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VINYL POLYMERIZATION. 439. VINYL POLYMERIZATION INITIATED BY POLY(ETHYLENE GLYCOL) DIGLYCOLIC ACID OR ITS SODIUM SALT

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ABSTRACT

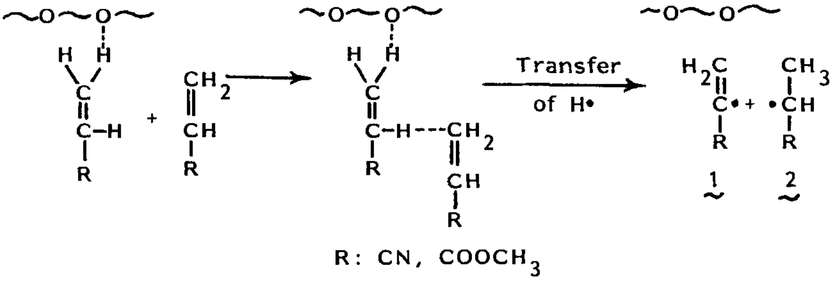
The polymerization of some kinds of vinyl monomer was found to occur in aqueous solutions of poly(ethylene glycol) diglycolic acid (PEG Acid) or sodium poly(ethylene glycol) diglycolate (PEG Acid Na) through radical mechanisms without any further initiator, as a so-called "uncatalyzed polymerization." Although the initiating radical species for PEG Acid was determined to be the same as that for PEG Acid Na by means of the spin-trapping technique, the initiating ability of PEG Acid was higher than that of PEG Acid Na. These results are assumed to be attributable to the difference in the initiation mechanisms of the two systems and in the incorporating abilities of monomer into the hydrophobic areas formed by PEG Acid and PEG Acid Na.

INTRODUCTION

As part of a series of studies on "uncatalyzed polymerization of vinyl monomers in water in the absence of copper(II) ion," which means radical polymerization initiated by water-soluble or water-insoluble, but hydrophilic, macromolecules without the addition of any ordinary free-radical initiator, we investigated the polymerization of vinyl monomers initiated by poly(ethylene glycol) (PEG-300; $\bar{M}_n$ 300) in aqueous solution and reported the following results. 1) Acrylonitrile (AN), methacrylonitrile, methyl methacrylate (MMA), methyl acrylate (MA), and methacrylic acid were polymerized by PEG-300, whereas styrene (St) was not [1, 2]. Such selectivity for vinyl monomer can be explained by the concept of "hard" and "soft" hydrophobic areas (HA) and monomers [3, 4]. According to this concept, a hard HA prefers to incorporate a hard monomer, and a soft HA prefers to incorporate a soft monomer. 2) The initiation mechanism expressed by Scheme 1 was confirmed by the spin-trapping technique [2].

Moreover, we found that some anionic macromolecular electrolytes containing sodium salt groups such as $-SO_3Na$ [5], $-COONa$ [3, 4, 6], and $-C_6H_4ONa$ [7] could initiate vinyl polymerization. The mechanism of hydrogen-atom transfer from the complexed monomer to the free monomer was proposed as the initiation mechanism, and the concept of hard and soft hydrophobic areas and monomers was applied to these polymerizations.

This article is concerned with vinyl polymerizations initiated by poly(ethylene glycol) diglycolic acid (PEG Acid), which is PEG with carboxylic acid groups at both ends, or sodium poly(ethylene glycol) diglycolate (PEG Acid Na), which is PEG with sodium carboxylate groups at both ends. The effects of the molecu-



SCHEME 1. Initiation mechanism for vinyl polymerization by PEG.

lar weight of PEG and the anionic end groups on the selectivity of vinyl monomer, the conversion of vinyl monomer, and the initiation mechanism in vinyl polymerizations are studied by using macromolecular electrolytes that consist of PEG main chains with anionic end groups as the parent polymers.

$HOOCCH_2O\text{-}(CH_2CH_2O)_n\text{-}CH_2COOH$

PEG Acid (n = 9, 23)

$NaOOCCH_2O\text{-}(CH_2CH_2O)_n\text{-}CH_2COONa$

PEG Acid Na (n = 9, 23)

$HO\text{-}(CH_2CH_2O)_n\text{-}H$

PEG-1000 (n = 23)

EXPERIMENTAL

Materials

PEG Acid (n = 9, 23) (Kawaken Fine Chemicals Co.) and PEG-1000 (n = 23) were dissolved in water, and the aqueous solutions were passed through a column filled with activated alumina in a stream of N_2 and lyophilized. The PEG Acid and PEG-1000 obtained were purified by repassage as aqueous and benzene solutions, respectively, through a column filled with activated alumina in a stream of N_2 before use.

The number in parentheses represents the degree of polymerization of the PEO chain. Peroxide groups and metallic ions were not found in the PEG Acid and PEG-1000 by the KI method and by fluorescence x-ray analysis, respectively. The PEG Acid aqueous solution, adjusted to pH 10 by addition of 3 *N* NaOH, was freeze dried to give PEG Acid Na. Moreover, it was confirmed by ESR that there were no free radicals in the PEG Acid, PEG Acid Na, and PEG used.

MA, MMA, *n*-butyl methacrylate (*n*-BMA), AN, and St were purified by the usual methods. Water was ion-exchanged and distilled. Sodium 2,4-dimethyl-3-nitrosobenzene sulfonate-d_8 (DMNS-d_8), for use as a water-soluble nitroso spin-trapping agent, was prepared by the method of Konaka and Sakata [8].

Polymerization Procedure

The polymerization was carried out in a sealed tube at 85°C with shaking. The reaction mixture was poured into a large amount of methanol to precipitate the polymer produced. After drying the product at 80°C *in vacuo,* the overall conversion of monomer was obtained from the weight of polymer. By subtracting the thermal conversion from the overall conversion, the corrected conversion could be calculated as follows:

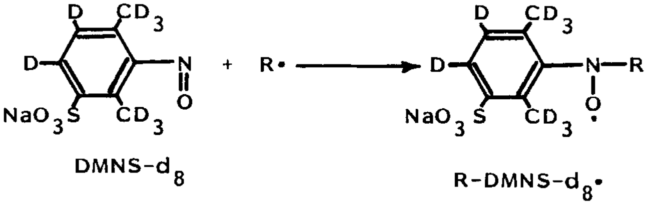
Corrected conversion (%) = [conversion (%) in the presence of parent polymer] - [conversion (%) in the absence of parent polymer] (1)

Observation by Transmission Electron Microscopy

The polymerization systems were examined by transmission electron microscopy (TEM) according to the method of Kunitake and Okahata [9]: 5.0 mg of parent polymer was dissolved in 1.0 cm^3 of water. The solution was mixed with 1.0 cm^3 of 2% aqueous uranyl acetate (a staining reagent) and sonicated for 20 s. The mixture was applied to carbon-coated grids. A Hitachi electron microscope (Hitachi HS-9) was used for the measurement.

Identification of the Initiating Radical Species

The determination of the initiating radical species was done by means of the spin-trapping technique described in a previous paper [10]. The primary alkyl radical, R•, was trapped by DMNS-d_8 to give the spin adduct (R-DMNS-d_8•), as shown in Eq. (2), and the accumulated stable radical was measured by ESR spectroscopy.



(2)

The reaction of PEG Acid (n = 23), PEG Acid Na (n = 23) or PEG (n = 23) with MA in water was carried out at 60°C without shaking in the presence of DMNS-d_8 in a flat-type ESR cell, which was rinsed with a stream of argon. After 1 h the ESR spectrum of the reaction mixture was taken at 60°C by using a JES-FE-1X spectrometer with 100 kHz field modulation.

RESULTS AND DISCUSSION

Polymerization of MA by PEG Acid or PEG Acid Na

To investigate the effects of both types of end groups on PEG Acid, PEG Acid Na, and PEG, polymerization of MA was carried out at 85°C for 3 h in aqueous solutions of PEG Acid (*n* = 9, 23), PEG Acid Na (*n* = 9, 23) or PEG (*n* = 9, 23). The results are shown in Figs. 1 and 2, where conversion in the absence of parent polymers refers to thermal polymerization. It was clear that these PEG parent polymers have high abilities to initiate the polymerization of MA. Thus, vinyl polymerization by these parent polymers can be regarded as an example of uncatalyzed polymerization. The initiating ability of these parent polymers is as follows:

PEG Acid > PEG > PEG Acid Na
PEG Acid (*n* = 23) > PEG Acid (*n* = 9)

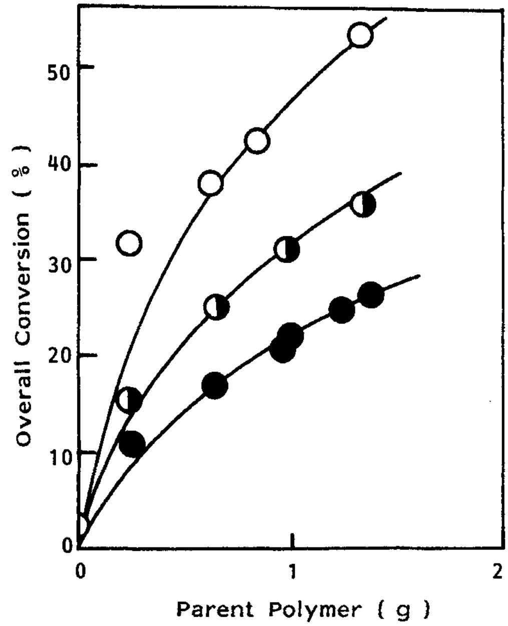


FIG. 1. Effects of the amount of PEG Acid (*n* = 9), PEG Acid Na (*n* = 9), and PEG (*n* = 9) on the conversion of MA. MA, 3 cm^3; H_2O, 10 cm^3; 85°C; 3 h; with shaking. (○) PEG Acid (*n* = 9); (●) PEG Acid Na (*n* = 9); (◑) PEG (*n* = 9).

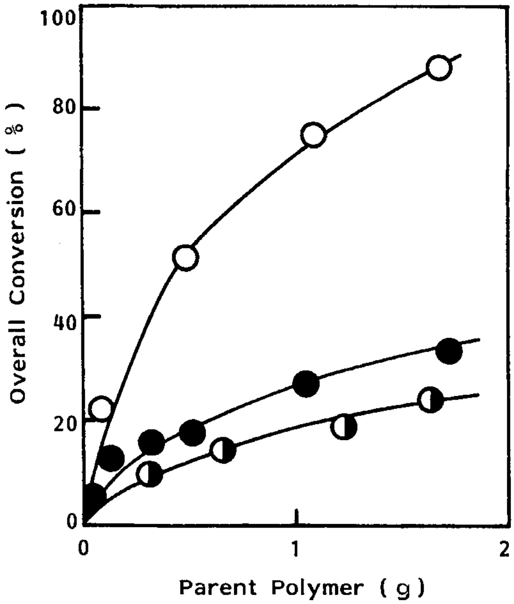


FIG. 2. Effects of the amount of PEG Acid (n = 23), PEG Acid Na (n = 23), and PEG (n = 23) on the conversion of MA. MA, 3 cm^3 ; H_2O, 10 cm^3 ; 85°C; 3 h; with shaking. (○) PEG Acid (n = 23); (●) PEG Acid Na (n = 23); (◑) PEG (n = 23).

PEG Acid Na (n = 23) > PEG Acid Na (n = 9)
PEG (n = 23) > PEG (n = 9)

Polymerization of Vinyl Monomers

The results of the polymerization of MA, MMA, n-BMA, AN, and St by these parent polymers (n = 23) in aqueous solution are summarized in Figs. 3-5).

As shown in these figures, the order of initiating ability for the five monomers are generally as follows: PEG Acid (n = 23) > PEG Acid Na (n = 23) > PEG (n = 23). However, the selectivities for vinyl monomer in these three polymerization systems tend to differ from each other.

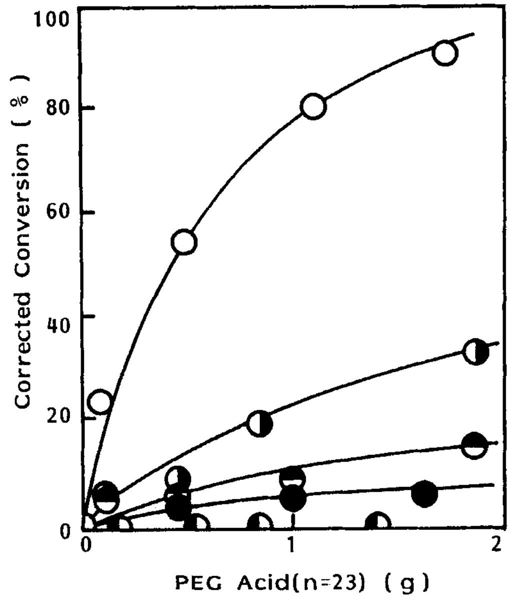


FIG. 3. Effects of the amount of PEG Acid (n = 23) on vinyl polymerization. Monomer, 3 cm^3; H_2O, 10 cm^3; 85°C; 3 h; with shaking. (○) MA; (◒) MMA; (●) n-BMA; (◑) AN; (◐) St.

Effect of Sodium Chloride on the Polymerization of MA by PEG Acid

We reported elsewhere that the polymerization of AN initiated by PEG was promoted by the addition of some types of alkaline metal halide, and this could be explained by assuming that the HA formed by PEG in aqueous solution became more stable owing to the interaction of PEG with the alkaline metal ions [11].

The promoting effect of sodium chloride was also found in the polymerization of MA initiated by PEG Acid (Fig. 6).

Observation of HA by TEM

In order to visualize the polymerization system, the aggregates of PEG Acid (n = 23), PEG Acid Na (n = 23), and PEG (n = 23) in water were observed by TEM. The results obtained are shown in Figs. 7(A), (B), and (C). It was clear

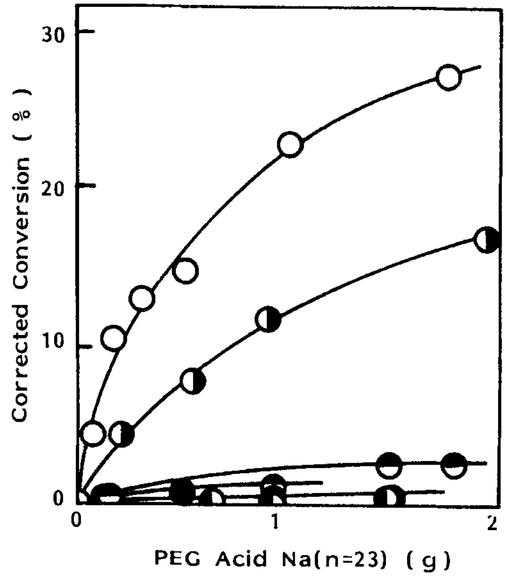


FIG. 4. Effects of the amount of PEG Acid Na ($n = 23$) on vinyl polymerization. Monomer, 3 cm^3; H_2O, 10 cm^3; 85°C; 3 h; with shaking. (○) MA; (◓) MMA; (●) *n*-BMA; (◑) AN; (◐) St.

from Figs. 7(A) and (C) that PEG Acid ($n = 23$) and PEG ($n = 23$) clearly form aggregates in water. However, Fig. 7(B) suggests that PEG Acid Na ($n = 23$) does not easily form aggregates in water. Although a large number of stable aggregates of small size were formed by PEG Acid ($n = 23$) in water, a small number of loose aggregates of larger size seem to be formed by PEG ($n = 23$) in water. We have called these aggregates "HA," where the polymerization commences.

The schematic representation of how HAs are formed by PEG Acid in aqueous solution is shown in Scheme 2.

Initiation Mechanism

The effects of 1,1-diphenyl-2-picrylhydrazyl (DPPH) or 1,3,5-triphenyl verdazyl (TPV) on the polymerization of MA with PEG Acid ($n = 23$) and PEG Acid Na ($n = 23$) were studied. The results in Table 1 confirm that these three kinds of polymerization system proceed through radical mechanisms.

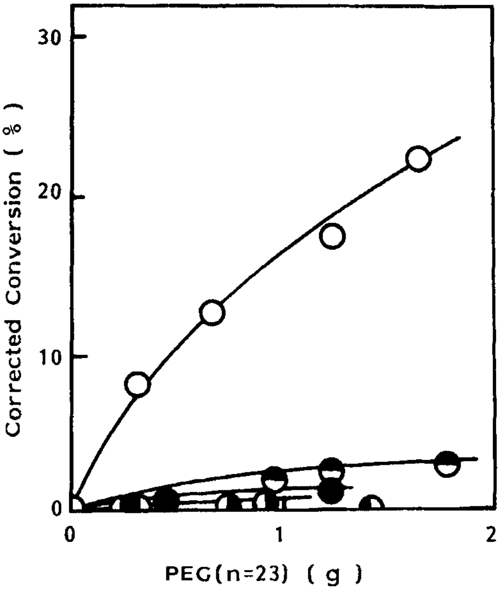


FIG. 5. Effects of the amount of PEG ($n = 23$) on vinyl polymerization. Monomer, 3 cm^3 ; H_2O, 10 cm^3 ; 85°C; 3 h; with shaking. (○) MA; (◒) MMA; (●) n-BMA; (◑) AN; (◐) St.

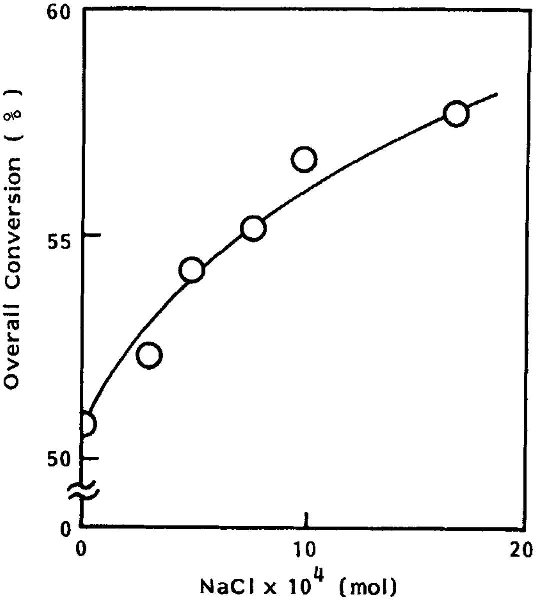


FIG. 6. Effects of the amount of NaCl on the conversion of MA initiated by PEG Acid ($n = 23$). MA, 3 cm^3 ; H_2O, 10 cm^3 ; 85°C; 3 h; with shaking.

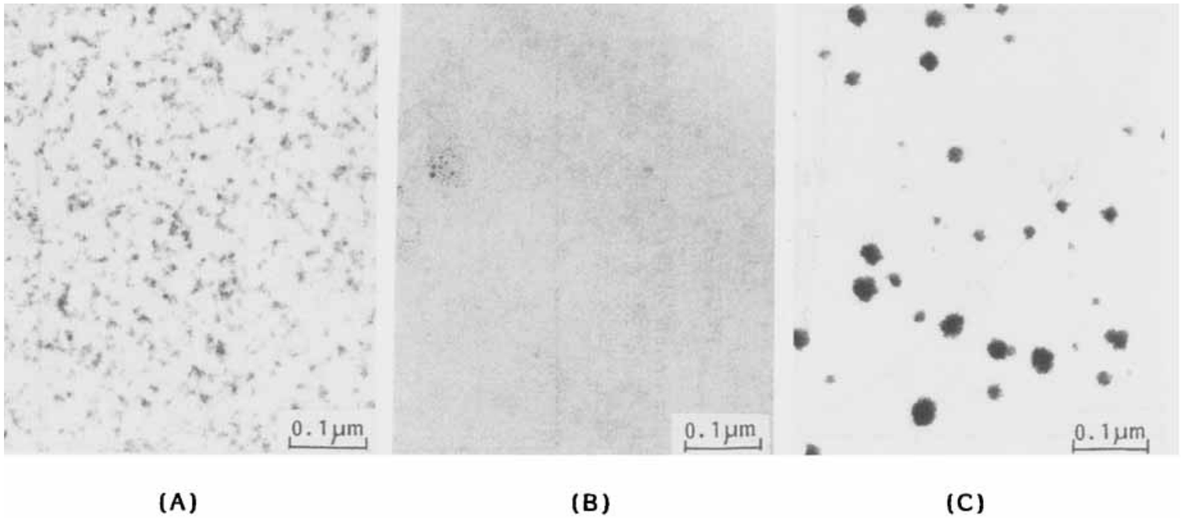
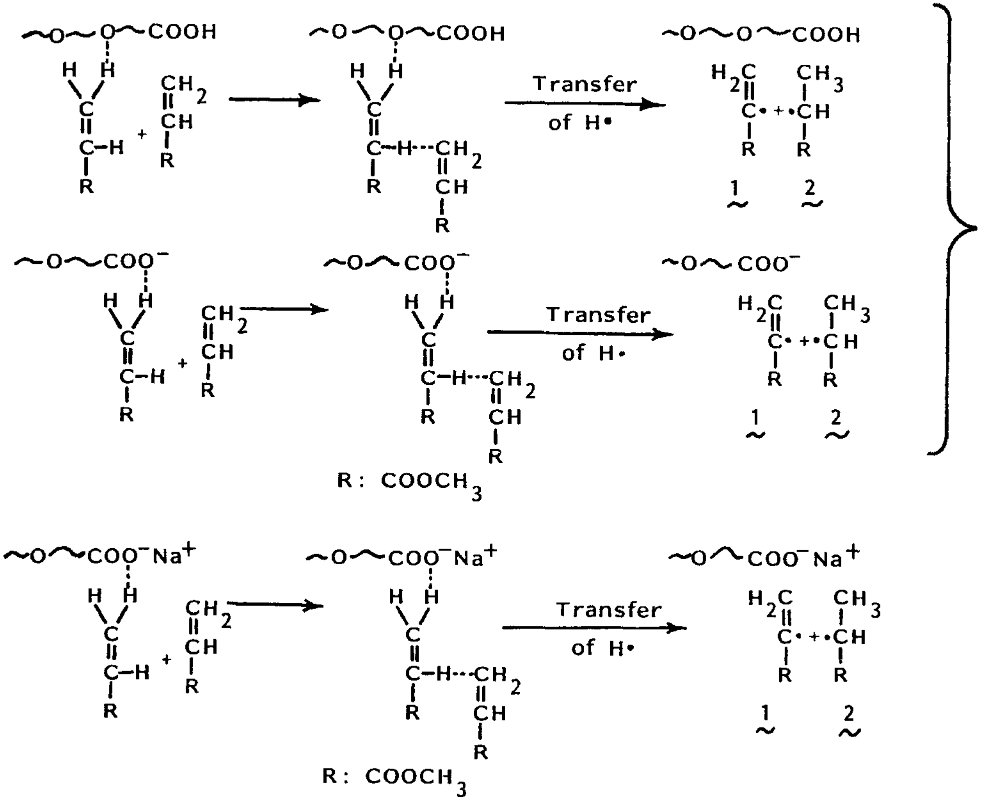


FIG. 7. Surface views of (A) PEG Acid ($n = 23$), (B) PEG Acid Na ($n = 23$), and (C) PEG ($n = 23$) in water.



(3)

(4)

SCHEME 2. Schematic representation of HAs formed by (A) PEG Acid and (B) PEG Acid Na in aqueous solution.

TABLE 1. Effects of Radical Scavenger on Polymerization of MA Initiated with PEG Acid (n = 23) and PEG Acid Na (n = 23)[a]

Initiator			
Type	Amount, g	Radical scavenger, g	Conversion, %
PEG Acid (n = 23)	0.51	None	51
PEG Acid (n = 23)	0.51	DPPH 0.15	0
PEG Acid (n = 23)	0.51	TPV 0.15	0
PEG Acid Na (n = 23)	0.51	None	17
PEG Acid Na (n = 23)	0.51	DPPH 0.15	0
PEG Acid Na (n = 23)	0.51	TPV 0.15	0

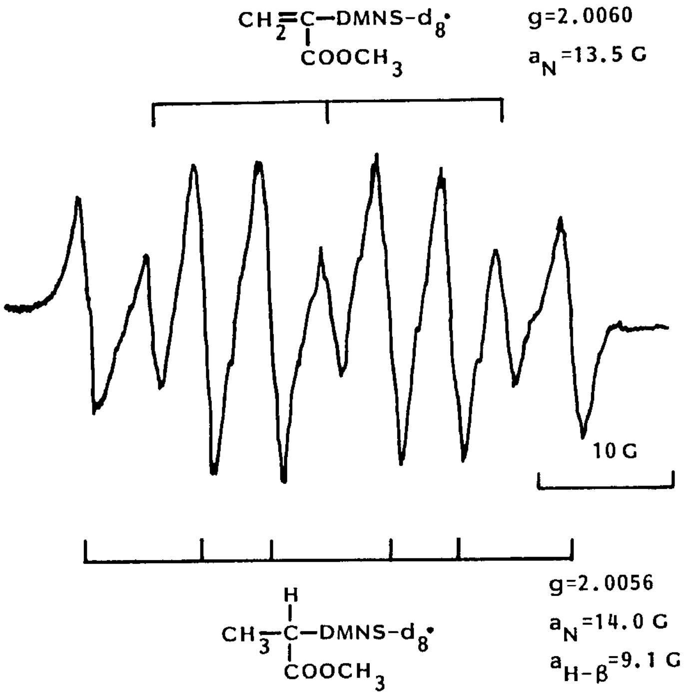
[a] MA, 3 cm^3; H_2O, 10 cm^3; 85°C; 3 h; with shaking.

The initiation mechanisms were studied by the spin-trapping technique. Figures 8(A) and (B) show the ESR spectra of the reaction mixtures obtained when MA was allowed to react with aqueous PEG Acid (n = 23) and PEG Acid Na (n = 23) solutions in the presence of DMNS-d_8 under the same condition. The same pattern was observed in both systems. The same spectral pattern had also been previously observed in the system MA/PEG-300/DMNS-d_8/H_2O [2], i.e., the initiating species in these three kinds of polymerization system was clearly the same. The triplet equivalent signals are assigned to the adduct of 1-methoxycarbonyl vinyl radical **1** to DMNS-d_8 (g = 2.0060, a_N = 13.5 G) (Eqs. 3 and 4 in Scheme 2). The sextet signals are assigned to the adduct of 1-methoxycarbonyl ethyl radical **2** to DMNS-d_8 (g = 2.056, a_N = 14.0 G, $a_{H\text{-}\beta}$ = 9.1 G) (Eqs. 3 and 4 in Scheme 2).

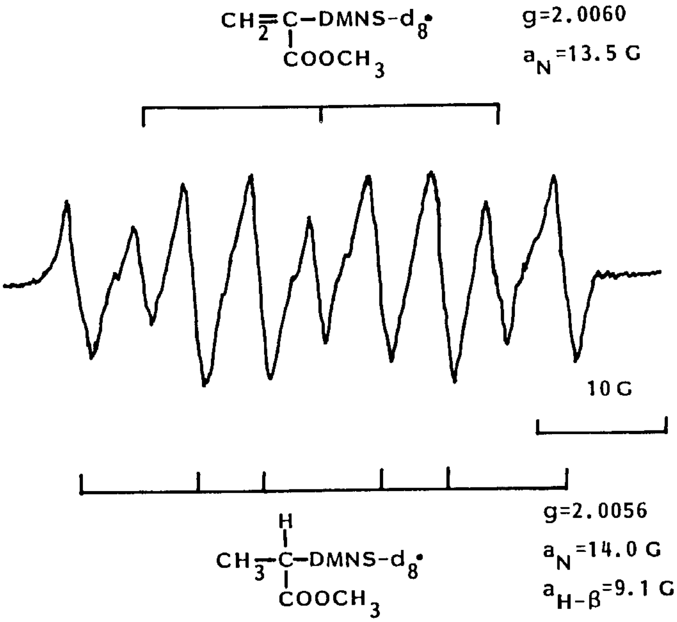
Considering the initiation mechanism proposed previously for the polymerization of MA by PEG (Scheme 1), and assuming the difference of the interaction of MA with PEG Acid and PEG Acid Na, we propose an initiation mechanism for the polymerization of MA by PEG Acid and PEG Acid Na expressed by Eqs. (3) and (4) in Scheme 2, respectively.

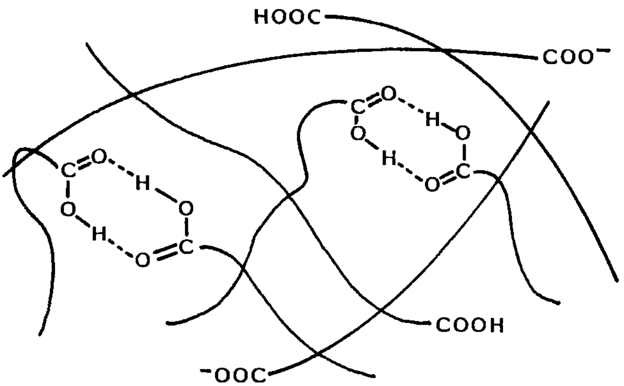
FIG. 8. ESR spectra of the systems of (A) MA/PEG Acid (n = 23)/DMNS-d_8 and (B) MA/PEG Acid Na (n = 23)/DMNS-d_8 in aqueous solution at 60°C after 1 h. MA, 0.1 mmol; PEG Acid (n = 23), PEG Acid Na (n = 23), 0.1 mmol; DMNS-d_8, 9.06 μmol; H_2O, 1.0 cm^3.

(A)

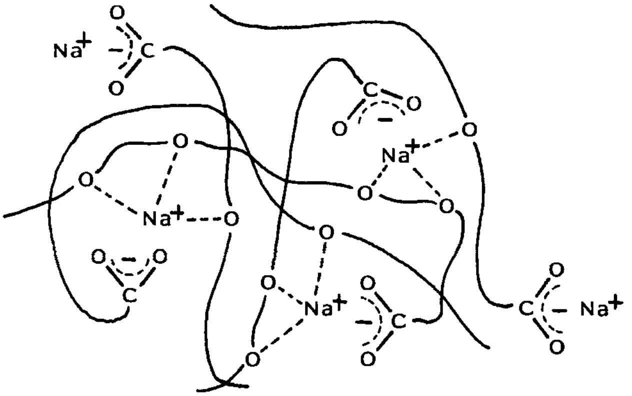

CH2=C(COOCH3)–DMNS-d8•
g=2.0060
aN=13.5 G
10 G
CH3–CH(COOCH3)–DMNS-d8•
g=2.0056
aN=14.0 G
aH-β=9.1 G

(B)


CH2=C(COOCH3)–DMNS-d8•
g=2.0060
aN=13.5 G
10 G
CH3–CH(COOCH3)–DMNS-d8•
g=2.0056
aN=14.0 G
aH-β=9.1 G



(A) HA formed by PEG Acid



(B) HA formed by PEG Acid Na

SCHEME 3. Initiation mechanisms of polymerization of MA by (A) PEG Acid and (B) PEG Acid Na.

The primary radical species **1** and **2** are considered to be generated by hydrogen-atom transfer from the complexed MA monomer to free MA monomer, as shown in Scheme 3.

Difference in Initiating Ability among PEG Acid, PEG Acid Na, and PEG

The order of the initiating ability of these PEG parent polymers for the polymerization of MA can be explained by the differences in the ease of HA formation in water and in the initiation mechanism.

The monomer selectivities can be easily explained by the concept of hard and soft HA and monomers.

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