

SYNTHESIS AND CHARACTERIZATION OF A NEW COMBLIKE POLYMER BASED ON POLY (VINYL METHYL ETHER-ALT- MALEIC ANHYDRIDE) BACKBONE

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ABSTRACT

A new comblike polymer host for polymer electrolyte was synthesized by reacting monomethyl ether of poly(ethylene glycol) with poly(vinyl methyl ether-alt-maleic anhydride) and endcapping the residual carboxylic acid with methanol. Butanone was selected as a solvent for the esterification in order to obtain a completely soluble product. The synthesis process was traced through by IR. Compared with the model compounds, the presumed structure of this comblike polymer has been proved to be valid by ^{13}C NMR. The comb polymer is a white rubbery solid. It can be dissolved in butanone and THF, and manifests good film forming ability.

INTRODUCTION

Polymer electrolytes composed of polymer host and alkali metal salt have been studied for many years because of their potential application in solid state high energy rechargeable batteries and other electrochemical devices^[1-3]. Among the host polymers, the most extensively studied is the poly(ethylene oxide) (PEO). PEO can readily dissolve metal salts and shows a high ionic conductivity (10^{-3} — 10^{-4}S/cm) at 100°C or so. However, its high crystallinity at room temperature hinders the ion transport and depresses the ionic conductivity to a level too low to meet the requirement of a room temperature electrolyte. In an attempt to suppress the crystallinity, a lot of approaches have been adopted to synthesize polymers consisting

mainly of amorphous PEO or poly (ethylene glycol)^[4-6].

To prepare comb-branched polymers in which oligo (ethylene oxide) side chains are attached to a polymer backbone is an effective way to obtain almost totally amorphous host polymer if the length of the side chains is appropriate to restrict the formation of crystal. The systems based on substituted methacrylate polymers have been reported by Banister^[7] and Tsuchida^[8]. A similar system was synthesized by Cowie^[9], but poly (itaconic acid) was used as starting material instead of poly (methacrylic acid). By using a backbone which has a low glass transition temperature T_g , a more conductive electrolyte system could be realized, for a polymer host with a low T_g would possess high segmental mobility and thus high ionic conductivity^[10-11]. Along this line, Hall and Smid synthesized comb-branched siloxane polymers^[12-13], the conductivity of which after doping with LiClO_4 was reported to be $1.6 \times 10^{-4} \text{ S/cm}$ at 25°C . Shriver and coworkers synthesized the comblike systems by selecting polyphosphazene polymer as main chain, poly (bis(methoxy-ethoxy-ethoxide phosphazene)) (MEEP)^[14]. The systems are completely amorphous and have an extremely low T_g of -80°C . The maximum conductivity ($2.6 \times 10^{-4} \text{ S/cm}$) was found for MEEP/ AgCF_3SO_3 at 30°C . However, most of the low T_g backbone comblike electrolyte systems are poor in mechanical stability. Therefore, some groups enhanced the dimensional stability of the electrolyte by making the low T_g comblike polymer host crosslinked, e. g., we have synthesized an allyl polyether grafted siloxane prepolymer, which was crosslinked with tetraethyl orthosilicate. The complex of this network polymer with alkali metal salt exhibits a high ionic conductivity of about $5 \times 10^{-5} \text{ S/cm}$ at 25°C ^[15].

Although its electrical and mechanical performances are both excellent, the preparation is too lengthy and tedious. In this work, we synthesized another low T_g comblike polymer host by grafting monomethyl ether of poly (ethylene glycol) onto the poly (vinyl methyl ether-alt-maleic anhydride) backbone.

Maleic anhydride based alternating copolymers are a group of high reactive bifunctional polymeric materials and commercially available. Recently, Rietman and his colleagues^[16] synthesized single-ion comblike polymer electrolytes by reacting monomethyl ether either with poly (styrene-alt-maleic anhydride) or with poly (ethylene-alt-maleic anhydride) and then treating with LiOH solution to form lithium salt. Just like other single-ion polymeric electrolytes, the ionic conductivities of them were still

low (ca. 10^{-7} S/cm) at room temperature and such a low level of conductivity is of no practical significance. Besides, in Rietman's work the resulting rubbery product after esterification was usually insoluble and this made the addition of Li ion to be very difficult. The present work is an approach alternative to Rietman's study, i. e. , to prepare polymer host for bi-ion conduction by reacting monomethyl ether of PEG with another maleic anhydride alternating copolymer, poly (vinyl methyl ether-alt-maleic anhydride) and endcapping the residual carboxylic acid group with methanol. In this paper, the method of avoiding gel formation during preparation and the results of structural characterization by IR and ^{13}C NMR will be reported.

EXPERIMENTAL

Materials

Poly (vinyl methyl ether-alt-maleic anhydride) and monomethylether of polyethylene glycols (PEGME) with MW of 350, 550 and 750, respectively, are all the commercial products of Aldrich Co. . They were used as received without further purification. Para toluene sulfonic acid (PTSA), C. P. grade (Shanghai 1st Chemical Reagent Factory) was dried under vacuum at 70°C for 12h before use. MEK was refluxed in the presence of C. P. grade P_2O_5 for 4h; methanol was at first dehydrated by using 4A molecular sieve, and then refluxed with metallic magnesium for 1h; acetone and n-hexane were both refluxed with CaH_2 for 4h. After refluxing all the solvents were distilled out before use.

Synthesis of the comblike polymer

(1) Preparation of the catalyst

A weighed amount of PTSA was dissolved into MEK so as to prepare a homogeneous solution in a container, sealed and reserved for use.

(2) Esterification

The esterification of MA with PEGME without gel formation was achieved at first by dissolving MA and PEGME (mole ratio 1:2) in the freshly distilled MEK, then injecting a definite volume of MEK solution of PTSA to the mixture under a flow of N_2 . The mixture was stirred continuously for 24h at 80°C . After the reaction came to the end, the mixture was transferred to a rotary evaporator to remove the MEK, then an excess amount of freshly distilled methanol (ca. 200-fold) was added to the residue so as to endcap the unreacted carboxyl group. The reaction

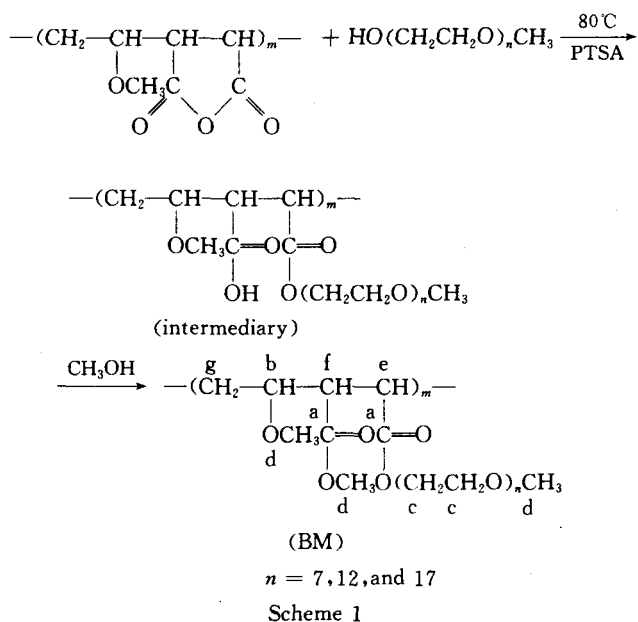
proceeded with continuous stirring for 24h at 60°C. The reaction mixture was then retransferred to the rotary evaporator for the removal of the excess methanol. Thereafter, the product was purified by reprecipitation by using distilled MEK as solvent, and n-hexane or dried petrol as precipitant. Generally, about four times of reprecipitation were necessary.

(3) Characterization of the structure

The IR spectra of the intermediary and end products were measured on a BIO-RAD FTS-7 spectrometer. A Varian unity-400 spectrometer was used to obtain the ^{13}C NMR spectra of the esterified MA (BM) and two model compounds, poly (ethylene-alt-maleic anhydride) (EM) and dimethyl ester of poly (vinyl methyl ether-alt-maleic anhydride) (MM).

RESULTS AND DISCUSSION

Scheme 1 summarizes the synthetic route for the comblike polymer host based on MA copolymer backbone.



Under the catalytic action of externally added acid, the esterification of the alternating maleic anhydride copolymer with low MW alcohol can only form a semi-ester, i.e., only one of the two carboxylic acids can be converted into ester^[17]. In our case of using PEGME as an esterification agent, similar result was obtained. The same result was also reported by Rietman^[16]. However, in contrast with the low MW monofunctional alcohol, the use of PEGME often results in an insoluble product. The formation of the

insoluble product would bring about many difficulties in the later operations of the synthesis work, e.g., purification, film formation and characterization. The gel formation might be caused by the presence of trace impurity of unmethylated PEG, which is very difficult to be removed from the bulk of PEGME completely. Then we tried to overcome this difficulty by allowing the esterification to proceed in solution, and have succeeded in obtaining completely soluble products. Several organic solvents such as DMF, cyclohexanone and MEK have been selected for the solution esterification. Among them, MEK seemed to be the most favourable. Although DMF is a good solvent for MA, it usually causes the product discoloured; as for the cyclohexanone, the solubility for the intermediary is rather poor. Besides, THF also manifests itself as a fairly good solvent for this esterification.

During the synthesis operation, it was found that after the completion of the first step of the reaction, the intermediary was very difficult to be obtained since it readily become an insoluble gel even if it was dried in an oven at the temperature as low as 50 °C. Thus the second step of the reaction was started by adding an excess amount of methanol right after the removal of MEK. Only in this way a completely soluble final product BM could be acquired.

The synthesis process was traced by IR. Fig. 1(a) shows the spectrum of the intermediary. The characteristic absorption of anhydride at 1857.8 and 1779.2 cm^{-1} appreciably lowered, while a strong absorption characteristic of the ester group at 1735.9 cm^{-1} appeared. This was an evidence that an appreciable amount of the anhydride has been esterified, although a part of which remained unreacted. The IR spectrum of the purified final product BM350 is shown in Fig. 1(b), both the absorption peaks at 1857.8 and 1779.2 cm^{-1} are absent, indicating that the anhydride has been converted completely. The strong absorptions at 1735.9 and 1106.6 cm^{-1} shows that the product is a polyester of poly (ethylene glycol). The assignment of the main absorption bands appeared in the IR spectrum of BM is listed in Table 1. It should be noted that sometimes a discernible absorption shoulder at 1710 cm^{-1} appeared in the IR spectrum of BM due to incomplete conversion of the carboxyl group. If an infinitesimal amount of dimethyl sulfate is added as a catalyst in the second step of the esterification, no such a shoulder can be detected. It means that the resulting BM contained no free $-\text{COOH}$ group.

Table 1 Assignment of IR spectrum for BM350

Peak (cm ⁻¹)	Assignment	Remarks
3303.9	—OH(CH ₂ OH)	νOH
2872.2	—CH ₃	ν _s CH ₃
1735.9		—
1452.7	—CO—OCH ₂ —	δ _{as} —CH ₂ —
1350.8	—CO—OCH ₃	δ _s —CH ₃
1197.7	—C—CO—O—	ν _{as} —C—O—
1106.6	—C—O—C—	ν _{as}

Note: ν, stretching; δ, bending; S, symmetry; as, asymmetry

The structure of BM was further examined by ¹³C NMR spectrum. According to the presumed formula of BM (see Scheme 1), there are four different carbons in the main chain, i. e. , one methylene carbon g and three tertiary carbons b, e and f. In the side chains, there are two carbonyl carbons a, three methyl carbons d, one of which belongs to the methoxyl group and the other two to the ester groups, and the methylene carbons c in the PEG group. The ¹³C NMR spectrum of BM 750 is shown in Fig. 2. In order to judge which signal represents its corresponding carbon in BM, it is necessary at first to study ¹³C NMR spectra of model compounds (EM, MA and MM) which are analogous to BM.

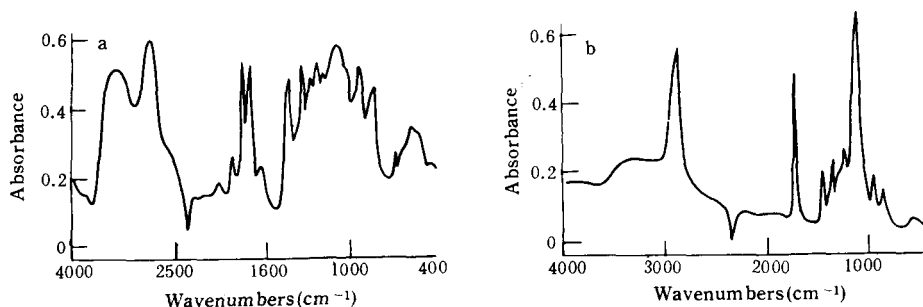


Fig. 1 IR spectra for (a)intermediary, (b)BM350

Fig. 3 shows the ^{13}C NMR spectrum of EM, the formula of which is shown as below. Except the solvent peaks, the spectrum exhibits only three sets of doublet signals. The splitting of the peaks is a result of the difference in the stereo-configuration for the anhydride group. From low to high field, we assign 175.6–173.4 ppm to the carboxyl carbons a; 47.8–45.8 ppm to the tertiary carbons b; 27.3–25.9 ppm to the secondary carbons c. The assignment was based on the disappearance of the signals of the quaternary carbons a in the carboxyl group and the inversion of the signals of the secondary carbons c in the methylene group in the DEPT spectrum of EM.

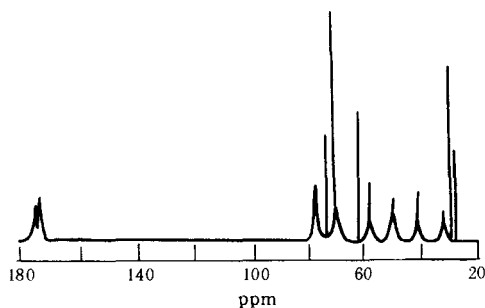
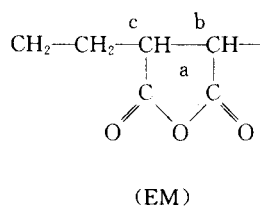


Fig. 2 ^{13}C NMR spectrum of BM 750

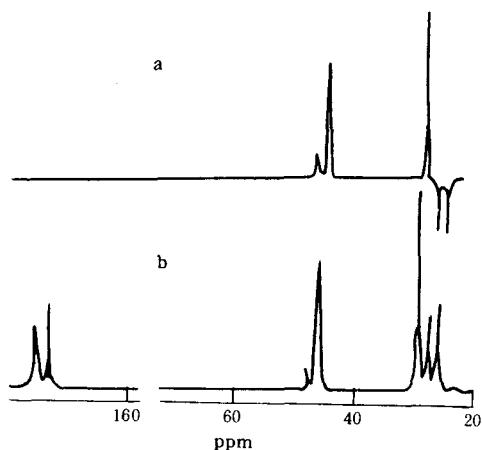
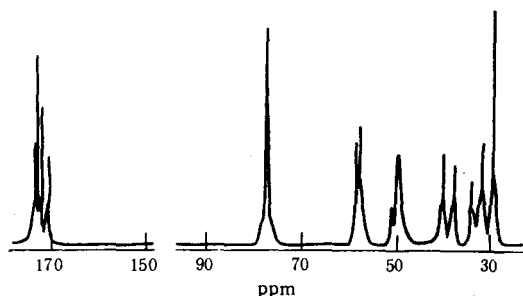
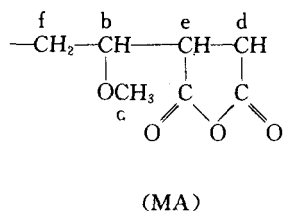
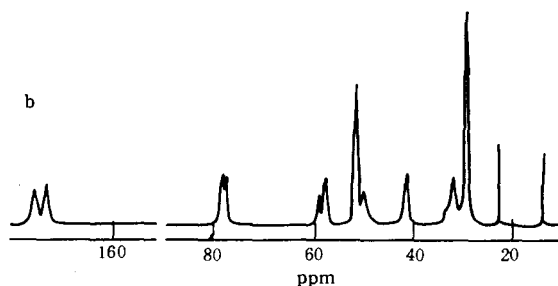
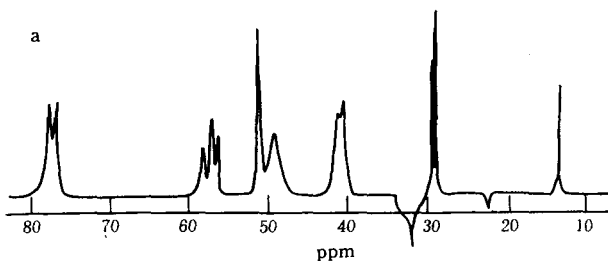
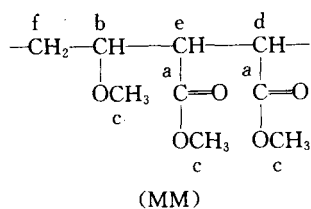


Fig. 3 ^{13}C NMR spectrum of EM (a) DEPT, (b) normal

The ^{13}C NMR spectrum of MA is shown in Fig. 4. From the formula of MA as shown below, the methoxyl group definitely complicates the chain structure of the copolymer, and increases the number and splitting of the signal. The presence of $-\text{OCH}_3$ would shift the signals of tertiary carbon b and adjacent secondary carbon f to the low field. The carbon in the methyl group of aliphatic methyl ether usually situates around 57 ppm^[18], so from low to high field the signals could be assigned as: a, quaternary carbon in the carboxyl group of maleic anhydride, 173.7–170.9 ppm; b, tertiary

carbon, 78.8—77.9ppm; c, primary carbon in the methoxyl group, 59.2—57.4ppm; d, tertiary carbon, 51.6—48.4ppm; e, tertiary carbon, 41.1—37.8ppm; and f, secondary carbon in the methylene group, 34.5—31.3ppm. For the model compound dimethyl ester of poly(vinyl methyl ether-alt-maleic anhydride)(MM), its formula is shown below and ^{13}C NMR spectrum in Fig. 5. From the assignment of the signals to carbons of the

Fig. 4 ^{13}C NMR spectrum of MAFig. 5 ^{13}C NMR spectrum of MM (a) DEPT, (b) normal

above discussed model compounds and the DEPT spectrum of this dimethyl ester of MA, signals of the carbons could be assigned as follows: a, quaternary carbon in the carboxyl group, 175.0—172.8ppm; b, tertiary carbon of methine group, 78.2—77.2ppm; methoxyl and methyl ester carbon, c, 58.4—56.6ppm; d,

methine carbon, 49.6—49.0ppm; e, methine carbon, 41.4—40.4ppm and f, secondary carbon of the methylene group, 31.9—31.6ppm. Compared with Fig. 5, the ^{13}C NMR spectrum of BM750 shown in Fig. 2 is quite similar to that of MM, except two additional signals situated in 72.8—69.9ppm and 61.2ppm. Apparently the former is the concentration of the secondary carbon c in the $-(\text{CH}_2\text{CH}_2\text{O})-$ group, while the latter is due to the carbon in the $-\text{CH}_2\text{OH}$ group^[18], which arises from the unreacted end of PEG mixed with PEGME. The fact that the PEGME contained a trace amount of PEG had been ascertained by ^1H NMR spectrum (not shown). Therefore, the assignment of the signals in BM ^{13}C NMR spectrum are: carbon a, 175.8—172.2; b, 78.2—77.2; c, 72.8—69.9; d, 57.5; e, 49.6; f, 41.1 and g, 32.1ppm. On the basis of the above results, the presumed structure of BM shown in Scheme 1 is now well confirmed.

Keywords:

Comblike polymer; Poly (vinyl methyl ether-alt-maleic anhydride); Esterification; Polymer electrolytes; IR spectra; ^{13}C NMR spectra

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