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Polymerization of Vinyl Monomers with Binary Initiator System of N-Chlorosuccinimide and Lewis Acids

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ABSTRACT

The polymerization of vinyl monomers with a binary system composed of N-chlorosuccinimide (NCS) and some Lewis acids was investigated by means of kinetic and spectral determinations. It was found that the NCS-$ZnCl_2$ system was the most effective as an initiator of radical polymerization of methyl methacrylate, and this polymerization was initiated by a radical produced via the reaction of NCS and $ZnCl_2$, and terminated bimolecularly. By applying a spin trapping technique to the reaction of NCS with $ZnCl_2$, it was shown that the initiating radical was N-succinimidyl radical which was obtained through a homolysis at the N—Cl bond.

INTRODUCTION

In previous papers [1, 2] the results of the radical polymerization of vinyl monomers initiated by the combined system of

N-chlorosuccinimide (NCS) with some protic acids such as p-toluenesulfonic acid [1], have been reported. In the course of studying the initiating activity of the above system, it was found that some Lewis acids could form excellent initiator system when combined with NCS. The present paper will describe the results obtained from the polymerization of vinyl monomers with these systems.

EXPERIMENTAL

Materials

NCS was used after purification according to the method described in the previous paper [1]. Methyl methacrylate (MMA), ethyl acrylate (EA), acrylonitrile (AN), styrene (St), and vinyl acetate (VAc) were purified and distilled in a stream of nitrogen just before use. Zinc chloride was a commercial grade sample which was used after drying at about 120°C for a few hours just before use. Stannic chloride and tetrachlorosilane were purified by distillation from their commercial grade samples. The pure-grade aluminum chloride and silver nitrate were used without further purification.

Procedures of Reaction and Polymerization

The reaction of NCS with Lewis acids and the polymerization with the above combined system were carried out according to the methods described in the previous paper [1].

The initiator activity of these systems for the polymerization was evaluated by measuring the polymer yield and the concentration of the unreacted NCS as a function of reaction time. The reactions were carried out in a glass tube which contained the required amounts of NCS, Lewis acid, and monomer in ethyl acetate. After an appropriate reaction time, the content of the tube was dispersed into a mixed solution of acetic acid and benzene (1:1) and the amount of unreacted NCS was determined iodometrically [1, 3].

RESULTS AND DISCUSSION

Polymerization of MMA with NCS in the Presence of Lewis Acids

The reactions of NCS with various Lewis acids and the polymerization of MMA with their systems were carried out in ethyl acetate. The results obtained are shown in Table 1.

TABLE 1. Reaction of NCS with Various Lewis Acids and Polymerizations of MMA with Their System in Ethyl Acetate[a]

Lewis acid	NCS reacted[c]	Polymer[d]	$\overline{P}_n \times 10^{-3}$[e]
$ZnCl_2$	21.7	15.2	9.8
$SnCl_4$	7.2	0.3	-
$SiCl_4$	98.5	0.2	-
$AlCl_3$	99.8	0.7	-
$AgNO_3$[b]	9.2	5.0	6.0
None	0	0.4	-

[a] Experimental conditions : [NCS] = 7.49×10^{-2} mole/liter; [Acid] = 1.49×10^{-1} mole/liter.

[b] [$AgNO_3$] = 1.49×10^{-2} mole/liter.

[c] Reacted at 80°C for 10 hr.

[d] Polymerized at 60°C for 12 hr.

[e] Number-average degree of polymerization ($\overline{P}_n$) was determined viscometrically in benzene [2].

Table 1 shows that $ZnCl_2$ and $AgNO_3$ in the presence of NCS can initiate the polymerization of MMA to give a high molecular weight polymer, and the resulting polymer yield corresponds reasonably well to the amount of NCS consumed. However, in the cases using $SiCl_4$ and $AlCl_3$ as Lewis acid, the polymer yield is quite low although the NCS is almost consumed. These results suggest that NCS reacted so rapidly with the Lewis acids that an inactive species for polymerization was formed. Since a white precipitate was immediately produced when NCS was mixed with these Lewis acids, the reaction probably takes place via a different mechanism than in the cases using $ZnCl_2$ and $AgNO_3$.

Table 2 shows the effect of solvents on the polymerization of MMA with the NCS-$ZnCl_2$ initiator system.

From Table 2 it is seen that the solvent used has a large effect on the polymerization yield, which also increases with an increase of the polar nature of the solvents.

To clarify the selectivity of various monomers toward polymerization with the NCS-$ZnCl_2$ initiator system, polymerizations were carried out in ethyl acetate at 60 C. The results are shown in Table 3, from which it is seen that this initiator system shows an excellent activity for the polymerizations of MMA, EA, and AN, and

TABLE 2. Polymerization of MMA with NCS and $ZnCl_2$ in Some Solvents at 60°C[a]

Solvent	Polymerization yield (%)
Acetonitrile	33.6
Ethanol	33.1
Acetone	15.0
Benzene	10.2
Ethyl acetate	9.5

[a] Polymerization conditions: [MMA] = 4.68 moles/liter, [$ZnCl_2$] = 1.46×10^{-1} mole/liter, [NCS] = 7.49×10^{-2} mole/liter, polymerized for 12 hr.

TABLE 3. Polymerization of Some Vinyl Monomers with NCS and $ZnCl_2$ at 60°C in Ethyl Acetate[a]

Monomer	Polymerization yield (%)
EA	35.4
AN	13.5
MMA	6.2
St	Trace
VAc	0

[a] Polymerization conditions: monomer = 5 ml, [NCS] = [$ZnCl_2$] = 7.49×10^{-2} mole/liter, polymerized for 6 hr.

a weak activity for St. However, no polymerization of VAc was observed with this system. A similar selectivity was observed in polymerizations with NCS—p-toluenesulfonic acid [1] and with N-bromosuccinimide—reduced nickel initiator system [4].

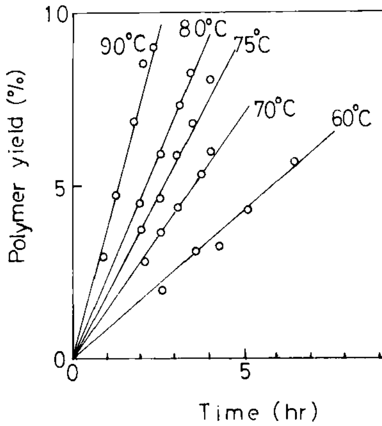


FIG. 1. Time-conversion curve of the polymerization of MMA with the NCS/$ZnCl_2$ system in ethyl acetate. [NCS] = [$ZnCl_2$] = 7.49×10^{-2} mole/liter, [MMA] = 4.68 moles/liter.

Kinetic Studies on the Polymerization of MMA with NCS-$ZnCl_2$ System

Figure 1 shows the time-conversion relationship in the polymerization of MMA initiated by the NCS-$ZnCl_2$ system in ethyl acetate at 60 to 90°C. Straight line relationships are obtained at every temperatures. When the rates of polymerization (R_p) calculated from Fig. 1 are plotted against the reciprocal of the absolute reaction temperature, the results are as shown in Fig. 2.

From the slope of this line, the apparent activation energy for overall polymerization is obtained to be 11.9 kcal/mole, from which the activation energy for initiation is calculated as 14.8 kcal/mole by using the reported values for propagation and termination of MMA [5].

Figure 3 shows the relationship between the concentration of NCS or $ZnCl_2$ in the initiator system and R_p. It is seen that R_p increases proportionally to the square root of the concentrations of both NCS and $ZnCl_2$.

Figure 4 shows the plot of R_p against to the concentration of MMA monomer. It is found that R_p is direct proportional to the monomer concentration. Consequently, R_p in the polymerization of MMA with the NCS-$ZnCl_2$ initiator system is expressed as

$$R_p = k[\mathrm{NCS}]^{1/2}[\mathrm{ZnCl_2}]^{1/2}[\mathrm{MMA}] \qquad (1)$$

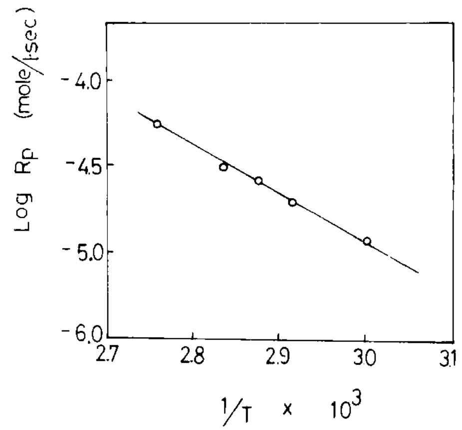


FIG. 2. Arrhenius plot of MMA polymerization with the NCS/ZnCl$_2$ system. [MMA] = 4.68 moles/liter, [NCS] = [ZnCl$_2$] = 7.49 × 10^{-2} mole/liter in ethyl acetate.

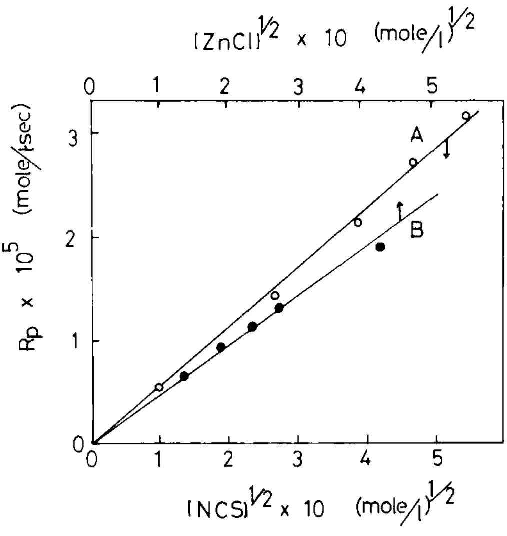


FIG. 3. Relationship between R$_p$ and [NCS] or [ZnCl$_2$]. [MMA] = 4.68 moles/liter in ethyl acetate. A: [ZnCl$_2$] = 7.49 × 10^{-2} mole/liter, [NCS] is changed. B: [NCS] = 7.49 × 10^{-2} mole/liter, [ZnCl$_2$] is changed.

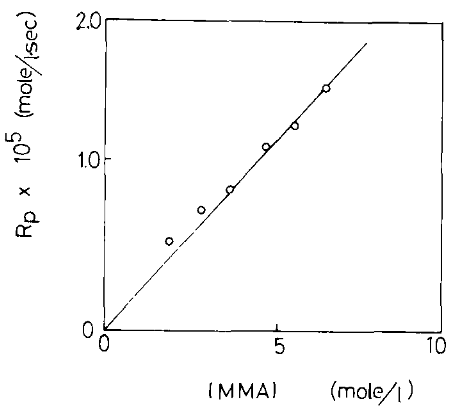


FIG. 4. Dependence of [MMA] on R_p. [NCS] = [$ZnCl_2$] = 7.49 × 10^{-2} mole/liter in ethyl acetate at 60°C.

Similar rate equations were found for the radical polymerizations with some redox initiator systems [6] and for the NCS—p-toluenesulfonic acid system [1].

Evaluation of Initiator Activity of the NCS-$ZnCl_2$ System

In order to evaluate the initiation efficiency of the NCS-$ZnCl_2$ system in MMA polymerization, the reaction of NCS with $ZnCl_2$ in the presence of MMA was investigated kinetically by determining the unreacted NCS. The results obtained at 80 to 120°C are shown in Fig. 5.

From Fig. 5, it is seen that the reaction proceeds according to second-order kinetics. When the logarithms of the rate constants (k_2) of the reactions are plotted against the reciprocal of the absolute temperatures, a straight line relationship is observed, as shown in Fig. 6.

From Fig. 6 the activation energy of the reaction is calculated to be 18.3 kcal/mole, and the activation enthalpy and entropy at 80°C are 17.6 kcal/mole and -28.8 e.u., respectively.

The efficiency of initiation of MMA polymerization with the NCS-$ZnCl_2$ initiator system was calculated by using

$$R_p = k_p/k_t^{1/2}(fk_2[\mathrm{NCS}][\mathrm{ZnCl_2}])^{1/2}[\mathrm{MMA}] \qquad (2)$$

$$k_p/k_t^{1/2} = 9.5e^{-4500/RT} \qquad (3)\ [7]$$

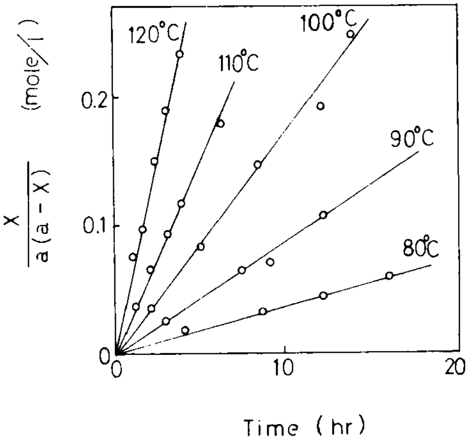


FIG. 5. Reaction of NCS with $ZnCl_2$ in ethyl acetate. [MMA] = 4.68 moles/liter, [NCS] = [$ZnCl_2$] = 7.49 × 10^{-2} mole/liter. a and X are the initial concentration of NCS and its consumed concentration, respectively.

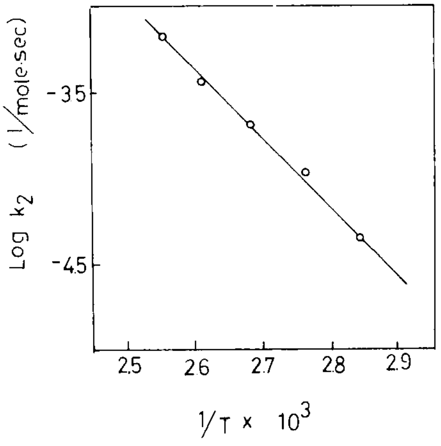


FIG. 6. Arrhenius plot of the reaction of NCS with $ZnCl_2$. [MMA] = 4.68 moles/liter, [NCS] = [$ZnCl_2$] = 7.49 × 10^{-2} mole/liter in ethyl acetate.

By introducing the values observed or calculated at 80°C, i.e., $[\mathrm{NCS}] = [\mathrm{ZnCl_2}] = 7.49 \times 10^{-2}$ mole/liter, $[\mathrm{MMA}] = 4.68$ mole/liter $k_2 = 4.78 \times 10^{-5}$ liter/(mole)(sec) and $R_p = 3.16 \times 10^{-5}$ mole/(liter)(sec), the efficiency of initiation of this system was found to be 0.29.

Interaction between NCS and $ZnCl_2$

The IR spectrum of the reaction mixture of NCS with $ZnCl_2$ in a liquid cell was determined in acetonitrile as a function of time. It is noted that the carbonyl absorption band of NCS at 1745 cm^{-1} does not change in the presence of $ZnCl_2$, and no band at 1725 cm^{-1} due to hydrogen bonding appears. This result is quite different from that observed in the reaction mixture of NCS with p-toluenesulfonic acid [1]. Accordingly, it seems that there is no interaction (e.g., formation of hydrogen bond) between the carbonyl oxygen of NCS and $ZnCl_2$.

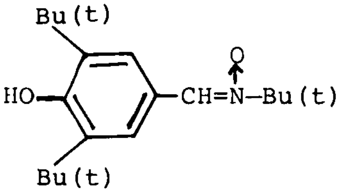
However, the fact that this system shows an excellent initiating activity, and that NCS reacts bimolecularly with $ZnCl_2$, suggests the possibility of an interaction. Since Lewis acid has been shown to have a high affinity for the chlorine atom in some organic halides (e.g., as in Friedel-Crafts reaction), an interaction between the chlorine atom in NCS and $ZnCl_2$ may exist, and such an interaction seems to play an important role in the production of initiating species for radical polymerization.

Detection and Identification of Intermediate Radical Species by Spin Trapping Technique

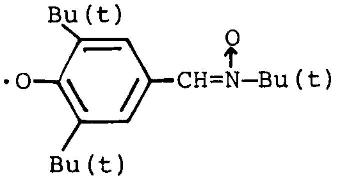
To detect and identify the radical species produced in polymerization with the NCS-$ZnCl_2$ system, electron spin resonance (ESR) measurement by the spin trapping technique was undertaken in a manner similar to that mentioned in the previous paper [1].

The reaction of NCS (3.74×10^{-2} mole/liter) with $ZnCl_2$ (1.89×10^{-2} mole/liter) in the absence of monomer was carried out in the presence of 3,5-di-tert-butyl-4-hydroxyphenyl-N-tert-butylnitrone (I) [7] (9.89×10^{-2} mole/liter) as a spin trapping agent in ethyl acetate for 1 hour at 70°C.

Figure 7 shows the ESR spectrum of the reaction mixture. The spectrum of this figure, consisting of 18 lines, is assigned to a phenoxy stable radical (II). The 18-line phenoxyl radical spectrum is attributed to hfc of the electron to the nitrogen and to the HC=N proton, with a secondary, in equivalent splittings by the two aromatic protons ($A_N = 5.05$ G, $A_{CH} = 2.60$ G, $A_m^H = 1.50$ and 1.70 G).



(I)



(II)

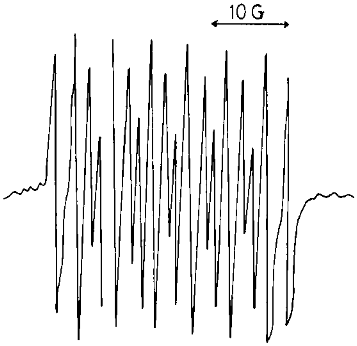
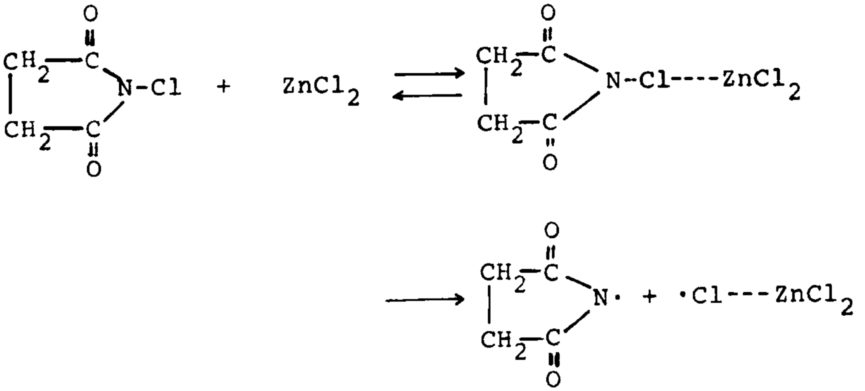


FIG. 7. ESR spectrum of the reaction mixture obtained in the presence of I for 1 hr at 70°C. [I] = 3.24×10^{-2} mole/liter, [NCS] = 3.74×10^{-2} mole/liter, and [$ZnCl_2$] = 3.32×10^{-2} mole/liter.

This indicates that a radical other than the carbon radical, which adds to the CH=N bond of I to yield a 6-line nitroxide ESR spectrum, probably succinimidyl nitrogen radical, is produced in this reaction, similar to the results obtained in the reaction of NCS with p-toluenesulfonic acid [1].

Initiation Mechanism of Polymerization

From the results of kinetic studies of the reaction of NCS with $ZnCl_2$ and the polymerization with this combined system and of spectral measurements of this reaction mixture, it is assumed that the polymerization proceeds via a radical mechanism and the initiating species may produce as follows:



(4)

According to this scheme, a complex between the chlorine atom in NCS and $ZnCl_2$ is formed, and the N—Cl bond in the complex is weakened by homolysis. This is different from the result described in the reaction between NCS and p-toluenesulfonic acid [1], in which a complex is formed by hydrogen bonding between the carbonyl oxygen of NCS and protic acid, and its N^+—Cl bond easily undergoes homolysis. Since it has been known to form a complex between the carbonyl oxygen in some ketones and esters and Lewis acids, weak interaction between carbonyl oxygen and $ZnCl_2$ in the present complex cannot be neglected.

Since protic acid and Lewis acid interact with different sites of NCS to form a complex, a cooperative effect of both acids on the polymerization of MMA might be expected. To check this point, p-toluenesulfonic acid (PTS) and $AgNO_3$ were used as protic and Lewis acids, respectively. The results are shown in Table 4.

TABLE 4. Cooperative Effect of PTS and $AgNO_3$ on the Polymerization of MMA in Ethyl Acetate at 60°C[a]

[PTS] (mole/liter)	[$AgNO_3$] (mole/liter)	Polymer yield (%)
1.50×10^{-2}	1.50×10^{-2}	12.7
0	1.50×10^{-2}	2.0
1.50×10^{-2}	0	4.2
0	0	0.2

[a] Polymerization conditions: [NCS] = 7.49×10^{-2} mole/liter, [MMA] = 4.68 moles/liter, polymerized for 9 hr.

As can be seen from Table 4, the rate of polymerization with the combined use of both acids to NCS markedly increases compared with their separate use, indicating the existence of a cooperative effect of both acids. This observation may also support the initiation mechanism of polymerization with the initiator system described by Eq. (4).

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