
Inhibitor, g	Polymer yield, %
None	26.1
Air	5.2
Hydroquinone (0.05)	0
p-Benzoquinone (0.05)	0

As can be seen from Table 2, hydroquinone, p-benzoquinone, and oxygen inhibited this polymerization.

Initiation Mechanism by this Binary System

From the results of polymerization kinetics, copolymerization, and the effect of radical inhibitors, it was clear that the polymerization of MMA by the system of NBS and reduced nickel in the absence of light proceeded via a radical mechanism. This conclusion was in agreement with that reported in the initiator system of carbon tetrachloride and reduced nickel [5].

Similarly, as was pointed out in a previous paper [5], the initiation of polymerization by this binary system may be expected to occur as follows:



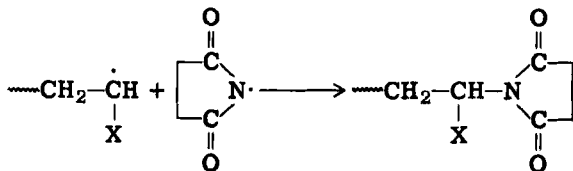
wherein the transition state complex between NBS and nickel atom is formed, and then one electron transfer from nickel atom to a nitrogen-bromine bond in NBS occurs.

This mechanism is characterized by the fact that only the succinimide radical is produced from NBS in the presence of reduced nickel, contrary to the homolysis of the nitrogen-bromine bond in NBS. Accordingly, the fact that this binary system can initiate the high polymerization of MMA and no bromine atom is incorporated in the resulting polymer may be explained from the above reaction scheme insofar as no chain transfer to NBS occurred.

The apparent activation energy for initiation of MMA polymerization by this system was quite low (3.8 kcal/mole) and the same as that for the system of reduced nickel and carbon tetrachloride [5]. This might indicate that the one electron transfer occurred readily.

A possible explanation of the finding that St hardly polymerizes and VAC does not polymerize at all (Table 1), contrary to MMA, may be related to the stability and reactivity of the initiating radical, i.e., because a succinimide radical is polarized and stabilized by a

resonance, it can act as both initiator and terminator of these polymerizations, as follows:



Similar primary termination was assumed in vinyl polymerizations by diethyldithiocarbamate radical $[(\text{C}_2\text{H}_5)_2\text{NCSS} \cdot]$ produced from the decomposition of tetraethyl thiuram disulfide [8, 9]. Recently, it was also postulated by Nakayama and Smets [10] that in the radical polymerization of maleimide the monomer chain transfer which yields a succinimide radical might occur as a unimolecular termination. Accordingly, such a primary termination might be important in the polymerizations of St and VAC, as is expected from the polar and resonance natures of both the succinimide radical and the growing polymer radical.

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