

The Characterization of Comblike Polymer Electrolyte by Means of NMR

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Abstract: The comblike polymers based on poly (styrene-*co*-maleic anhydride) backbone with poly (ethylene glycol) methyl ether as side chains were synthesized and characterized by ^1H NMR, with the result compared with that of IR. It is found that it is both feasible and simple to synthesize this kind of compounds with the help of ^1H NMR.

Keywords: ^1H -NMR, poly (styrene-*co*-maleic anhydride), IR, polymer solid electrolyte.

Introduction

Polymer solid electrolytes are a class of solid materials whose properties lie between those of solids and liquids, and they have been widely used in energy resources, metallurgy, environmental protection, electro-chemistry device and so on^{1,2}.

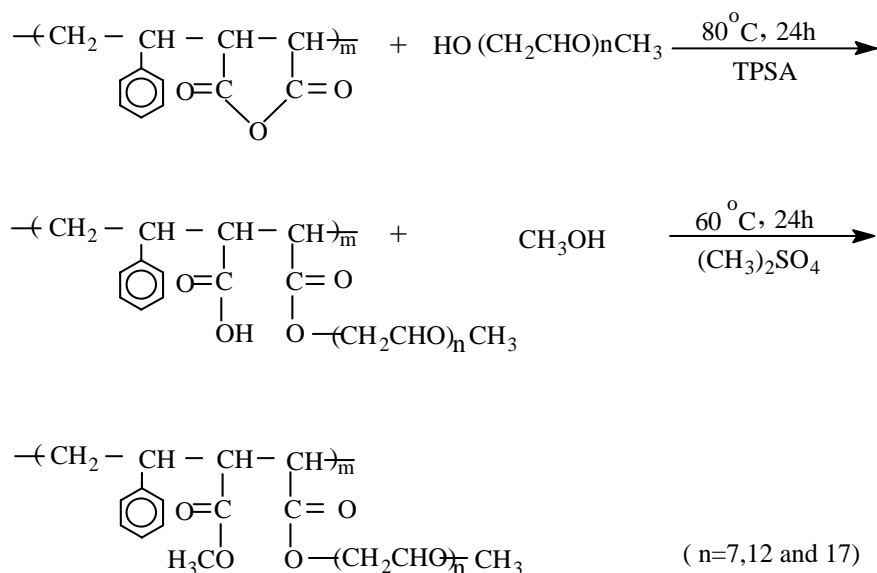
Inoue had pointed out that polystyrene derivative with many poly (ethylene oxide) PEO side chain could make conductivity reach 10^{-5} S/cm. They think that the flexibility of the backbone is not necessarily the important factor to achieve a high conductivity³. But we synthesized the comblike system of methyl vinyl ether/maleic anhydride and poly (ethylene glycol) methyl ether (PEGME) of styrene/maleic anhydride⁴⁻⁶, and found that glass transition temperature of the chief side chain is correlated with conductivity⁶. In order to make the glass transition temperature of backbone close to room temperature and observe the influences of the macromolecule motion of backbone relative to side chain, ionic conductivity, and even the ion conductor with a unique style of high conductivity. We selected the rigid styrene-*co*-maleic anhydride as backbone with benzene ring being side chain and synthesize the comblike polymers with poly (styrene-*co*-maleic anhydride) (PScMA) as backbone and poly (ethylene glycol) methyl ether as side chains. The polymers are characterized by ^1H -NMR and IR, and excellent results are obtained.

Experimental

Poly (ethylene glycol) methyl ether with MW of 350, 550 and 750 (Aldrich) were used

as received. We weighted PEGME and PScMA (mole ratio= 2:1), added butanone and PScMA in retrieving device, after that, added PEGME and a little toluene-p-sulfonic acid (TPSA), mixed, reacted 24 hours at 80°C. After the reaction was completed, the pressure of the mixture was reduced in order to remove butanone, then, added 300 time as large methyl alcohol and a little (CH₃)₂SO₄ (as catalyst). The crude product was formed by circumfluent reaction 24 hours at 60°C. After removing methyl alcohol, let the crude product settled with acetone as solvent and hydride petrol as precipitating agent. The product is usually settled for 3 times and then a pure sample is obtained. The reaction is shown schematically below.

Scheme 1



The product was kept in mixed solution of acetone and methyl alcohol, with $n = 7, 12, 17$ denoted as PS33, PS53, PS73.

¹H NMR experiment: JEOL FX-100 NMR spectrometer, observe frequency: 99.55MHz, spectrum wide: 2KHz, 90° pulse, 16K data point, accumulated: 50 time, dissolved in CDCl₃.

The IR spectra of the intermediate and end products were measured on a BIO-RAD FTS-7 spectrometer using KBr plate technique.

Results and Discussion

The sample structures: HO(CH₂CH₂O)_nCH₃ ($n = 7, 12, 17$), with side chains M.W. = 350, 550, 750, consist of 3 different chemical shift groups. After two steps of esterification reaction, three kinds of products with the lengths of side chains different: PS33, PS53, PS73, were obtained. In the NMR spectrum, the -OH peak was not be found, implying that the esterification reactions had taken place. The assignment of the main peaks in the ¹H NMR spectrum is listed in **Table 1**.

Table 1. ¹H NMR spectral assignment of PS33, PS53, PS73, 350, 550 and 750

	PS33	PS53	PS73	350	550	750
-OH				3.88	3.88	3.81
-CH ₂ CH ₂ O-	3.06,3.43	3.09,3.45	3.13,3.45	3.53, 3.69	3.46, 3.66	3.53, 3.64
-CH ₃	3.70	3.69	3.69	3.39	3.42	3.37
-CH ₂ -	1.99	1.93	1.92			
-CH-C ₆ H ₆	1.56	1.56	1.56			
-CH-COOCH ₃	1.28	1.29	1.27			
-CH-COO(CH ₂ CH ₂ O) _n CH ₃	3.70	3.69	3.69			

We had calculated the area integrals of each peak and found that the ratio of O(CH₂CH₂O)_nCH₃ and (CH₂CHCHCH)_m is about 1:1 (listed in **Table 2**). If this structure is half-ester⁷, the molecular formula of PS33, PS53, PS73 can then be written as C₂₈H₄₄O₁₁, C₃₈H₆₄O₁₆, C₄₈H₈₄O₂₁. The data of fine products showed that the principle value is in agreement with the measured value. This structure is half-ester, and the molecular structure is given in **Scheme 2**.

Scheme 2.

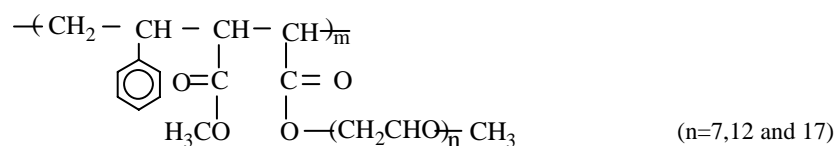


Table 2. Peak area integrals of HO(CH₂CH₂O)_nCH₃ and (CH₂CHCHCH)_m

	PS33	PS53	PS73
O(CH ₂ CH ₂ O) _n CH ₃	1.7	1	0.35
(CH ₂ CHCHCH) _m	2	1.2	0.5

In addition, the IR spectrum of PS53 showed that the absorption peaks of 1777.7 cm⁻¹ and 1853.2cm⁻¹ had disappeared, and implying that the acid anhydride had been transformed. The strong characteristic absorption peaks at 1733.4cm⁻¹ and 1163.1cm⁻¹ were poly (ethylene glycol) methylether, while the peak of polyether at 1107.5cm⁻¹ and the peak of -OH at 3341.3cm⁻¹ had been disappeared. It showed that PEGME and impurity had been cleared after being settled and purified repeatedly. The assignment of the main absorption band appearing in the IR spectrum is listed in **Table 3**.

Table 3. Assignment of main absorptions in IR spectrum of PS53

assignment	absorption peaks (cm ⁻¹)
-CO-O-	1733.4, 1163.1
-CO-	1104.9
C-O-C	1104.9
-COOCH ₃	1452.5, 1357.3
-CH ₃	2876.5

We thus conclude that the determination of the structures of this series of compounds by $^1\text{H-NMR}$ method is not only easy to operate and fast but also accurate, compared with IR and elemental analysis.

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