

SYNTHESIS AND POLYMERIZATION OF OLIGO (OXYETHYLENE) MACROMONOMER

ZHANG Shengshui (张升水), LIU Qingguo (刘庆国)

(Laboratory of Solid State Ionics, University of Science and Technology Beijing, Beijing 100083)

YANG Leiling (杨蕾玲)

(Beijing Research Institute of Chemical Industry, Beijing 100013)

FARRINGTON, Gregory C.

(Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA.)

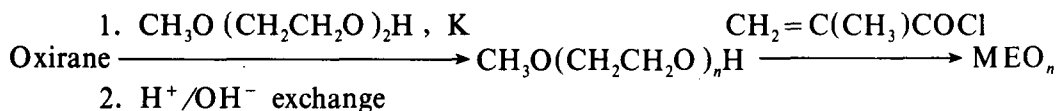
ABSTRACT

This paper reports the synthesis of methoxyoligo (oxyethylene) methacrylate (MEO_n , n is the repeating unit number of $(\text{CH}_2\text{CH}_2\text{O})$ in the macromonomer), and its polymerization in different solvents. MEO_n is prepared through such two independent reactions as (1) anionic polymerization of oxirane initiated by potassium alkoxide and (2) end-capping of methoxy oligo (oxyethylene) by methacrylic group. The n value can be conveniently controlled over the range of 5 ~ 30 by varying the molar ratio of oxirane to initiator and the molecular weight distribution of MEO_n be narrowed by increasing reaction time only in step (1). MEO_n thus obtained shows a rapid polymerization in water and benzene respectively, and both give water-soluble polymers as long as suitable conditions are used.

INTRODUCTION

Many publications have recently been devoted to the synthesis of macromonomers since they provide a convenient approach towards preparing well-defined graft polymers. As a result the types of new macromonomers are increasingly explored^[1 ~ 4]. Among macromonomers ever studied oligo (oxyethylene) macromonomer seems to be even more interesting as an intermediate for the preparation of amphiphilic graft copolymers due in part to the non-ionically hydrophilic property of poly (oxyethylene)^[3, 6 ~ 9]. Majority of the previous publications on the synthesis of oligo (oxyethylene) macromonomers are involved in the use of aromatic alkali metals salts such as cumylpotassium, diphenylmethyl potassium and naphthalene potassium, which frequently introduces hydrophobic groups into polymers and then reduces water-solubility of the polymers. More recent works have noticed that potassium alkoxides, especially potassium methoxide, can be employed as initiator in the ring-opening polymerization of oxirane, but their poor solubility in organic solvents impairs considerably, even eliminates, the initiating efficiency^[3, 6, 7]. Even if prepared successfully by using potassium alkoxides, monoalkyloxyoligo (oxyethylene) will be contaminated by small amount of bihydroxyoligo (oxyethylene) glycol ether, and consequently causes partial crosslinking of the resultant polymers owing to the presence of double vinyl end-group^[5]. In this work we will report the synthesis of oligo (oxyethylene) methacrylate (MEO_n with a general formula of

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_{n-1}\text{OCH}_3$, the designed scheme is as follows:



where n distributes from 5 to 30. Polymerization of MEO_n is studied in water and benzene solution, respectively.

EXPERIMENTAL

1. Materials

All reagents should be ensured to be free of moisture before reaction.

(1) Oligo (oxyethylene) monomethoxyl ether (MeEO_n). In an ice-salt bath oxirane was carefully dissolved in THF solution of potassium salt of monomethoxybiethylene glycol, then the reactor was sealed off. The reactor was transferred into 25 °C water-bath, and allowed to react for 36h with vigorous stirring. Small amount of water was dropwise added to terminate the reaction and the resultant product was purified by flowing the solution through a couple column of anion/cation exchanging resins. The product in a yield of more than 70% is colorless liquid to white wax-like solid, depending on the n value in the formula of $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. The n value was calculated from ^1H -NMR data and determined directly by GPC, respectively, and the results are consistent with each other. IR, 3430 (s, OH); 1095 (s, C—O—C); 1440 (m, OCH_2) cm^{-1} . ^1H -NMR (CDCl_3), δ ppm, 2.90 (1H, OH); 3.3 (3H, — CH_3); 3.5 ~ 3.9 (4nH, — $\text{OCH}_2\text{CH}_2\text{O}$ —).

(2) End-capping of MeEO_n by methacrylic group. To a well stirred solution of MeEO_n and triethylamine in chloroform cooled in a water-ice bath under a nitrogen atmosphere the methacryloyl chloride was dropped very slowly during 0.5h. After all the chloride had been added, the reaction was left to proceed for 1h at 0 °C, and 16h at room temperature. The precipitates formed during reaction were filtered off and the filtrate was carefully evaporated in reduced pressure. The crude product was purified by flowing its chloroform solution through silica gel column with the same solvent as eluant. The desired compound in a yield of around 75% was obtained by freeze-drying under vacuum. The purity of macromonomers was monitored by Cl elemental analysis (0%), IR (no characteristic peaks of the reactants such as —OH, —COCl). ^1H -NMR results (in CDCl_3) for MEO_{16} : 1.88 (3H, — CH_3); 3.31 (3H, — OCH_3); 3.58 (62H, — $\text{OCH}_2\text{CH}_2\text{O}$ —); 4.23 (2H, — COOCH_2 —); 5.50 and 6.04 (2H, $>\text{C}=\text{CH}_2$) ppm.

2. Polymerization

Polymerization of MEO_n was carried out under nitrogen atmosphere in water or benzene respectively, a common polymerization procedure was followed in these conditions: (1) 60 °C for both polymerization solvents, (2) calculated amount of initiator, 2,2'-azobisisobutyronitrile (ABIN) for benzene solvent and $\text{K}_2\text{S}_2\text{O}_8$ for water, was used, and (3) hexane as precipitator for the former and ethyl ether for the latter. Homopolymers above-prepared were all transparent elastomers with

an average molecular weight of $1 \sim 8 \times 10^4$ estimated by GPC.

3. Measurements

(1) IR scan was run on a Bruker IFS 113V FI-IR spectrometer and $^1\text{H-NMR}$ on Varian FT-80A apparatus. A Water ALC/GPC 224 column was used to analyze gel permeation chromatogram.

(2) DSC analysis was carried out under nitrogen atmosphere by using a Stanton Redcroft Thermal Analyzer with a scan rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) was taken as the mid-point temperature of the base-line shift observed during the transition from glass to rubber-like state, and the crystallinity (X_c) is calculated from the formula of $X_c = \Delta H / \Delta H^0 \times 100\%$ where ΔH^0 (188.1J/g) is the standard melting enthalpy of pure crystalline PEO^[10].

RESULTS AND DISCUSSION

1. Preparation of MeEO_n

It has been well-known that pure potassium salt of methoxybi(oxyethylene) glycol (MeEO_2K) is difficult to be dissolved in organic solvents, thus the solubility of MeEO_2K in THF has become a key to enhancing activity of initiator in the ring-opening of oxirane. In this work an appropriate amount of methoxybi(oxyethylene) glycol (MeEO_2H) is used to dissolve MeEO_2K so as to reach a homogeneous reaction system, but it will raise a broad molecular weight distribution of the target products. A solution to this problem is to increase polymerization time so as to ensure a sufficient chain transfer in the course of polymerization, which is considered to be favorable for obtaining narrow molecular weight distribution. GPC data demonstrate that all the $(\text{MeO}_n)_s$ synthesized here possess a $\overline{M}_w/\overline{M}_n$ value of less than 1.10 in spite of their different average molecular weight. Another essential factor for the achievement of well-defined MeEO_n is absolutely free of moisture, otherwise, a hard-isolation bihydroxyl product $[\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$ is formed, which then produces crosslinked polymer in the next reaction. A summary for the synthesis of MeEO_n is listed in Table 1, in which the n values determined from the correlation between the amount of consumed oxirane and used total amount of $\text{MeEO}_2\text{K}(\text{H})$ are rather larger than those estimated by other methods. The reason is the loss of volatile oxirane in ring-opening polymerization. In order to promote initiating efficiency it is necessary to choose potassium salt as initiator because of its relative lower ionic pairing in organic solvents.

Table 1 Summary for the polymerization of oxirane^{a)}

EO mole	MeEO_2H mmole	MeEO_2K mmole	$\text{MeEO}/\text{MeEO}_2\text{H}(\text{K})$ in mole	Yield ^{b)} %	Calcd	n value by GPC ^{c)}	n value by NMR ^{d)}
1.0	54.6	36.4	12.0	80	10.6	10.1	8.9
1.0	38.1	20.5	17.1	75	14.8	13.8	11.9
1.0	29.8	12.8	23.5	74	19.4	17.4	16.2
.0	21.7	8.4	33.2	70	25.2	22.1	20.4

a) Reactions were carried out at 25°C and near 1 atm with THF as solvent.

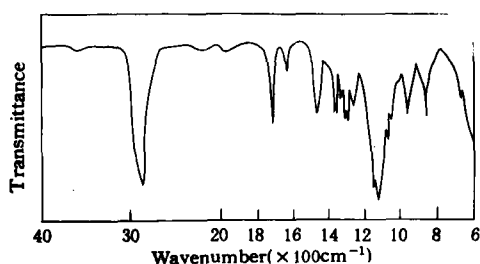
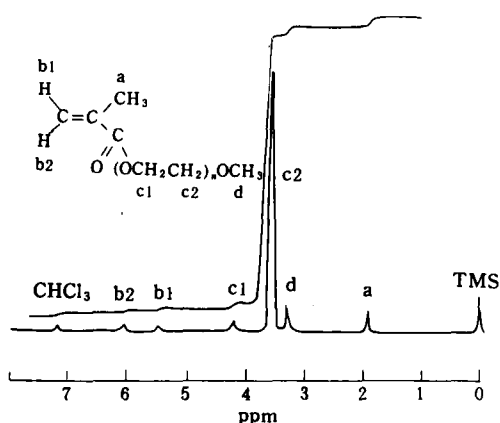
b) Estimated based on the amount of added oxirane.

c) Calibrated with PEO standard sample.

d) Calculated from the ratio of the integral area of protons in $\text{CH}_2\text{CH}_2\text{O}$ and CH_3 .

2. Esterification of MeEO_n with methacryloyl chloride

Majority of aprotic organic solvents are available for this reaction due mainly to an amphiphilic property of the MeEO_n , hence in this work chloroform is preferably chosen for the sake of the convenience of after-treatment. Meanwhile, triethylamine is also used as catalyst to remove hydrochloride produced during esterification. The obtained MEO_n is a colorless liquid to white wax-like solid, depending on the n value, but has no definite melting point since a spontaneous polymerization occurs very easily even below its melting point. Typically IR and ^1H -NMR spectra for MEO_{16} are shown in Fig.1 and Fig.2, respectively, both of which confirm the chemical structure of MEO_n . A few characteristic peaks in IR spectrum are assigned as follows: 1120 (s, $\nu_{\text{C}-\text{O}-\text{C}}$); 1724 (s, $\nu_{\text{C}=\text{O}}$); 1640 (s, $\nu_{\text{C}=\text{C}}$); 1280 (s, $\nu_{\text{as. CO}-\text{C}}$); 1150 (s, $\nu_{\text{s. CO}-\text{O}}$); 1470 (s, $\delta=\text{CH}_2$). Proton peaks of ^1H -NMR are marked in corresponding spectrum. The purity of MEO_n is in addition checked by the following data: ester content of ca. 96% (determined by saponification) and an unsaturation degree of 95% (titrated by bromine).

Fig.1 IR spectrum of MEO_{16} Fig.2 ^1H -NMR spectrum of MEO_{16} in CDCl_3

3. Free-radical polymerization of MEO_n

As an amphiphilic macromonomer MEO_n can be rapidly polymerized in many common solvents. Table 2 summarizes the free-radical polymerization of MEO_n in water and benzene, respectively. From Table 2 it has been found that

Table 2 Summary for the polymerization of MEO_n ^{a)}

n	Mass (g)	Solvent	Volume (ml)	Initiator (mg)	Yield (%)	$\bar{M}_n \times 10^{-4}$ ^{b)}	Water solubility
8	2.0	benzene	20	15	63	6.2	yes
		water	20	15	52	1.1	yes
12	2.0	benzene	20	20	88		no
		water	20	20	57	4.7	yes
16	2.0	benzene	20	25	68	8.4	yes
		water	20	25	93		no
22	2.0	benzene	20	25	72	5.6	yes
		water	20	25	92		no

a) All polymerizations were proceeded for 16h.

b) Estimated by GPC with PEO (2000) as standard sample.

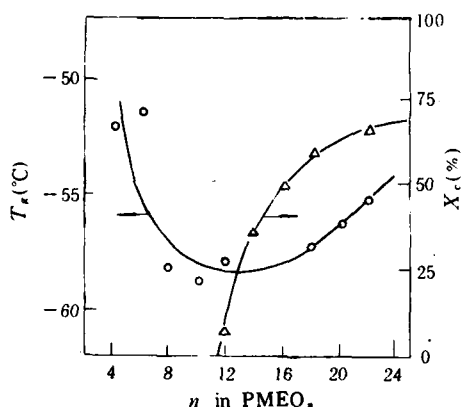


Fig.3 Glass transition temperature (T_g) and crystallinity (X_c) for homopolymers of $(\text{MEO})_n$.

polymeric gel is formed much easier in water than in benzene, which might be avoided or at least alleviated by lowering the concentration of monomer or increasing suitably the amount of initiator. On the other hand, the trend of gelation seems to be become more prominent with increasing of the n value in MEO_n , this phenomenon implies that there is a close relation between side-chain length and gelation. Hence it is reasonable to infer that gelation results from the physical entanglement of the oligo (oxyethylene) side chains rather than from the chain transference between the side chains and progressing macromolecules as MEO_n concentration exceeds a certain limited value. The DSC results for the homopolymer (PMEO_n) of MEO_n are indicated in Fig.3, from which a minimum glass transition temperature (T_g) of ca. -58°C is observed, whereas crystallinity (X_c) is enhanced initial-rapidly and then slowly with increasing n value after the n value exceeds 12. It seems to be an interesting fact that thermal behavior of PMEO_n is mainly decided by the structure of polymeric backbones for less n values and by the structure of oligo (oxyethylene) side chains of the polymers for larger n values.

Keywords :

Macromonomer ; Oligo (oxyethylene) ; Amphiphilic monomer ; Free-radical Polymerization

Acknowledgement The authors would like to thank Ms. Xi X.Q. and Prof. Jin S. Z. of the Institute of Chemistry, Academia Sinica for their helpful discussions on structural analyses of the compounds. This work was in part supported by Beijing Zhongguancun Associated Center of Analysis and Measurement under contract No. 92J31FQ-881.

REFERENCES

- [1] Rempp, P. and Franta, E., *Advances in Polymer Science*, **1984**, 58, 1.
- [2] Quirk, R. P., *Rubber Chem. Technol.*, **1984**, 3, 557.
- [3] Masson, P.; Beinert, G.; Franta, E. and Rempp, P., *Polym. Bull.*, **1982**, 7, 17.
- [4] Xie, H. Q., *Polymer Bulletin (in Chinese)*, **1990**, 3, 161.
- [5] Sun, F.; Feng, L. X. and Yang, S. L., *Chinese J. Appl. Chem.*, (in Chinese), **1987**, 4(4), 40.
- [6] Gnanou, Y. and Rempp, P., *Makromol. Chem.*, **1987**, 188, 2111.
- [7] Ito, K.; Yokoyama, S. and Arakawa, F., *Polym. Bull.*, **1986**, 16, 345.
- [8] Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S. and Itsuno, S., *Macromolecules*, **1991**, 24, 2348.
- [9] Chao, D.; Itsuno, S. and Ito, K., *Polym. J.*, **1991**, 23, 1045.
- [10] Griffin, L. C., in "Physical Constant of Linear Homopolymers", Springer-Verlag, Berlin, **1968**, p.120.