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Effect of Polyethyleneglycol on Polymerization of Methyl Methacrylate Initiated by Sodium Salt-Type Macromolecular Electrolytes[a]

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Summary

The effects of polyethyleneglycol (PEG) on the radical polymerizations of methyl methacrylate initiated with the aqueous solutions of such macromolecular electrolytes as sodium polyphenolate and sodium polycarboxylate were studied. PEG was found to promote the polymerizations initiated by such sodium salt-type's macromolecular electrolytes.

Introduction

Recently, we found that the polymerization of MMA was initiated by the system of polyethyleneglycol-300 (PEG-300; $\overline{M}_n$=300), copper(II) ion, and water (OUCHI et al. 1982).

In another study, we studied the effect of PEG-300 on the radical polymerization of methyl methacrylate (MMA) initiated by an aqueous solution of sodium polystyrenesulfonate (PSS-Na) and reported a dramatic promotion of the polymerization by PEG-300 (IMOTO et al. 1982).

In order to reconfirm such a promoting effect of PEG on the polymerization, the present paper deals with the effect of PEG on the radical polymerization of MMA initiated with the aqueous solutions of the other sodium salt-type's macromolecular electrolytes than PSS-Na.

The polymerization of MMA by such sodium salt-type's macromolecular electrolytes has already concluded to belong to the uncatalyzed polymerization; that is, the polymerization proceeds through the following processes: (1) macromolecular

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[a] Vinyl Polymerization. 415.

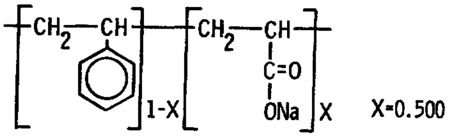
electrolytes form the hydrophobic areas (HA) in the water phase; (2) MMA is incorporated into the HA; (3) in the HA the polymerization proceeds. And the polymerization proceeds through a radical mechanism.

Experimental

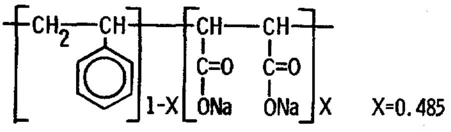
Materials PEG-300 ($\bar{M}_n$=300) and PEG-2000 ($\bar{M}_n$=2000) were afforded by Sanyo Kasei Co. Ltd. Since the additional activities of polyethyleneglycols treated with the bulk passage through an activated alumina column filled activated in a stream of N_2 did not differ from those of polyethyleneglycols treated with anhydrous sodium sulfite as a reductant, as shown in Fig. 1, the former treatment was applied to this system.

The existences of peroxide group and metallic ion in PEG were not observed by the KI method and fluoresence-X-ray analysis, respectively. Also, it was reconfirmed by ESR spectrum that any free radical was not included.

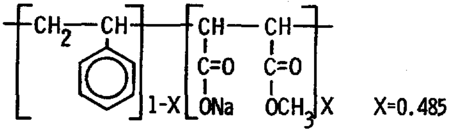
Sodium poly-p-vinylphonolate (PVPh-Na) was prepared by mixing poly-p-vinylphenol ($\bar{M}_w$=3400) with 8 times moles of NaOH in an aqueous solution (OUCHI et al. 1982). Poly(styrene-alt-disosium maleate)[poly(St-alt-disodium maleate)], Poly(styrene-alt-methyl maleate)[poly(St-alt-sodium methyl maleate)] (OUCHI et al. 1982) were prepared according to the previous papers. Sodium carboxymethyl cellulose (CMC-Na) was resprecipitated from 2 % -NaOH aqueous solution with methanol.



poly(St-co-AA-Na)



poly(St-alt-disodium maleate)



poly(St-alt-sodium methyl maleate)

Sodium p-(1,3,5,7-tetramethyl)octylbenzenesulfonate (DBS-Na) was of commercial grade and used without further purification.

MMA was purified by the usual method. Water was ion-exchanged and distilled. NaOH was of commercial grade and used without further purification.

Procedures MMA, sodium salt of macromolecular electrolyte, PEG, and water were placed in a tube. The tube was sealed i.vac. after thawing with nitrogen, and heated at 85°C with shaking. The reaction mixture was poured into a large amount of methanol to precipitate the polymer produced. The conversion of the monomer was calculated from the weight of the polymer.

The number-average degree of polymerization, $\bar{P}_n$, of poly(MMA) was determined from the intrinsic viscosity in benzene at 30°C by using Welch's equation (WELCH 1962).

Results and Discussion

Effect of PEG on the Polymerization of MMA by Various Na Salts of Macromolecular Electrolyte

The effect of PEG-300 on the polymerization of MMA initiated by PVPh-Na, poly(St-co-AA-Na), poly(St-alt-disodium maleate), CMC-Na, or DBS-Na is shown in Table 1. In spite of the difference in the kinds of sodium salt of macromolecular electrolyte, the polymerizations were always found to be accelerated by PEG-300. Such a promoting effect by PEG was also found in the case of PSS-Na. Now, the polymerization of MMA by the sodium salt-type's macromolecular electrolyte is reported to be initiated by the mechanism shown in Scheme 1 (IMOTO et al. in press). Since PEG-300 may take Na-ions as quests and increase the concentration of naked polymeric ions, the interaction between the naked polymeric ions and the $\delta+$ charged vinyl group of MMA becomes easier. Thus, PEG-300 could promote the polymerization.

Effect of the Amount of PEG-300 or PEG-2000 on the Polymerization of MMA by PVPh-Na

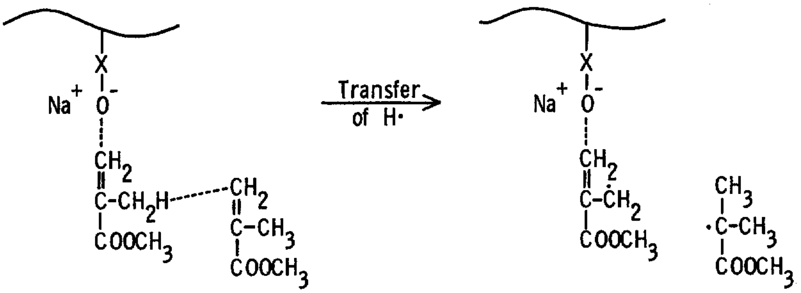
Varying the amount of PEG-300 or PEG-2000, the polymerizations of MMA by NaOH aqueous solution of PEG in the presence of 0.1 g of PVPh and the absence of PVPh were carried out. The results are shown in Fig. 1. Since the polymerization of MMA was initiated by PEG-300 or PEG-2000 even if in the absence of PVPh, the corrected conversion of MMA by PVPh-Na can be obtained by Eq. (1).

Corrected conversion =(Conversion by the system of PVPh/NaOH/PEG)-(Conversion by the system of NaOH/PEG) (1)

The remarkable decrease of the conversion of MMA was seen in Fig. 1 when the fed amount of PEG-2000 exceeded a certain limit. It is considered that this phenomenon is concerned with the formation of HA by PVPh-Na in the water phase. That is, in the region of the higher concentration of PEG having high molecular weight, the macromolecules entangle with each other and the formation of appropriate HA to incorporate MMA becomes difficult.

Effect of the Amount of PEG-300 on $\overline{P}_n$ of poly(MMA)

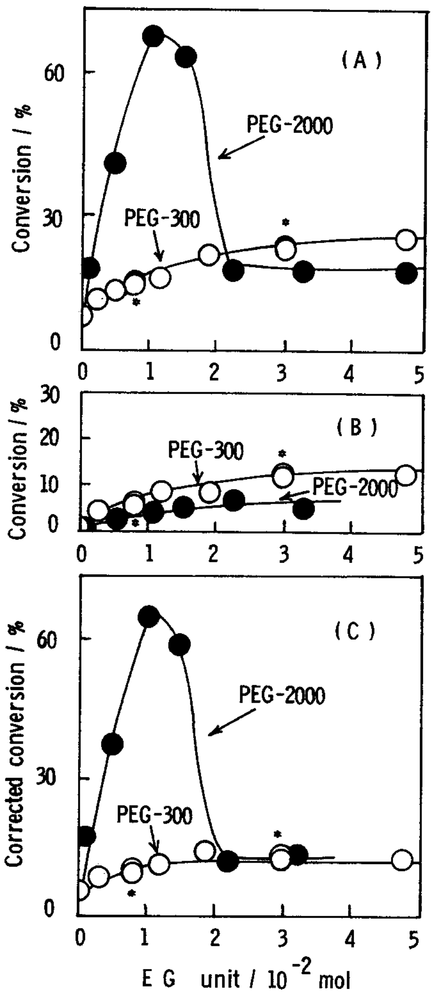
Figure 2 shows the effect of the amount of PEG-300 on $\overline{P}_n$ of poly(MMA) produced by the system of PVPh/NaOH/PEG-300/H_2O/MMA. $\overline{P}_n$ of poly(MMA) decreased slightly with the amount of PEG-300.



Scheme 1. Initiation mechanism of the polymerization of MMA by Na salt-type's macromolecular electrolyte.

Acknowlegment

We express our sincere thanks to Sanyo Kasei Co. Ltd. for providing PEG-300 and PEG-2000.



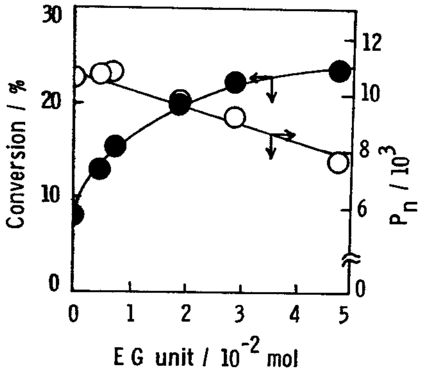


Fig. 2. Effect of the amount of PEG-300 on $\bar{P}_n$ of poly(MMA) produced. MMA 3 cm^3, PVPh 0.1 g, NaOH 0.274 g, H_2O 10 cm^3; 85°C, 3 h, with shaking.

Fig. 1. Effect of molecular weight of PEG on the polymerization of MMA initiated by NaOH aqueous solution of PVPh in the presence of PEG. MMA 3 cm^3, NaOH 0.274 g, H_2O 10 cm^3, 85°C, 3 h, with shaking. ○ PEG-300, ○* PEG 300 treated with anhydrous sodium sulfite, ● PEG-2000.

(A), (C) in the presence of 0.1 g of PVPh.

(B) in the absence of PVPh.

TABLE I

Polymerization of MMA Initiated by Sodium Salt-Type's Macromolecular Electrolytes in the Presence of PEG-300[a]

Na Salt-Type's Macromolecular Electrolytes / g	Conversion[c] / %	
	No PEG-300	PEG-300
PVPh-Na 0.11[b]	8.3, 8.5	14.8[d], 15.9[d]
DBS-Na 0.10	38.1, 39.0	66.0[d], 68.1[d]
CMC-Na 0.10	1.1, 1.1	6.1[e], 6.7[e]
Poly(St-co-AA-Na) 0.03	7.0, 7.2	34.4[e], 36.5[e]
Poly(St-alt-disodium maleate) 0.03	5.8, 6.0	17.9[f], 18.2[f]
Poly(St-alt-sodium methyl maleate) 0.03	4.0, 4.1	9.0[f], 9.4[f]

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

[b] PVPh 0.10 g, NaOH 0.27 g; Mole ratio of NaOH per unit of PVPh = 8.

[c] The conversion of MMA in the absence of PEG and macromolecular electrolyte was 1.02 % (blank test).

[d] PEG-300 0.5 cm^3. [e] PEG-300 1.0 cm^3. [f] PEG-300 0.1 cm^3.

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