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Vinyl Polymerization by Binary Systems of N-Benzoyloxysuccinimides and p-Toluenesulfonic Acid

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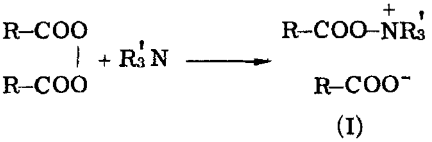
ABSTRACT

The binary systems of N-acyloxyimides with p-toluenesulfonic acid (PTS) were found to serve as effective initiators for the radical polymerization of such vinyl monomers as methyl methacrylate (MMA), methyl acrylate, and acrylonitrile. N-Benzoyloxysuccinimide (NBS), N-acetoxysuccinimide, and N-benzoyloxyphthalimide were used as the N-acyloxyimides. The polymerization of MMA with the NBS/PTS system depended upon the solvents used. The results of copolymerization of MMA with styrene initiated by this system and of the application of the spin trapping technique indicated that polymerization proceeded through a radical mechanism. A kinetic study on the polymerization of MMA with this system in ethanol was also investigated. The observed overall activation energy was 18.2 kcal/mole. The rate of polymerization (R_p) was expressed as $R_p = k[\mathrm{NBS}]^{0.2}[\mathrm{PTS}]^{0.5}[\mathrm{MMA}]^{1.0}$. From the results obtained, the initiation mechanism of vinyl polymerization by the NBS/PTS system was proposed and discussed.

INTRODUCTION

In a previous paper [1] it was found that N-hydroxysuccinimide, a nitrogen analog of peracid, served as an effective initiator for radical polymerizations of acrylate monomers.

It has recently been found that combined systems of N-acyloxyimides, nitrogen analogs of diacyl peroxide, and p-toluenesulfonic acid (PTS) induce radical polymerization of vinyl monomers. This binary initiator system seems to be interesting in connection with the initiation mechanism for the diacyl peroxide/tertiary amine initiator systems in which the reaction is considered to proceed as follows [2]:

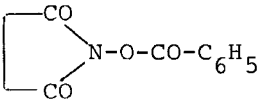


$$\begin{matrix}R\text{–}COO\\ |\\ R\text{–}COO\end{matrix} + R'_3N \longrightarrow \underset{(I)}{\begin{matrix}R\text{–}COO\text{–}\overset{+}{N}R'_3\\ \\ R\text{–}COO^-\end{matrix}} \qquad (1)$$

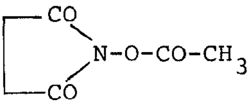
$$I \longrightarrow R\text{–}COO\cdot + \cdot\overset{+}{N}R'_3 + R\text{–}COO^- \qquad (2)$$

Thus the structure of N-acyloxyimides used here seems to resemble that of the reaction intermediate (I) in Eq. (1). The present paper deals with the results of vinyl polymerization with the binary initiator systems of N-acyloxyimides and PTS.

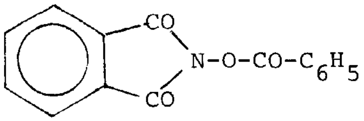
N-benzoyloxysuccinimide (NBS), N-acetoxysuccinimide (NAS), and N-benzoyloxyphthalimide (NBP) were used as N-acyloxyimides.



(NBS)



(NAS)



(NBP)

EXPERIMENTAL

NBS was prepared by the reaction of N-hydroxysuccinimide (NHS) with benzoyl chloride in pyridine and recrystallized from ethanol: mp 139-140°C (Ref. 3, 136°C). NAS was prepared by reaction of NHS with acetic anhydride and recrystallized from ethanol: mp 132-133°C (Ref. 4, 131-132°C). NBP was prepared by reaction of N-hydroxyphthalimide with benzoyl chloride in pyridine and recrystallized from ethanol: mp 176-178°C (Ref. 5, 174-175°C). Commercially available PTS was purified by recrystallization from ethyl acetate. Phenyl-tert-butylnitrone (PBN), a spin trapping reagent, was prepared according to the method of Emmons [6] and recrystallized from petroleum ether: mp 73°C (Ref. 6, 76°C). The solvents and monomers were used after purification by the usual methods.

Polymerizations were carried out in sealed tubes which were degassed by a freezing and thawing method.

The viscosity-average molecular weight ($\bar{M}_v$) of the poly(MMA) obtained was viscometrically determined in benzene at 30°C by using [7]:

$$\log \bar{M}_v = 5.34 + 1.32 \log [\eta] \tag{3}$$

The reaction of NBS with PTS was carried out in the presence of PBN, a spin trapping agent, in an ESR tube which was degassed and sealed under vacuum. The ESR spectrum of the reaction mixture was recorded by using a JES-ME-3X spectrometer with 100 kHz modulation.

RESULTS AND DISCUSSION

Polymerization of MMA with the NBS/PTS System

In order to see whether NBS, a nitrogen analog of diacyl peroxide, can induce vinyl polymerization, the polymerization of MMA with NBS was carried out at 80°C in bulk for 5 hr. The results obtained are shown in Table 1.

According to the results, NBS itself is not effective as an initiator but in the presence of PTS it serves as an excellent initiator for MMA. Its initiator activity depends upon the solvents used. Among them, ethanol strongly accelerates this polymerization.

NAS and NBP were also used in the polymerization of MMA in ethanol, and the results are shown in Table 1. The NAS/PTS and NPS/PTS systems can also induce the polymerization of MMA, but they are not as effective as the NBS/PTS system. The viscosity-average molecular weights ($\bar{M}_v$) of the poly(MMA) obtained from these systems are as high as $(1.72 \sim 4.4) \times 10^5$.

TABLE 1. Polymerization of Methyl Methacrylate (MMA) with N-Acyloxyimides and PTS Systems[a]

Imide	[Imide] (mole/L)	[PTS] (mole/L)	Solvent	Temperature (°C)	Time (hr)	Yield (%)	$\overline{M}_v \times 10^{-5}$
NBS	0.046	0	Bulk	80	5	4.8	
-	0	0	Bulk	80	5	3.3	
NBS	0.023	0.079	Ethanol	60	10	61.9	2.50
NBS	0.023	0.079	Acetone	60	10	26.3	
NBS	0.023	0.079	Chloroform	60	10	22.2	
NBS	0.023	0.079	Benzene	60	10	18.8	
NBS	0.023	0.079	Acetonitrile	60	10	14.8	
NBS	0.023	0.079	Ethyl acetate	60	10	8.6	
NBS	0.023	0.079	Tetrahydrofuran	60	10	8.5	
NBA	0.023	0.079	Ethanol	60	10	16.8	1.72
NBP	0.023	0.079	Ethanol	60	10	14.0	4.43

[a] [MMA] = 4.68 mole/L.

TABLE 2. Polymerization of Some Vinyl Monomers with the NBS/PTS system at 60°C for 10 hr in Ethanol[a]

Monomer	Yield (%)
Methyl methacrylate	61.9
Acrylonitrile	58.6
Methyl acrylate	56.8
Styrene	4.4
Vinyl acetate	Trace

[a] Monomer = solvent = 5 mL, [PTS] = 0.079, [NBS] = 0.023 mole/L.

TABLE 3. Copolymerization of Styrene and Methyl Methacrylate (MMA) with the NBS/PTS System at 60°C in Ethanol

	Mole % of MMA
In the monomer mixture	51.9
In the copolymer	51.2

Polymerizations of Some Vinyl Monomers by the NBS/PTS System

Some vinyl monomers were polymerized by the NBS/PTS system at 60°C for 10 hr. The results are shown in Table 2. This binary initiator system is found to be effective for MMA, methyl acrylate, and acrylonitrile (electron-accepting monomers) while it gives only low yields in the polymerization of electron-donating styrene (St) and vinyl acetate.

Copolymerization of St and MMA with the NBS/PTS System

To see whether this polymerization proceeds through a radical mechanism, the copolymerization of St (2.36 mole/L) and MMA (2.55 mole/L) with the NBS/PTS system was carried out at 60°C. As shown in Table 3, the molar ratio of MMA to St in the resulting copolymer is about 1, indicating that this polymerization propagates via a free-radical intermediate.

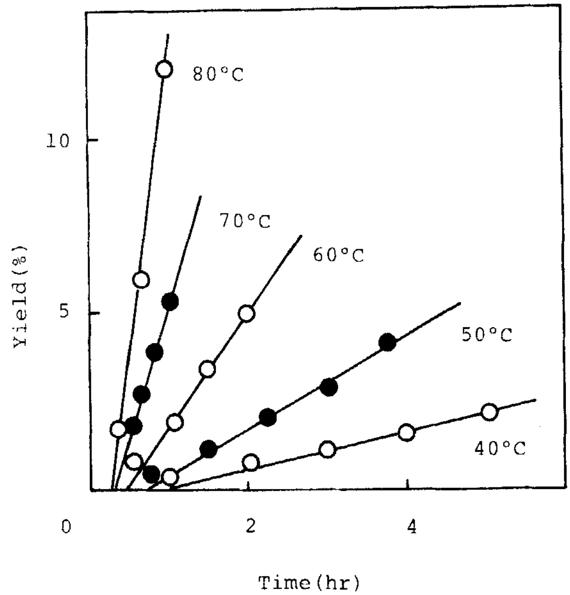


FIG. 1. Time-conversion curves in the polymerization of MMA with the NBS/PTS system in ethanol. [NBS] = 2.3×10^{-2} mole/L, [PTS] = 7.9×10^{-2} mole/L, [MMA] = 4.68 mole/L.

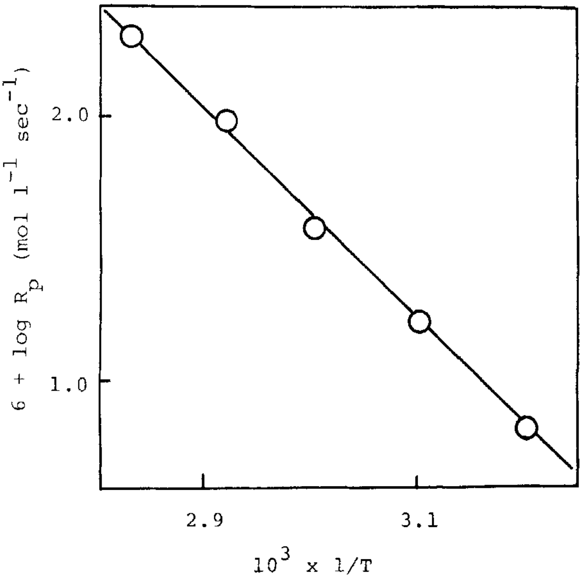


FIG. 2. Arrhenius plot in the polymerization of MMA with the NBS/PTS system in ethanol. [NBS] = 2.3×10^{-2} mole/L, [PTS] = 7.9×10^{-2} mole/L, [MMA] = 4.68 mole/L.

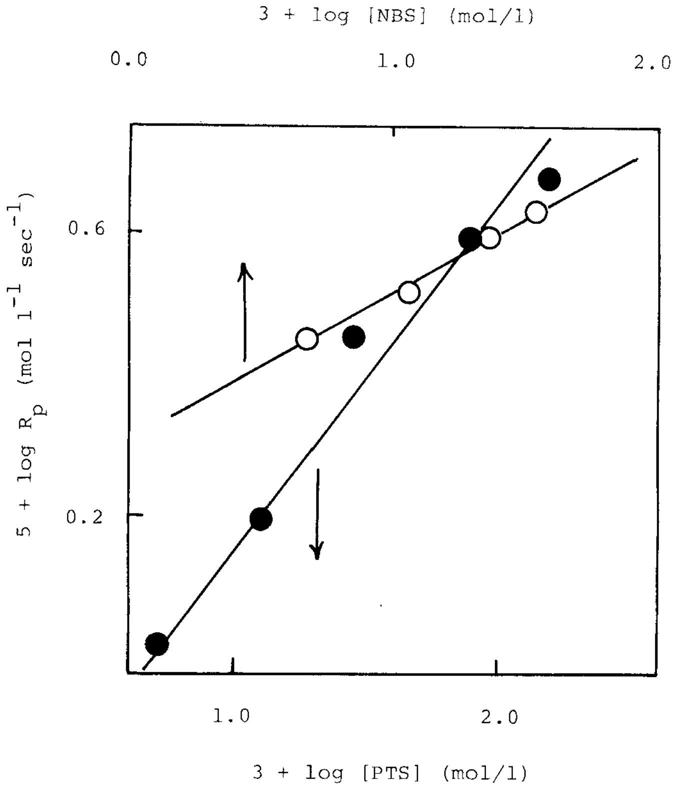


FIG. 3. Relationship between the polymerization rate (R_p) and the concentration of the initiator system in ethanol at 60°C. [MMA] = 4.68 mole/L, ○ : [PTS] = 7.9×10^{-2} mole/L, ● : [NBS] = 2.3×10^{-2} mole/L.

Kinetic Study of the Polymerization of MMA with the NBS/PTS System

The polymerization of MMA with the NBS/PTS system was studied kinetically in ethanol. Although poly(MMA) is insoluble in ethanol, the polymerization system is homogenous in the initial stage under the present conditions because MMA is a good solvent for its polymer.

Figure 1 shows the time-conversion obtained in the temperature range from 40 to 80°C. This polymerization shows a short induction period which becomes even shorter with an increase in the reaction temperature.

Figure 2 shows an Arrhenius plot of the rate of polymerization

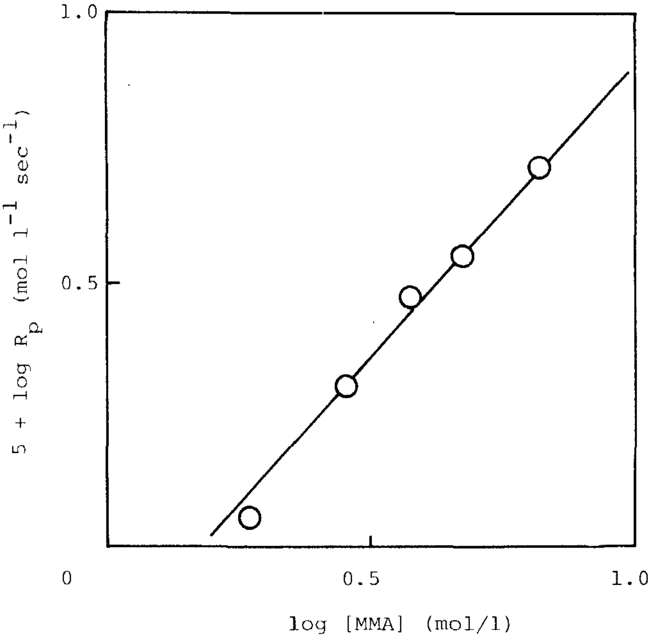


FIG. 4. Relationship between the polymerization rate (R_p) and the monomer concentration at 60° C in ethanol/ethyl acetate mixture. [NBS] = 2.3×10^{-2} mole/L, [PTS] = 7.9×10^{-2} mole/L, ethanol: 30 vol%. Ethyl acetate was used as a diluent.

(R_p) obtained from the time-conversion curves in Fig. 1 with the reciprocal polymerization temperature. From the slope of the straight line in Fig. 2, the overall activation energy of this polymerization is calculated as ~18.2 kcal/mole, which is somewhat lower than that (20 ~ 21 kcal/mole) by azobisisobutyronitrile.

The effects of the concentrations of NBS and PTS on R_p were investigated at 60° C at a constant concentration of MMA. The results are shown in Fig. 3. From the slopes of both straight lines, R_p is found to depend on the 0.2 order of the NBS concentration and on the 0.5 order of the PTS concentration. The reason for the lower order NBS concentration is uncertain at the present time.

Figure 4 shows the relationship between R_p and the MMA concentration observed at 60° C when ethyl acetate was used as a diluent to keep the ethanol concentration constant (30 vol%). From this figure, R_p is proportional to the first order of the MMA concentration.

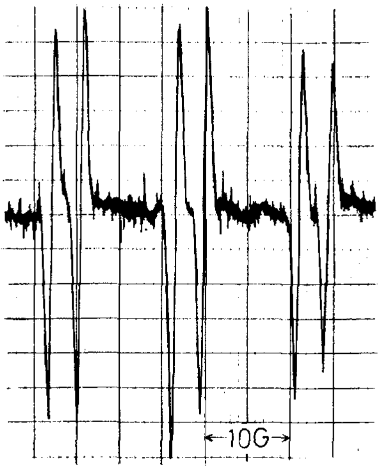
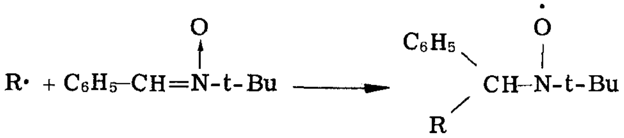


FIG. 5. ESR spectrum of the mixture of NBS with PTS in the presence of PBN after being reacted at 60°C for 2 hr in ethanol/ethyl acetate (50:50 vol/vol) mixture. [NBS] = 4.6×10^{-2} mole/L, [PTS] = 9.5×10^{-2} mole/L, [PBN] = 2.8×10^{-2} mole/L.

Initiation Reaction by the NBS/PTS System

As shown above, the results of copolymerization of St and MMA with the NBS/PTS system reveal that this polymerization proceeds through a radical mechanism. In order to get further information on the initiation mechanism by this initiator system, the reaction of NBS with PTS was carried out in an ethanol-ethyl acetate mixture in the presence of phenyl-tert-butylnitrone (PBN), a spin trapping agent.

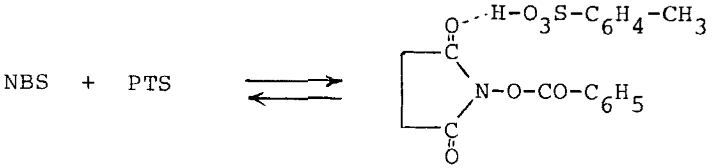
Figure 5 shows the ESR spectrum obtained from this reaction mixture. The nitroxyl radical observed is formed by the addition of some radical (R·) to PBN (Eq. 4). However, the radical produced cannot be identified at the present time.

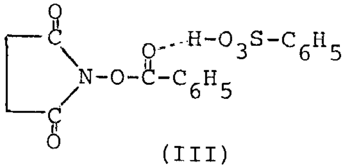


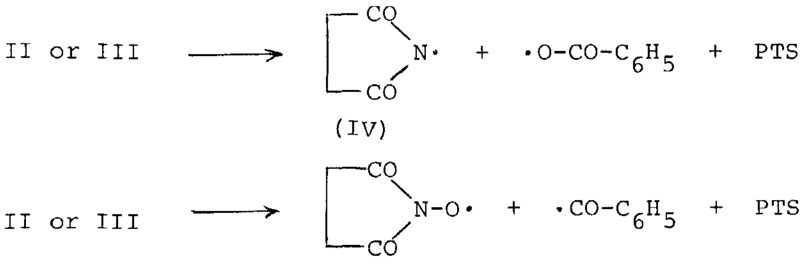
$$R\cdot + C_6H_5{-}CH{=}\overset{\overset{O}{\uparrow}}{N}{-}t{-}Bu \longrightarrow \begin{array}{l} C_6H_5\diagdown \\ \qquad CH{-}\overset{\overset{\bullet}{O}}{\overset{|}{N}}{-}t{-}Bu \\ R\diagup \end{array} \qquad (4)$$

The possible initiation mechanism of this system seems to be expressed in Eqs. (5)-(7).

NBS can interact with PTS through hydrogen-bonding between the carbonyl groups in NBS and the acidic hydrogen of PTS. A similar interaction is also assumed between N-chlorosuccinimide and PTS,


(II) (5)


(III) (6)


(IV)

(V) (7)

which can act as a radical initiator [8]. This hydrogen-bonded complex (II or III) closely resembles the N-acyloxyammonium intermediate in the acyl peroxide/tert-amine system. Therefore, this complex decomposes homolytically into benzoyloxy and succinimidyl radicals, IV (Eq. 6), to initiate polymerization.

However, the scission of the O–CO bond in NBS is also possible because the N-oxyl radical (V) is considered to be fairly stable and because photolysis of NBS causes homolysis of both the N–O and the O–CO bonds. The results of photosensitized vinyl polymerization with N-acyloxyimide compounds will be published in the near future [9].

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