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SYNTHESES OF LITHIUM OLIGOETHER PHENYLSULFONATES

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ABSTRACT

Lithium oligoether phenylsulfonates, a new kind of oligoether salts which are used in ionic conductive polymers, were synthesized. IR, ^{1}HNMR spectra and elemental analyses were used to characterize their chemical structures. DSC results exhibit that the salts have low glass transition temperature (-30°C~ -20 °C). They are viscous liquids at ambient temperature and could be used as low temperature molten salts in polymer electrolytes.

Keywords: oligoether salts, organic lithium salts

INTRODUCTION

It has been twenty years since the beginning study on application of polymer solid electrolytes (PSE) in all-solid-state lithium cells, but they are not practical until now. The main reason is the lower ionic conductivity of polymer solid-state electrolytes ($\sigma \sim 10^{-5}$ Scm^{-1} at ambient temperature without plasticizers).

The organic salts, which were added into the PSE, were reported much as organic lithium sulfonates, especially the lithium oligoether alkylsulfonates [1~2]. Because of the donative effect of alkyl groups, it makes larger the electron cloud density of sulfonic anions so that lithium cations are attracted more tightly by static electrical force which results in the more difficult dissociation of the salts. In this paper, lithium oligoether phenylsulfonates synthesized all have phenyl groups. Due to the conjugative effect of phenyl groups, it decreases the electron cloud density of sulfonic groups. Thus the static electrical force which the lithium cations are drawn by lowers down and then the salts dissociate more easily. It is hopeful

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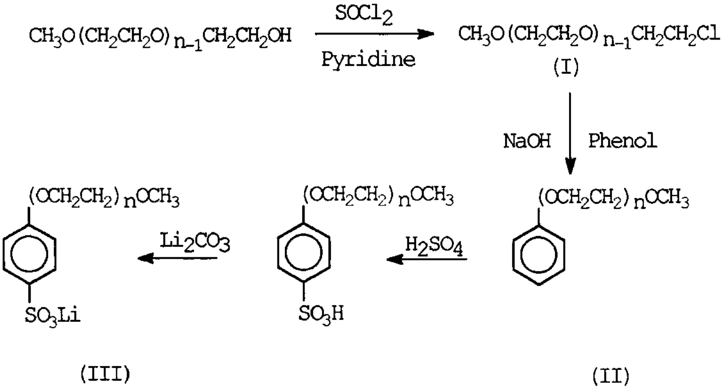
that higher ionic conductivity could be achieved compared to that of lithium oligoether alkylsulfonates with the same addition.

Referred to literatures [3–5], a new type of organic lithium salts, lithium p-(methoxy oligo(ethyleneoxy)) phenylsulfonates, were designed and synthesized. The route is listed as follows:



where n=2 (a), 7.3 (b), and 11.8 (c).

The above mentioned compounds were determined by IR and ^{1}HNMR spectra and elemental analyses. The thermal, electrical and electrochemical properties of these lithium oligoether phenylsulfonates and their application in liquid and polymer electrolytes will be reported in other articles.

EXPERIMENTAL

1. Reagents:

Diethylene glycol monomethyl ether (n=2) was purchased from Shanghai No. 3 Reagent Factory and used after distillation under reduced pressure. Poly(ethylene glycol) monomethyl ether with average molecular weights of 350 (n=7.3) and 550 (n=11.8) were bought from Aldrich Chemical Co. Inc. and used as received. Thionyl chloride was purified by distillation before use. Tetrahydrofuran, pyridine and methanol were treated as anhydrous ones.

2. Measurements:

The boiling points in this experiment were not adjusted. IR spectra were measured by Beckman Microlab 620 MX. ^{1}HNMR spectra were carried out by Varian FT-80A (TMS used as internal standard material) and elemental analyses were determined by Carlo Erba 1106 for C, H, ICP emission spectra for Li and chemical methods for Cl, S. The Perkin-Elmer DSC-7 was used to investigate the glass transition temperature (T_g) of these lithium oligoether phenylsulfonates in a temperature range from -100 °C to 60 °C with scanning rate of 20 °C / min under nitrogen atmosphere.

3. Syntheses:

3.1 Methoxy oligo(ethyleneoxy) ethylene chloride (I) [3]:

To a well-stirred solution of poly(ethylene glycol) monomethyl ether 0.10 mole, absolute pyridine 0.11 mole and dry THF 300ml, cooled below 5 °C in an ice-water bath, 0.12 mole of $SOCl_2$ was added dropwise in half an hour in order to keep the temperature lower than 10 °C. The mixture was then heated slowly to about 70°C and maintained refluxing for 4 hours at which gas evolution had nearly ceased. After cooling, the precipitates formed during the reaction were filtered and the solid body was washed several times with THF. The filtrate and the washing solution were mixed up and then concentrated on a rotary evaporator. The residue was poured into 300 ml of water and extracted with chloroform. The extract was washed with 10% Na_2CO_3 aqueous solution and water respectively until the pH value was neutral and then dried with anhydrous $MgSO_4$ for 24 hours. Removal of the solvent followed by distillation under vacuum gave the pure products. However, (I_c) with n=11.8 cannot be distilled. It could be used directly in the following reaction as crude product after the chloroform was removed.

I_a (n=2): colorless transparent liquid, b.p. 32.0~33.5 °C/ 9.4 mmHg, yield 72%. IR(cm^{-1}): 2885 (ν_{C-H}), 1122 (ν_{C-O-C}), 670 (ν_{C-Cl}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.36 (s, 3H, 1*CH_3), 3.46~3.83 (m, 8H, 2*OCH_2CH_2). Elemental analysis: found C% 43.14, H% 7.81, Cl% 25.52; calculated C% 43.32, H% 7.94, Cl% 25.63.

I_b (n=7.3): yellow transparent liquid, b.p. 94~284 °C/ 0.1~0.3 mmHg, yield 68%. IR(cm^{-1}): 2880 (ν_{C-H}), 1120 (ν_{C-O-C}), 670 (ν_{C-Cl}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.32 (s, 3H, 1*CH_3), 3.45~3.90 (m, 29H, 7.3*OCH_2CH_2). Elemental analysis: found C% 49.28, H% 8.58, Cl% 9.51; calculated C% 50.34, H% 8.66, Cl% 9.63.

I_c (n=11.8): orange transparent liquid, yield 66%. IR(cm^{-1}): 2875 (ν_{C-H}), 1120 (ν_{C-O-C}), 670 (ν_{C-Cl}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.31 (s, 3H, 1*CH_3), 3.45~3.88 (m, 47H, 11.8*OCH_2CH_2). Elemental analysis: found C% 51.03, H% 8.71, Cl% 6.08; calculated C% 51.80, H% 8.81, Cl% 6.24.

3.2 Methoxy oligo(ethyleneoxy) benzene (II) [4]:

In a three-necked round bottom flask, were placed 0.15 mole phenol, 0.15 mole NaOH, 0.5g tetrabutyl ammonium bromide and 200 ml distilled water. After the solids dissolved with stirring, 0.10 mole methoxy oligo(ethyleneoxy) ethylene chloride (I) was added dropwise. The reaction was carried on in refluxing state for 8 hours. After cooling, the mixture was extracted with chloroform. The extract was washed to neutral with water and dried by anhydrous $MgSO_4$ for 24 hours. After filtered, the solvent was removed from the filtrate and the residue was distilled under vacuum to give pure products. When n=11.8, i.e. (II_c), however, the residue must be distilled to remove little amount of phenol to give a crude product and used as so.

II_a (n=2): colorless transparent liquid, b.p. 104~108 °C/ 0.4~0.7 mmHg, yield 84%. IR(cm^{-1}): 2870 (ν_{C-H}), 1600, 1495 ($\nu_{C=C\ of\ Ph}$), 1246 (ν_{C-O-Ph}), 1110 (ν_{C-O-C}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.33 (s, 3H, 1*CH_3), 3.59~4.12 (m, 8H, 2*OCH_2CH_2), 6.79~7.31 (m, 5H, 1*C_6H_5). Elemental analysis: found C% 66.84, H% 8.17; calculated C% 67.35, H% 8.16.

II_b (n=7.3): orange liquid, b.p. 143~296 °C/ 0.2~1.5 mmHg, yield 79%. IR(cm^{-1}): 2860 (ν_{C-H}), 1600, 1495 ($\nu_{C=C\ of\ Ph}$), 1246 (ν_{C-O-Ph}), 1110 (ν_{C-O-C}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.19 (s, 3H, 1*CH_3), 3.49~3.95 (m, 29H, 7.3*OCH_2CH_2), 6.68~7.22 (m, 5H, 1*C_6H_5). Elemental analysis: found C% 59.50, H% 8.32; calculated C% 60.45, H% 8.67.

II_c (n=11.8): orange liquid, yield 65%. IR(cm^{-1}): 2870 (ν_{C-H}), 1600, 1500 ($\nu_{C=C\ of\ Ph}$), 1245 (ν_{C-O-Ph}), 1110 (ν_{C-O-C}). ^{1}HNMR (in $CDCl_3$) δ (ppm): 3.18 (s, 3H, 1*CH_3), 3.48~3.97 (m, 47H, 11.8*OCH_2CH_2), 6.61~7.20 (m, 5H, 1*C_6H_5). Elemental analysis: found C% 57.63, H% 8.47; calculated C% 58.54, H% 8.80.

3.3 Lithium p-(methoxy oligo(ethyleneoxy)) phenylsulfonates (III) [5]:

A mixture of 0.10 mole of compound (II) and 0.10 mole 90% sulfuric acid was stirred vigorously at about 100 °C for 10 hours, poured into 300 ml distilled water. The oily products were removed by extraction with chloroform, and the aqueous solution was neutralized by adding excess of lithium carbonate. The mixture was refluxed for fifteen minutes and then cooled down. After removal of the precipitates and evaporation of the filtrate to dryness, the residue was dried under vacuum at about 80 °C for 4 hours, and finally extracted with absolute methanol. The product (III) was obtained by evaporating the extract to dryness and by further drying under reduced pressure at 80 °C for 48 hours.

III_a (n=2): white viscous liquid, yield 65%. T_g=-27.0 °C. IR(cm^{-1}): 2890 (ν_{C-H}), 1610, 1508 ($\nu_{C=C\ of\ Ph}$), 1255 (ν_{C-O-Ph}), 1125 (ν_{C-O-C}), 1186, 1043 ($\nu_{S=O}$). ^{1}HNMR (in D_2O) δ (ppm): 3.28 (s, 3H, 1*OCH_3), 3.54~4.11 (m, 8H, 2*OCH_2CH_2), 6.95 (d, 2H, J=8.8Hz) and 7.70 (d, 2H, J=8.8Hz) for AA'BB' system of Ph. Elemental analysis: found C% 44.41, H% 5.67 , S% 11.03, Li% 2.54; calculated C% 46.81, H% 5.32 , S% 11.35, Li% 2.48.

III_b (n=7.3): pale yellow brown viscous liquid, yield 43%. T_g=-22.4 °C. IR(cm^{-1}): 2870 (υ_{C-H}), 1600, 1503 ($\nu_{C=C\ of\ Ph}$), 1250 (ν_{C-O-Ph}), 1130 (ν_{C-O-C}), 1225, 1035 ($\nu_{S=O}$). ^{1}HNMR (in D_2O) δ (ppm): 3.32 (s, 3H, 1*OCH_3), 3.66~4.13 (m, 29H, 7.3*OCH_2CH_2), 7.03 (d, 2H, J=8.8Hz) and 7.25 (d, 2H, J=8.8Hz) for AA'BB' system of Ph. Elemental analysis: found C% 49.06, H% 6.69, S% 6.79, Li% 1.48; calculated C% 50.30, H% 7.02, S% 6.25, Li% 1.37.

III_c (n=11.8): pale brown viscous liquid, yield 39%. T_g=-29.5 °C. IR(cm^{-1}): 2870 (ν_{C-H}), 1600, 1500 ($\nu_{C=C\ of\ Ph}$), 1250 (ν_{C-O-Ph}), 1126 (ν_{C-O-C}), 1250, 1045

($\nu_{S=O}$). ^{1}HNMR (in D_2O) δ (ppm): 3.38 (s, 3H, 1*OCH_3), 3.74~4.17 (m, 47H, 11.8*OCH_2CH_2), 7.09 (d, 2H, J=8.8Hz) and 7.80 (d, 2H, J=8.8Hz) for AA'BB' system of Ph. Elemental analysis: found C% 49.89, H% 6.86, S% 5.20, Li% 0.98; calculated C% 51.47, H% 7.60, S% 4.49, Li% 1.14.

DISCUSSION

When methoxy oligo(ethyleneoxy) benzene reacts with sulfuric acid, the donative effect and much space hindrance of methoxy oligo(ethyleneoxy) groups make the reaction produce only mono-substituted sulfonic product at the given conditions, and the sulfonic group is located at the para position. This could be proven by ^{1}HNMR results which exhibit that there are two pairs of coupling peaks at a range of δ 6.9 ~ 7.8 ppm which are characteristic peaks of hydrogen atoms of 1,4-disubstituted benzene.

With the increase of unit value (n) of oligoether, it enhances the coordinative ability of oligoethers, acting as open chain crown ethers, to metal lithium cations. While neutralizing sulfuric acid with lithium carbonate, a coordinative complex having little amount of lithium sulfate and lithium carbonate formed due to the coordination of oligoether oxygen atoms to lithium cations. But these coordinative inorganic salts could be removed by treating dry crude product with anhydrous methanol several times.

It is shown from DSC curves that the glass transition temperatures (T_g) of these lithium oligoether phenylsulfonates are all located in a range between -30°C to -20°C and the salts are in viscous states at ambient temperature. Thus, they could be applied in polymer solid electrolytes as low temperature molten salts. It is anticipated that higher ionic conductivity could be obtained since their additions could reach a larger amount in polymers.

REFERENCES

1. T.Hamaide and A.Guyot, *The Second International Symposium on Polymer Electrolytes*, pp. 71-74 (June 14-16, 1989 at Siena, Italy)
2. S.S.Zhang, Z.H.Deng and G.X.Wan, *Chin. J. Polym. Sci.*, 9(4), 326 (1991)
3. Saverio Zuffanti, *J. Am. Chem. Soc.*, 62, 1044 (1940)
4. L.W.Deady, R.D.Topson and J.Vaughan, *J. Chem. Soc.*, 2094 (1963)
5. Y.Muramoto and H.Asakura, *Nippon Kagaku Kaishi*, 11, 1948 (1975)