

POLYMERIZATION OF ETHYLENE METHYL PHOSPHATE IN THE PRESENCE OF SODIUM POLY(ETHYLENE GLYCOL)ATE*

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Abstract Poly(ethylene methyl phosphate)-poly(ethylene glycol)-poly(ethylene methyl phosphate) triblock copolymers carrying hydroxyl group at both chain ends were synthesized with sodium poly(ethylene glycol)ate as initiator. The effects of the factors such as solvent, amount of the initiator and reaction time were investigated. The copolymers were characterized by IR, ^1H -NMR, $^1\text{H}\{^{31}\text{P}\}$ -NMR, ^{13}C -NMR, $^{31}\text{P}\{^1\text{H}\}$ -NMR, and DSC. High molecular weight of the copolymer and high yield of the polymerization were achieved within 3 min at 25°C . The polymerization process was studied by $^{31}\text{P}\{^1\text{H}\}$ -NMR and transesterification was found during longer polymerization time.

Keywords Ethylene methyl phosphate, Sodium poly(ethylene glycol)ate, Telechelic polymer, Block copolymer

INTRODUCTION

Polyphosphates are of great interest in a variety of applications including flame retardation^[1], adhesion promoters and processability either by their solubility in common solvents^[2] or by the lowering of glass transition temperature^[3, 4]. Furthermore they possess attractive plasticizing properties due to the presence of P-O-C linkages in the polymer chain^[5]. Polyphosphates with backbones related to nucleic acids and teichoic acids have been proposed for use in biomedical applications, especially as drug carriers^[6] because of their biocompatibility and biodegradability.

Many current researches on biomaterials have focused on copolymers of different types. Over the past years, copolymers containing phosphoester units have been reported^[7-9]. In contrast with random copolymers, block and graft copolymers can not only provide new materials with properties intermediate between those of the parent homopolymers, but also provide additional unique morphologies and physical properties due to microphase separation.

Telechelic polymers are becoming of increasing interest because they are ideal precursors for use in coupling reactions or chain extensions that can lead to a variety of polymer architectures including blocks, grafts and networks^[10]. One of the possible routes of the synthesis of telechelic polymers is based on the initiation with the difunctional initiator. This method is applied in our preparation of polyphosphate diols. In this article, we prepared polyphosphate diols through ring-opening polymerization of 2-methoxy-2-oxo-1, 3, 2-dioxaphospholane, i.e. ethylene methyl phosphate (EMP) using sodium poly (ethylene glycol)ate as initiator.

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EXPERIMENTAL

Materials

Poly(ethylene glycol)(PEG) was thoroughly dried under high vacuum at 120°C for 10 h and used without further purification. Average molecular weight of the pure PEG sample measured by end-group titrimetric method was 320. The average degree of polymerization n was calculated to be 7. All other solvents and reagents were purified and dried by conventional methods.

Characterization

IR spectra were obtained on a Magna 550 spectrometer. ^1H -NMR and ^{13}C -NMR spectra were recorded on a JEOL FX-90Q spectrometer or a Bruker DPX-300 spectrometer using CDCl_3 as solvent and TMS as the internal standard. ^{31}P -NMR spectra were measured on a Bruker DPX-300 apparatus with 85% H_3PO_4 as an external standard. The number average molecular weights were determined by ^1H -NMR spectroscopy from the intensity ratio of signals from PEG segment at $\delta = 3.59$ and from the EMP segment at $\delta = 4.23$ along with the average degree of polymerization of PEG. Differential scanning calorimetry (DSC) measurements were carried out on a Rigaku TAS-100 thermal analyzer at a heating rate of 10°C/min.

Preparation of the Monomer

2-methoxy-2-oxo-1, 3, 2-dioxaphospholane was prepared according to Edmundson^[11]. To a mixture of phosphorus trichloride (412.5 g, 3 mol) and dry CH_2Cl_2 (350 mL) ethylene glycol (186 g, 3 mol) was added drop-wise over 5 h with vigorous magnetic stirring. Gaseous HCl evolved was evacuated from the reaction flask at reduced pressure (water pump). After complete addition of ethylene glycol, the solution was stirred at room temperature for another 0.5 h and then the solvent was evaporated under reduced pressure. The residue was distilled under vacuum to give 287 g of 2-chloro-1, 3, 2-dioxaphospholane in 75.6% yield (b.p. 42°C/1600 Pa). The oxidation of 2-chloro-1, 3, 2-dioxaphospholane was carried out by bubbling O_2 through benzene solution at 50 °C for 24 h. After removal of benzene, the residue was distilled under vacuum to give a colorless liquid of 2-chloro-2-oxo-1, 3, 2-dioxaphospholane in 85% yield (88 ~ 90°C/106 Pa).

A mixture containing a calculated amount of 2-chloro-2-oxo-1, 3, 2-dioxaphospholane (41.4 g, 0.29 mol) and dry benzene (250 mL) was cooled to -5°C and then a mixture of dry methanol (9.3 g, 0.29 mol) and dry triethylamine (29.3 g, 0.29 mol) was added drop-wise with stirring and cooling. The temperature of the reaction mixture was maintained between -5°C and 0°C. After the methanol and triethylamine mixture was completely added, the resulting mixture was stirred at room temperature for 1.5 h. The triethylamine hydrochloride was filtered off and the filtrate was concentrated. The residue was distilled under vacuum to give 28.6 g of 2-methoxy-2-oxo-1, 3, 2-dioxaphospholane in 71% yield (b.p. 99~101°C/106 Pa).

Preparation of the Macroinitiator

2 mmol of PEG, 4.2 mmol of sodium hydride and 20 mL of THF were placed in a heated argon purged reactor equipped with magnetic stirring bar and reflux condenser. The reaction mixture was stirred at 60°C for 16 h and filtered.

Polymerization

Polymerization experiments were carried out in CH_2Cl_2 solution at 20°C under stirring in a preheated argon purged reactor. EMP, solvent and initiator solution were sequentially introduced into the reactor with syringes through rubber septums. The polymerization was terminated by introduction of ten-fold excess of acetic acid (in diethyl ether) with regard to Na. After being concentrated, the residue was poured into benzene to give a solution and then washed with diethyl ether three times and dried under vacuum to a constant weight.

RESULTS AND DISCUSSION

Synthesis of Telechelic Polyphosphate

It was reported that EMP was polymerized in CH_2Cl_2 with potassium tert-butoxide as initiator^[12]. In a search for polyphosphate carrying end-functional groups, we employed sodium polyglycolates as macroinitiators in the synthesis of poly(2-methoxy-2-oxo-1, 3, 2-dioxaphospholane) (PEMP). Many experiments were carried out at different conditions in order to obtain high conversion rates of the monomer. At first, when we chose THF as solvent in the polymerization, the results showed that the polymer chain precipitated before the monomer was completely consumed. Later we found that the polymerization proceeded fast in CH_2Cl_2 , and after 3 min the monomer was almost entirely consumed.

The results of the block copolymerization are presented in Table 1. These data demonstrate that PEMP-*b*-PEG-*b*-PEMP with the expected molecular weight and composition were obtained in good yields. The block copolymer compositions were calculated from $^1\text{H-NMR}$ spectra as described in the experimental part.

Table 1. Results of the anionic polymerization of EMP initiated with sodium poly(ethylene glycol)ate in CH_2Cl_2 at 25°C^a

Sample	Yield (%)	Mole ratio of EO ^b to EMP		M_n^c
		Fed	Found	
1	95	26:74	26.4:73.6	3000
2	94	19:81	19.7:80.3	4200
3	92	12:88	12.8:87.2	6900
4	96	7:93	7.3:92.7	12500

a) the polymerization time was 3 min, b) EO: ethylene oxide,

c) estimated from $^1\text{H-NMR}$ spectra ($\pm 10\%$)

The influence of reaction time on the polymerization is shown in Figs. 1 and 2. The yield and molecular weight of the copolymer was increased with the increase of the reaction time within 3 min, then both decreased and leveled off with increase of the reaction time. This may be explained by the transesterification during the polymerization. In fact, a living character has been observed for the polymerization when the polymerization time is within 3 min. This behavior is supported by the linear correspondence between the degree of polymerization and the monomer/initiator mole ratio (Fig. 3).

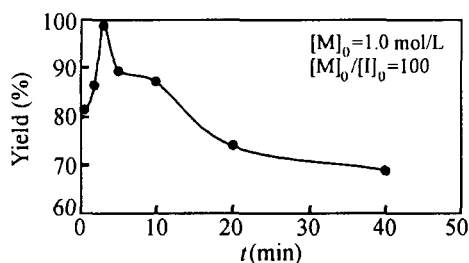


Fig. 1 The relationship between polymer yield and polymerization time

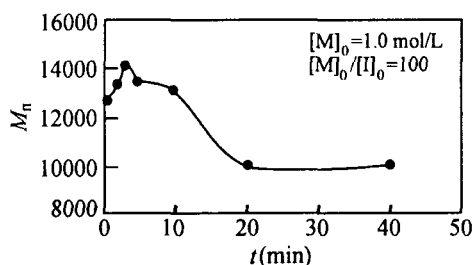


Fig. 2 The relationship between polymer molecular weight and polymerization time

Characterization of Telechelic Polyphosphate

The IR spectra of the polymer show that the most important and identifying PEMP peaks were $\nu_{\text{P=O}}$ appearing as a sharp singlet at 1269 cm^{-1} and $\nu_{\text{P-O-C}}$ at $1038, 986\text{ cm}^{-1}$. The peak at 1110 cm^{-1} was assigned to $\nu_{\text{C-O-C}}$ from PEG segment. Polymers gave a broad absorption peak at the region of $3200\sim 3600\text{ cm}^{-1}$ due to the terminal hydroxyl groups. As expected, the hydroxyl absorption

became stronger when the molecular weight of the polymer decreased.

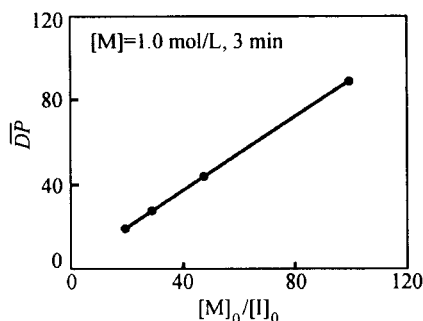


Fig. 3 Dependence of $\overline{DP}$ on the $[M]_0/[I]_0$ mole ratio in the polymerization

The ^1H -NMR and $^1\text{H}\{^{31}\text{P}\}$ -NMR spectra of polyphosphate diol are shown in Figs. 4 and 5. $^1\text{H}\{^{31}\text{P}\}$ -NMR spectrum exhibited, besides the signals corresponding to PEG (at $\delta = 3.59$) and PEMP chain ($\delta = 4.23$ (CH_2OP) and 3.77 (CH_3OP)), an additional signal at $\delta = 3.67$ which was assigned to methylene protons connected to the terminal hydroxyl groups. The ^1H -NMR spectrum gave an expected splitting of a CH_3OP singlet into a doublet due to the P-H coupling, $^3J_{\text{PH}} = 11.25$ Hz, CH_2OP protons signals are more complicated and are not discussed here.

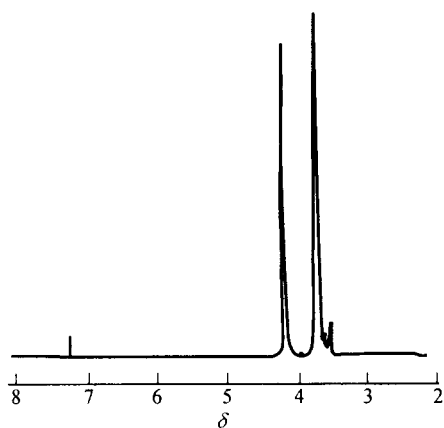


Fig. 4 ^1H NMR spectrum of polyphosphate diol (EO mol%=16.3%, 3min)

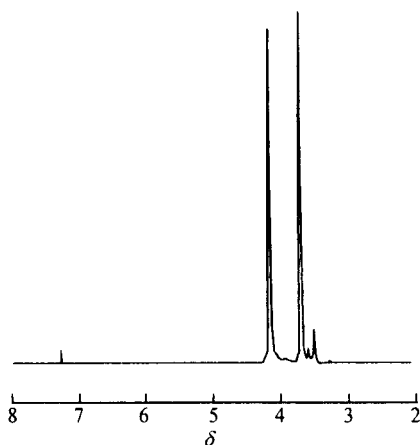


Fig. 5 $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of polyphosphate diol (EO mol% = 16.3%, 3min)

Additional information about the block structure of polyphosphate was obtained by ^{13}C -NMR studies. Figure 6 shows the typical ^{13}C -NMR spectrum of the polymer. In comparison with the spectra of PEG and PEMP, it is clear that peaks at 54.48 and 66.16 correspond to CH_3 and CH_2 in PEMP segments and the peak at 70.28 belongs to CH_2 in PEG segments. Another two small peaks at 66.80 and 69.71 may be due to POCH_2 and CH_2OH in the end groups.

$^{31}\text{P}\{^1\text{H}\}$ NMR studies was used to investigate the side reactions during the longer polymerization time. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the polymer shown in Fig. 7 indicated that the signal at $\delta = 17.6$ due to the monomer was not present in the purified polymer. Besides a sharp singlet at -0.41 (linear repeating unit), the polymer gave three additional signals at $\delta = 0.87$, 0.20 and -1.69 respectively, which were the chemical shifts of the acyclic triesters of phosphoric acid. The two singlets at $\delta = 0.87$ and -1.69 may be explained by the transesterification in the polymerization. The loop structures led by intramolecular chain transfer gave a signal at $\delta = 0.87$,

while the branched structures led by intermolecular chain transfer with side chain rupture gave a signal at $\delta = -1.69$. The signal at $\delta = 0.20$ might be due to the terminal structure.

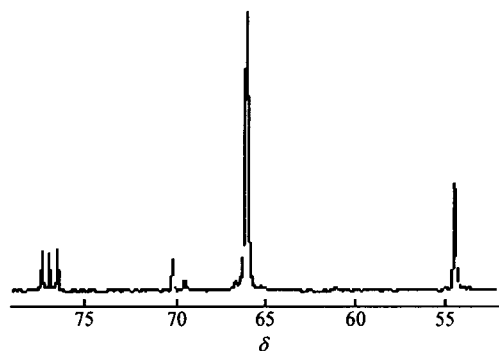


Fig. 6 ^{13}C -NMR spectrum of polyphosphate diol (EO mol%=16.3%, 3min)

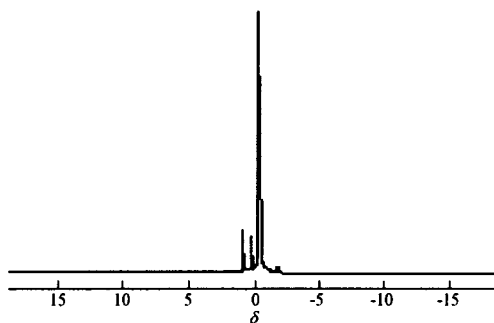
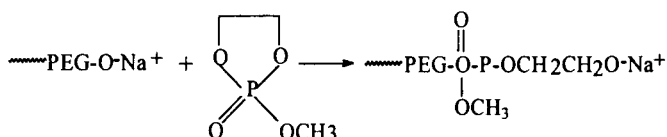


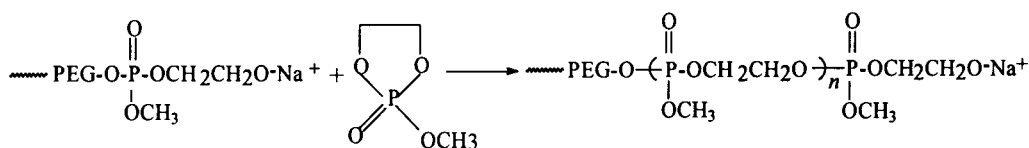
Fig. 7 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of polyphosphate diol (EO mol%=16.3%, 240 min)

Penczek *et al.*^[13] investigated the polymerization of EMP initiated by $\text{Al}(\text{O}^i\text{Pr})_3$ and found that exclusively linear polymer could be formed at low conversion, and transesterification occurred later during the polymerization. According to our experimental data, the polymerization mechanism is proposed as follows:

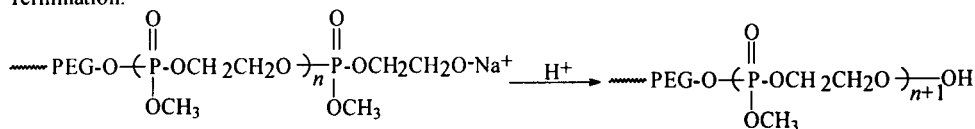
Initiation:



Propagation:



Termination:



Intermolecular transesterification:

