

NETWORK CROWN ETHER POLYMERS WITH CENTRIC FUNCTIONAL GROUP (IV) SYNTHESIS OF NETWORK CROWN ETHER POLYMER WITH PENDANT DIETHYLAMINO THIAALKYL GROUP AND ITS PLATINUM COMPLEX*

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ABSTRACT

The title polymer was prepared from 5-diethylamino-3-thia-pentyl glycidyl ether and diethylene glycol bisglycidyl ether via ring-opening copolymerization. It was found that this reaction could be catalyzed by sodium, but not Lewis acid. The obtained polymer can coordinate with platinum compound, and the platinum complex is a new kind of catalyst for the hydrosilylation of olefins with triethoxysilane.

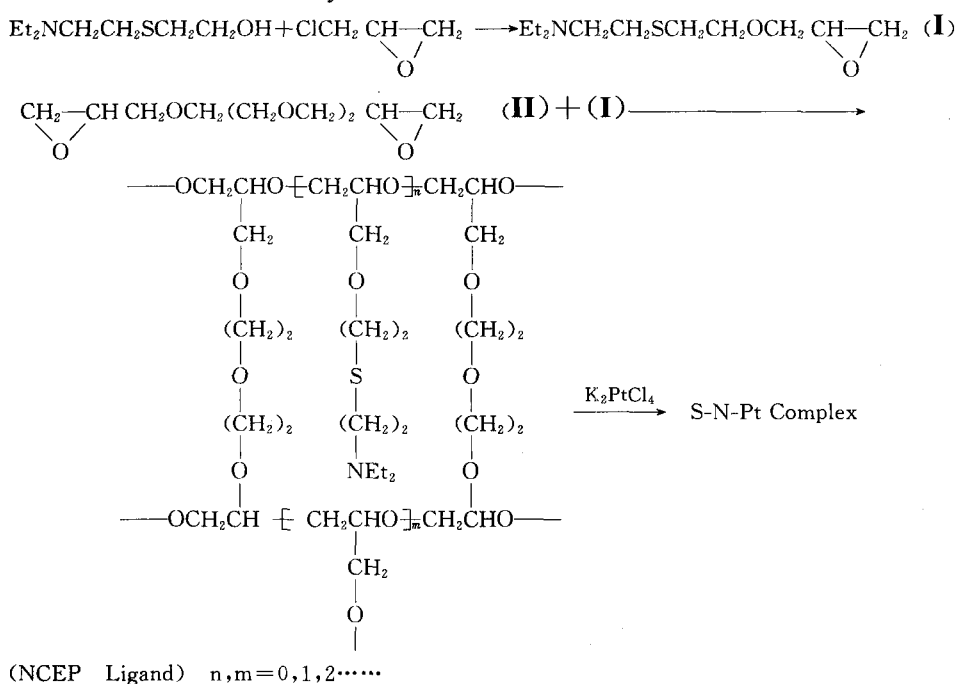
INTRODUCTION

It is well known that the crown ether polymers possess a number of merits as compared with monomeric crown ethers. For example, they can easily be recovered from reactants and products and be reused several times. However, their applications are strongly confined due to the multi-step synthetic procedure, which usually uses monomeric crown ethers as starting material. Consequently, it is of great practical and theoretical significance to note the simple methods for the syntheses of crown ether polymers from non-crown ether monomers via polymerization directly. In 1981, Butler et al. synthesized linear crown ether polymers from 1,2-bis(ethenyloxy)benzene, 1,2-bis(ethenyloxyethyloxy)benzene via cyclopolymerization^[1]. Cyclopolymerization of divinyl ethers of oligo(oxyethylene)s was reported by Yokota et al.^[2]. We also found a route to synthesize network crown ether

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polymers (NCEPs) from non-crown ether monomers, oligo(oxyethylene)s bisglycidyl ether and monoglycidyl ethers, via ring-opening polymerization or copolymerization^[3]. The NCEP is a special kind of crown ether polymer. They may be considered as crosslinked polyether, but their structural units are composed of oxyethylene and oxypropylene chain units. In 1990, we had made another important progress in this field. A series of quaternary ammonium salt-containing NCEP were synthesized by ring-opening copolymerization of ω -chlorohexyl glycidyl ether with ethylene glycol bisglycidyl ether, diethylene glycol bisglycidyl ether, or triethylene glycol bisglycidyl ether in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as catalyst, followed by quaternarization with triethyl amine or tributyl amine^[4]. The quaternary ammonium salt-containing side chain is attached to the network structural units of NCEP. As we know, this is the first example of NCEP with centric functional group. The main demerit is that the yield of quaternarization is low, i. e. the nitrogen content of polymers is about 0.1% only. In this paper, we wish to report a new modified route for the preparation of NCEP with centric functional group, and the obtained polymer is successfully used as polymer ligand of soft metal salt. The catalytic characteristic of the platinum complex for the hydrosilylation of olefins with triethoxysilane is described here also. The synthetic scheme is shown below:



EXPERIMENTAL

PMR, IR, MS, and XPS were obtained on EM-360L spectrometer, Nicolet 170 SX FT-IR spectrometer, ZAB 3F HF-HF mass spectrometer, and Kratos XSAM 800 electron energy spectrometer, respectively. GLC was carried out on 102G model chromatography, using thermal conductivity detector, SE-30 stationary phase, and silylanized white matrix. Diethylene glycol bisglycidyl ether was synthesized as reported^[3]. 5-Diethylamino-3-thia-pentyl alcohol was prepared according to literature^[5].

Synthesis of 5-diethylamino-3-thia-pentyl glycidyl ether (I)

A mixture of β -diethylamino- β -hydroxy diethylsulfide (8.85 g, 0.05 mol), potassium hydroxide (2.8 g, 0.05 mol), epichlorohydrin (9.25 g, 0.10 mol), PEG-400 (1 g, 2.5 mmol), and 25 ml of dichloromethane was stirred at 35°C for 12 h. After filtration, the filtrate was distilled under reduced pressure. 7.0 g of 5-diethylamino-3-thia-pentyl glycidyl ether was obtained as colourless liquid in 60% yield at 126–128°C/6.7 Pa. Calcd for $C_{11}H_{23}NSO_2$: N 6.00, S 13.74%; Found: N 5.98, S 13.68%. PMR: 1.05 (t, 6H), 2.2–3.1 (m, 13H), 3.2–3.9 (m, 4H) ppm. IR: 2928, 2878, 1458, 1378, 1253, 1109, 1070, 911, 856, 700 cm^{-1} . MS: m/z 223 (M^+), 101 ($H_2CCH(O)CH_2OCH_2CH_2^+$), 87 ($H_2CCH(O)CH_2OCH_2^+$), 86 ($H_2C=N^+Et_2$, base peak).

Ring-opening copolymerization of 5-diethylamino-3-thia-pentyl glycidyl ether (I) and diethylene glycol bisglycidyl ether (II)

A mixture of diethylene glycol bisglycidyl ether (1.795 g, 8.22 mmol), 5-diethylamino-3-thia-pentyl glycidyl ether (1.918 g, 8.22 mmol), sodium (10.1 mg, 0.44 mmol) was stirred at ambient temperature for 0.5 h under nitrogen, and then at 120°C for 1.5 h. The reactants turned brown transparent solid after cooling. The solid was ground to powder, and then washed with distilled water until the rinsed water remained neutral. After extracting with acetone in a Soxhlet apparatus for 12 h, drying at 120°C/0.67 KPa for 8 h, 3.1 g of copolymer was obtained as slightly grey powder in a yield of 83.5%. Calcd: N 3.19, S 7.29; Found: N 2.12, S 4.85%. The nitrogen and sulfur contents are much less than that calculated. It was found that the linear polymer of 5-diethylamino-3-thia-pentyl glycidyl ether could dissolve in acetone. Thus, a part of it did not participate in the

formation of copolymer, and washed out as homopolymer by acetone in the extractive process.

It was also found that the Lewis acid could not catalyze this reaction. This phenomenon may be ascribed to the strongly coordinate ability of Lewis acid to sulfur in 5-diethylamino-3-thia-pentyl glycidyl ether. As the polymerization reaction proceeded smoothly if we used chlorohydrin or 2-alkoxymethyl oxirane instead of 5-diethylamino-3-thia-pentyl glycidyl ether as a component in copolymerization.

Synthesis of platinum complex

A mixture of the polymer ligand (NCEP ligand, 1.0 g); K_2PtCl_4 (0.15 g), and 50 mL of acetone was stirred at reflux temperature under argon for 72 h. After filtration, the solid product was washed with acetone, distilled water, acetone, successively, and dried at 120°C/0.67 KPa for 12 h. The platinum complex was obtained as slightly yellow elastomer (1.1 g). Calcd: Pt 6.38, Cl 2.37%; Found: Pt 5.62, Cl 2.05%. The atomic ratio of N : S : Cl is equal to 1 : 1 : 2, and that of S : Pt is equal to 3.43 : 1. IR : 2920, 2872, 1460, 1107 cm^{-1} . XPS : $Pt_{4f7/2}$ 72.2, S_{2p} 163.4, Cl_{2p} 197.7 eV. The binding energy of $Pt_{4f7/2}$ is 0.9 eV less than that in K_2PtCl_4 , 0.9 eV more than that in platinum foil. The S_{2p} binding energy increases 0.6 eV as compared with that in NCEP ligand, and the Cl_{2p} binding energy is almost the same as that in *cis*-(Et_2S) $_2PtCl_2$ (197.6 eV)^[6]. These can be interpreted as the result of formation of the expected platinum complex. Considering the elemental analysis data, we can conclude that the platinum exists as $PtCl_2$ in the complex.

Hydrosilylation experiments.

Hydrosilylation experiments were carried out in a 5 ml plane-bottomed flask connected with a condenser to the upper end of which a drying system was attached. 5.0 mmol of olefin and a weighed amount of platinum complex were stirred for 30 min before triethoxysilane was added. The reaction was monitored by GLC, and the yield of hydrosilylation product was determined by standard sample and standard curve^[7].

RESULTS AND DISCUSSION

Recently, we synthesized a number of polysiloxane-supported platinum coordinate catalysts in which the platinum atoms were anchored to polysiloxane via bidentate type ligands including $-CH_2CH_2SCH_2CH_2NMe_2$.

and found that they are not only effective catalysts for the hydrosilylation of olefins, but also have different catalytic characteristics from that of ordinary monodentate type supported platinum coordinate catalysts^[7]. Thus, we will expect that the title platinum complex is also an effective hydrosilylation catalyst, and it is interesting to compare with the above mentioned silicone-supported sulfide-amine platinum complex. The catalytic characteristics of the platinum complex are investigated via the following ways.

1. Influence of temperature on the activity of platinum complex

Dec-1-ene is used as substrate to test the catalytic activity at a series selected temperature. The platinum complex exhibits high catalytic activity in the temperature range of 120 to 135°C, that is similar to that of silicone-supported one. The induction period decreases with the increasing of temperature, but the yield of decyltriethoxysilane has small or no variation from 120 to 135°C. However, higher yield is obtained with title complex at 130°C, the most suitable temperature for it, as compared with using silicone-supported one at its suitable temperature, 120°C. The results are shown in Fig. 1.

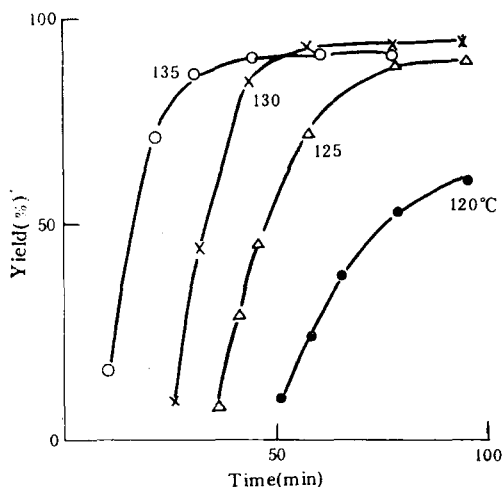


Fig. 1 Plot of the yield of decyltriethoxysilane vs. time at a series of temperature
Conditions: Decene 5.0 mmol, $\text{HSi}(\text{OEt})_3$ 5.0 mmol, S-N-Pt 1.44×10^{-3} mmol of Pt

2. Influence of the amount of S-N-Pt used

The yield of decyltriethoxysilane is about 93% and not sensitive to the variation of the amount of S-N-Pt used from 2.88×10^{-3} to 1.44×10^{-4} mmol of Pt, and the highest turnover number is 32,000 by using the latter amount. It is similar to that of silicone-supported complex. The results are illustrated in Fig. 2.

3. Influence of the kind of olefin on the activity and selectivity of S-N-Pt

Dec-1-ene, dodec-1-ene, allyl phenyl ether, and allyl glycidyl ether are used as substrates to test the catalytic activity and selectivity of S-N-Pt. The differences between S-N-Pt and silicone-supported sulfide-amine

platinum complex are remarkable. The yields of decyltriethoxysilane, dodecyltriethoxysilane, γ -triethoxysilylpropyl phenyl ether, γ -triethoxysilyloxymethyloxirane are 93, 58, 49, and 34%, respectively, as compared with 80, 62, and 75% by using silicone-supported sulfide-amine platinum complex as catalyst. It is obvious that the selectivity bases on the size and polarity of substrate, as the activity of decene is higher than that of dodecene, and the activity of aliphatic olefin is higher than that of unsaturated ether.

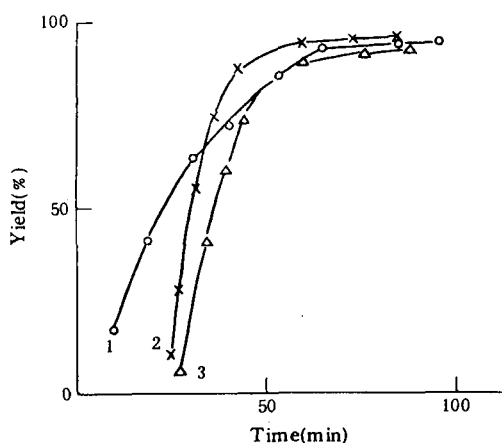


Fig. 2 Plot of the yield of decyltriethoxysilane vs. time with various amount of S-N-Pt at 130°C. The amount of S-N-Pt being used in (1), (2), (3) are 1.44×10^{-4} , 1.44×10^{-3} , and 2.88×10^{-3} mmol of Pt, respectively. Other conditions are the same as given in Fig. 1

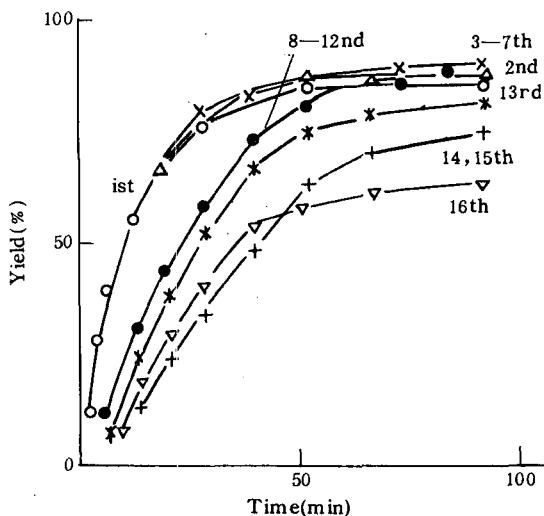


Fig. 3 Plot of the yield of decyltriethoxysilane with 1.44×10^{-3} mmol of Pt at 130°C through different runs. (○) 1st; (△) 2nd; (×) 3-7th; (●) 8-12nd; (*) 13rd; (+) 14, 15th; (▽) 16th

4. Recovery and reuse of the platinum complex

Decene is used as substrate to test the recovery and reuse properties of platinum complex. S-N-Pt can be used sixteen runs, and the yield of decyltriethoxysilane is unchanged in the region of error at first to twelfth run. However, the induction period becomes longer gradually. It is worthy to note that the silicone-supported catalyst can be used five runs only, and the yield of adduct decreases remarkably at the fifth run. This can be ascribed to the stronger complexation ability of NCEP, as compared with that of silylanized silica carrier. The results of S-N-Pt being repeatedly used are shown in Fig. 3.

Keywords:

Crown ether; Crown ether polymer; Platinum complex; Hydrosilylation catalyst

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