Synthesis and Transport Properties of Thin Film Composite Membranes. I. Synthesis of Poly(phenylene Oxide) Polymer and Its Sulfonation

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Synopsis

The synthesis of sulfonated poly(phenylene oxide) polymer was investigated. The poly(phenylene oxide) was synthesized through oxidative coupling from 2,6-dimethyl-phenol with copper (I) chloride-pyridine catalyst and sulfonated using chlorosulfonic acid. The effects of catalyst concentration, solvent, and other experimental variables on the kinetics of the polymerization of poly(phenylene oxide) and its subsequent sulfonation are reported in detail.

INTRODUCTION

The present series of papers is concerned with the synthesis and transport properties of sulfonated poly(phenylene oxide) thin film composite membranes for reverse osmosis applications. Part I deals with the synthesis of sulfonated poly(phenylene oxide) (SPPO) polymer while Part II will deal with the preparation of thin film composite membranes of sulfonated poly(phenylene oxide) (SPPO)–polysulfone (PS) (SPPO–PS) membranes and its applications for the purification of Alberta tar sands waste waters using reverse osmosis.

During the past few years considerable progress has been made in the development of thin film composite membranes of various polymers and their development has been described in detail in an article by Cadotte and Petersen[1] in 1981. The synthesis of poly(phenylene oxide) and its sulfonation has been described in a report to the Office of Saline Water Research and Development in 1971 by Chludzinski et al.[2] of the General Electric Co., while some properties of sulfonated poly(phenylene oxide) membrane systems have been reported by LaConti.[3] Huang et al. have recently reported work on ionically crosslinked poly(acrylic acid) composite thin film membranes cast onto a porous polysulfone substrate.[4]
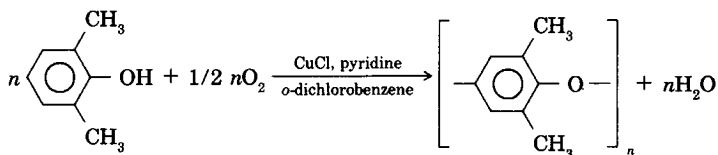
EXPERIMENTAL

Materials

2,6-Dimethylphenol (Gold Label, 99.8% purity), copper(I) chloride (Purified Grade, 99% purity) and o-dichlorobenzene (99% purity) were obtained from Aldrich Chemicals. Chlorosulfonic acid (practical grade), anhydrous magnesium sulfate (Baker Analytical Reagent Grade, 99.4% purity) and chloroform (Baker Analytical Reagent Grade, 99.2% purity) were obtained

from J. T. Baker Chemicals. Pyridine (Fisher Certified Reagent, 99% purity) was from Fisher Scientific. The oxygen used was high purity, 99.6% supplied by Union Carbide Ltd., while the polysulfone (MW = 30,000) was obtained from Polyscience Inc.

Experimental Procedures

The intrinsic viscosity of the PPO polymer was measured using a Ubbelohde viscometer and the ion exchange capacity (IEC) of hydrogen form SPPO polymer was obtained using the acid–base back titration method. Infrared spectra were determined by a Perkin-Elmer Model 337 Infrared Spectrophotometer. Thermal analyses of polymers were carried out by Perkin-Elmer Differential Scanning Calorimeter (Model DSC-4) and thermogravimetric analyzer (Model TGS-2).

Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) from 2,6-Dimethylphenol Using CuCl–Pyridine–O_2[6-11]

$$n \underset{CH_3}{\overset{CH_3}{\bigcirc}}\!\!-OH + 1/2\, nO_2 \xrightarrow[\text{o-dichlorobenzene}]{\text{CuCl, pyridine}} \left[-\underset{CH_3}{\overset{CH_3}{\bigcirc}}\!\!-O- \right]_n + nH_2O$$
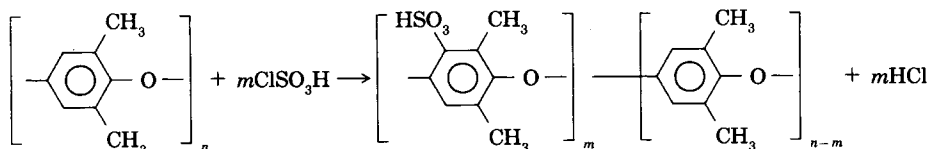
The oxidative condensation polymerization was carried out in a closed system at constant temperature of 20°C permitting quantitative measurement of the rate and extent of oxygen adsorption. To a 100-mL two-necked flask with a magnetic stirrer connected to an oxygen buret, filled with o-dichlorobenzene, were added o-dichlorobenzene as solvent, finely divided copper (I) chloride and pyridine as catalysts, and 602 mg of anhydrous magnesium sulfate as drying agent (solution volume 15 mL). After flushing the system with oxygen, the mixture was preoxidized by rapid stirring under oxygen for 30–60 min to give a dark green solution. At this point (zero time) the monomer 2,6-dimethylphenol in o-dichlorobenzene solvent (solution volume 10 mL) in a funnel was added in quickly (total reactant volume 25 mL), with rapid and constant stirring, and the absorption of oxygen at atmospheric pressure was recorded as a function of time. The reaction was continued in each case until absorption of oxygen ceased, and allowed for an additional 30 min. During the reaction, the color of the reaction mixture was changed from dark green, through yellow and orange, to brown.

After polymerization, 75 mL of methanol acidified with 1 vol % conc. HCl, an excess relative to the copper salt, was added to the reaction mixture, a procedure which deactivated the catalyst. The precipitated polymer was filtered off on a tared sintered glass funnel and washed with additional acidified methanol. After the crude polymer was dried superficially under vacuum, it was reprecipitated from solution in 20 mL of benzene by adding 80 ml of acidified methanol. After refiltering and rewashing with deionized

water and acidified methanol, the polymer was dried at 1 mm Hg vacuum at 65°C for 24 h and weighed.

Sulfonation of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)[5,12]

$$\left[-\!\!\left\langle \bigcirc \right\rangle\!\!\overset{CH_3}{\underset{CH_3}{}}\!\!- O- \right]_n + m ClSO_3H \rightarrow \left[-\!\!\left\langle \bigcirc \right\rangle\!\!\overset{HSO_3 \quad CH_3}{\underset{CH_3}{}}\!\!- O- \right]_m \!\!-\!\! \left[-\!\!\left\langle \bigcirc \right\rangle\!\!\overset{CH_3}{\underset{CH_3}{}}\!\!- O- \right]_{n-m} + m HCl$$

Commercial grade poly(phenylene oxide) (PPO) powder was used to make SPPO. The specification of PPO was: electrical grade, lot No. 691-111, intrinsic viscosity in chloroform = 0.45 (30°C) = 0.51 (25°C) obtained from the General Electric Co. The sulfonation was carried out in a chloroform solvent system at ambient conditions using chlorosulfonic acid as the sulfonating agent. The sulfonation step had to be controlled so that the small quantity of sulfonable material (ethanol and water) in chloroform used as a solvent for PPO was determined and removed prior to PPO sulfonation by neutralization with chlorosulfonic acid. The PPO was then added to the neutralized chloroform and dissolved by stirring for about 30 min at room temperature to form a 3–6 wt % solution. Finally the proper amount of chlorosulfonic acid was introduced via an additional funnel over a period of 20 min while the solution was stirred vigorously to sulfonate the PPO to the desired ion exchange capacity (IEC) and allowed to react for an additional 30 min at room temperature. The precipitated polymer was separated, and the liquid was discarded. The polymer was dissolved in methanol. The solution was poured into a Pyrex glass tray forming a film of about 1–2 mm thickness, and allowed to dry in air for 24 h at room temperature. The dried polymer sheet was then shredded into pieces of about 2 mm particle size and washed with deionized water until the wash water showed no sulfate or chloride and had a pH above 4. This hydrogen form SPPO was filtered, spread out, and air-dried. If the polymer was desired in the sodium form, it was treated with 0.1N NaOH, filtered, washed with deionized water, and air-dried.

Kinetics of the Sulfonation of Poly(phenylene Oxide)

2.4 g (0.02 mol) of PPO was added to the 50 mL of neutralized chloroform with chlorosulfonic acid and dissolved by stirring for 1 h at constant temperature 20°C. At this point (zero time), 2.33 g (1.33 mL, 0.02 mol) of chlorosulfonic acid in 1:1 chloroform/methanol solvent (solution volume 50 mL) in an additional funnel was added quickly (total reactant volume 100 mL) with vigorous stirring. At the proper time, the sulfonation was killed by addition of 100 mL of deionized water. To check the excess amount of neutralizing chlorosulfonic acid which could sulfonate PPO into SPPO, the PPO solution was also killed at zero time before adding chlorosulfonic acid solution as a blank test. The precipitated polymer was separated and the liquid was discarded. The purification and drying procedures were identical

to the sulfonation procedure of PPO. From the ion exchange capacity (IEC) measurement with $0.1N$ NaOH back titration for dried SPPO polymer, the conversion of PPO repeating units into SPPO was calculated, and the concentrations of PPO, SPPO, and chlorosulfonic acid were calculated from the conversion.

RESULTS AND DISCUSSION

Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)

The particular system chosen for the preparation of poly(2,6-dimethyl-1,4-phenylene oxide) was the oxidative condensation polymerization of 2,6-dimethylphenol in o-dichlorobenzene solvent under oxygen gas at atmospheric pressure, using catalysts complexes derived from copper (I) chloride and pyridine, although there were many other methods,[6] since this method showed rapid oxidation rate, high yield, inexpensive raw material, and easy intrinsic viscosity control.

In Figure 1, a plot of oxygen consumption vs. time was a straight line for most of the course of the reaction, usually with a short induction period. It was thus convenient to record the rate of reaction simply as the rate of oxygen consumption.

It was shown earlier[7,8] that the ratio of ligand pyridine to copper is an important factor influencing the rate and course of oxidative coupling of 2,6-dimethylphenol. Our data on such a study in o-dichlorobenzene are summarized in Table I. As shown in Figure 2, they indicated a maximum rate at a ligand pyridine to copper mole ratio of 100. The earlier studies reported a maximum at a ratio of 100 in o-dichlorobenzene[8] and 15–30 in nitrobenzene.[7]

In Figure 3, the dependence of the intrinsic viscosity of PPO on the ligand pyridine to copper mole ratio is given, showing that the intrinsic viscosity increased with increasing ligand ratio at constant copper (I) chloride con-
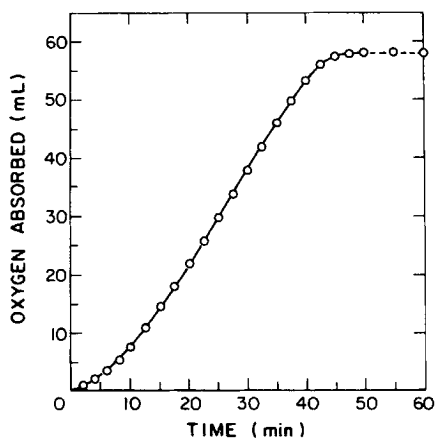

Fig. 1. Oxidation of 2,6-dimethylphenol $0.2M$ in the presence of copper (I) chloride $0.005M$, pyridine $0.5M$, and anhydrous magnesium sulfate $0.2M$ in o-dichlorobenzene solvent (solution volume 25 mL) at 20°C, $p_{0_2} = 1$ atm, batch #17.

TABLE I

Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) by Oxidation of 2,6-Dimethylphenol with Copper–Amine Catalyst[a]

Batch no.	Pyridine (M)	Copper (I) Chloride (M)	Ligand[b] Ratio (N/Cu)	R_{max}[c] $\times 10^3$ (mol/L min)	Oxygen[d] absorbed (%)	Fractional[e] yield ($f_{c\infty}$)	Intrinsic[f] viscosity (dL/g)
3	0.5	0.01	50	4.64	114	0.889	0.56
4	0.25	0.005	50	2.93	109	0.859	0.37
5	1	0.005	200	1.71	83.0	0.910	0.75
6	2	0.005	400	1.86	84.5	0.940	0.79
8	1	0.01	100	4.00	96.4	0.899	0.77
9	2	0.02	100	4.71	97.3	0.940	1.05
10	0.25	0.0025	100	3.57	99.3	0.867	0.34
14	0.75	0.005	150	4.71	98.9	0.905	0.61
15	0.5	0.0025	200	3.29	88.8	0.911	0.35
16	0.5	0.02	25	4.00	96.6	0.932	0.52
17	0.5	0.005	100	5.71	103	0.918	0.49
18	0.375	0.005	75	5.43	101	0.905	0.39
General Electric (Lot No. 691-111)							0.51

[a] 2,6-Dimethylphenol 0.2M, o-dichlorobenzene solvent, anhydrous MgSO₄ 0.2M, total reactant volume 25 mL, 20°C, atmospheric pressure.
[b] Mol pyridine/mol copper (I) chloride.
[c] Maximum rate of oxidation calculated from oxygen absorption.
[d] Ratio to the theoretical oxygen consumption.
[e] Dry weight ratio of the isolated PPO to the theoretical value.
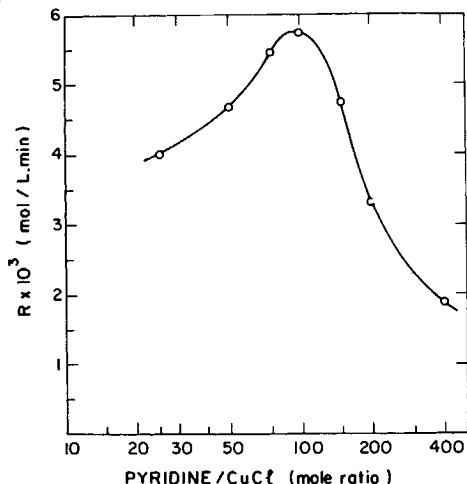[f] In chloroform solvent at 25°C.

Fig. 2. Dependence of maximum rate of oxygen absorption on the ligand ratio, copper (I) chloride 0.0025–0.02M, pyridine 0.375–2M, 2,6-dimethylphenol 0.2M, and anhydrous magnesium sulfate 0.2M in o-dichlorobenzene solvent (solution volume 25 mL), 20°C, p_{O_2} = 1 atm.

centration and decreased with increasing ligand ratio at constant pyridine concentration. This means intrinsic viscosity increased with increasing catalyst concentration as shown in Figure 4. From the Mark–Houwink–Sakurada equation[13] and the linear relationship between the logarithm of the intrinsic viscosity and logarithm of the catalyst concentration at a fixed ligand ratio 100, the molecular weight of PPO and degree of polymerization were found to be nearly proportional to the catalyst concentration at a fixed ligand ratio.

Sulfonation of Poly(phenylene Oxide)

In order to make good polymer for the membranes, the sulfonation step had to be controlled so that the small quantity of sulfonable material in the chloroform was determined and removed prior to PPO sulfonation by
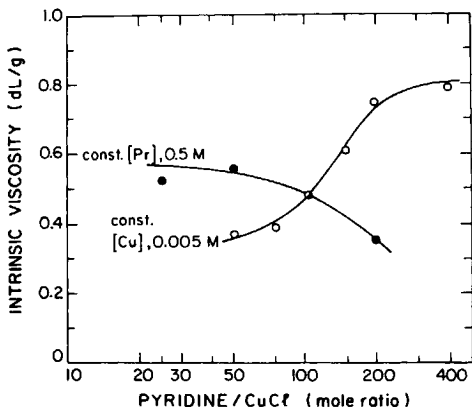

Fig. 3. Dependence of intrinsic viscosity of poly(phenylene oxide) on the ligand ratio, 2,6-dimethylphenol 0.2M, and anhydrous magnesium sulfate 0.2M in o-dichlorobenzene solvent (solution volume 25 mL), 20°C, p_{O_2} = 1 atm.
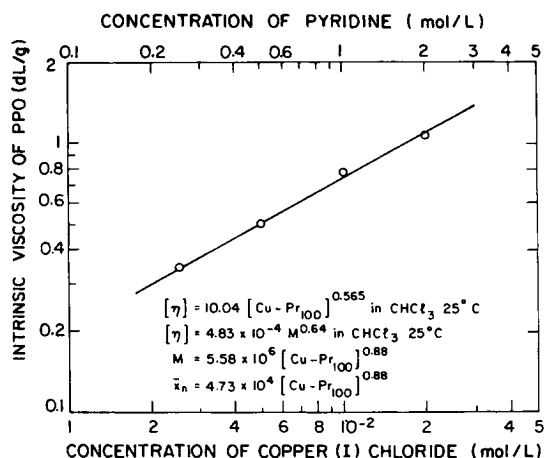
Fig. 4. Effect of changing catalyst concentration on intrinsic viscosity of poly(phenylene oxide) at a fixed ligand ratio (N/Cu = 100), 2,6-dimethylphenol 0.2M, and anhydrous magnesium sulfate 0.2M in o-dichlorobenzene solvent (solution volume 25 mL), 20°C, p_{O_2} = 1 atm.

neutralization with chlorosulfonic acid and finally the proper amount of chlorosulfonic acid was introduced to sulfonate the PPO to the desired IEC value. The results of 12 PPO sulfonating batches during this study are listed in Table II. Generally, targeted IEC was met within about 10%, even though the sulfonable material (ethanol and water) in the chloroform solvent was as high as 0.8 wt %, and the sulfonation step was fairly predictable.

Kinetics of the Sulfonation of Poly(phenylene Oxide)

Since many kinetic studies on the sulfonation of aromatic compounds had led to the conclusion that it is an S_E2 reaction with monomeric SO_3 as the effective reacting species[14] and the irreversible reaction at low tem-

TABLE II
Sulfonation[a] History of Sulfonated Poly(phenylene Oxide)

Sample	PPO[b] (g)	CHCl$_3$[c] (g)	ClSO$_3$H (g)		IEC (meq/g)	
			Neutral	Sulfon.	Targeted	Actual
SPPO-1	10	298	6.03	2.15	1.61	1.72
2	30	447	9.04	9.47	2.23	2.30
3	20	447	9.04	6.41	2.25	2.55
4	30	447	9.04	11.21	2.55	2.58
5	30	447	9.04	11.21	2.55	2.53
6	30	447	9.04	14.09	3.05	2.83
7	30	447	9.04	8.61	2.06	1.85
8	30	447	9.04	9.37	2.21	2.07
9	10	149	3.01	3.38	2.35	2.13
10	10	149	3.01	3.38	2.35	2.39
11	10	149	3.01	2.87	2.06	2.20
12	10	149	3.01	2.55	1.86	2.10

[a] At ambient condition, relative humidity 25–55%.
[b] Intrinsic viscosity in chloroform = 0.45 (30°C) = 0.51 (25°C).
[c] Determined sulfonable material 0.8 wt % (ethanol base).

perature below 100°C,[15,16] the sulfonation of PPO at 20°C was assumed to be irreversible and that the sulfonation rate is proportional to the concentration of the phenylene oxide repeating unit and the concentration of the chlorosulfonic acid:

$$PPO + ClSO_3H \underset{k_r}{\overset{k}{\rightleftharpoons}} SPPO + HCl$$
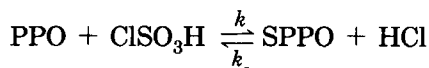
At low temperature, $k_r \simeq 0$

$$\frac{d[SPPO]}{dt} = k[PPO]^m[ClSO_3H]^n$$

Let $[SPPO] \equiv c$, $[PPO] \equiv p = p_0 + c_0 - c$, and $[ClSO_3H] \equiv a = a_0 + c_0 - c$. Assuming $m = n = 1$, we obtain

$$\frac{dc}{dt} = kpa = k(p_0 + c_0 - c)(a_0 + c_0 - c)$$

After integration,

$$\frac{1}{(a_0 - p_0)} \ln\frac{(a_0 + c_0 - c)p_0}{(p_0 + c_0 - c)a_0} = \frac{1}{(a_0 - p_0)} \ln\frac{ap_0}{a_0 p} = kt$$

From the experimental results shown in Table III and Figure 5, this assumption was shown to be correct.

Thermal Analysis of Polymers

From the results of thermal analyses with differential scanning calorimetry (DSC) and thermogravimetry (TG) as shown in Figure 6, the hydrolysis of the hydrogen form polymer was detected starting at 110°C and sodium form SPPO polymer was stable to its decomposition temperature, about 250°C, having lost SO_3. So, the drying temperature of SPPO polymers at 1 mm Hg vacuum was set at room temperature (hydrogen form) and 70°C (sodium form).

Infrared Analysis of Polymers

Infrared spectra were obtained from KBr pellet method (1 wt % PPO) or directly from polymer film samples (0.2 mil SPPOH or SPPONa). As shown in Figure 7, infrared data on the samples of SPPO showed some changes in the structure compare to the PPO. Some peaks, at the frequency of 1070 and 675 cm^{-1}, appeared with sulfonation. These bands are due to the —SO_3^- groups. Another —SO_3^- band at 1200 cm^{-1} overlapped with the aromatic ether band. Some peaks, at the frequency of 1120, 825, 775, and 755 cm^{-1}, disappeared with sulfonation. This suggests that the substitution state of aromatic nuclei is changed from 1,2,4,6 substitution to 1,2,3,4,6 substi-

TABLE III
Calculation for Kinetic Analysis for the Sulfonation of Polyphenylene Oxide) at 20°C

t (s)	CHCl$_3$ (mL)	CH$_3$OH (mL)	IEC (meq/g)	X[a]	[SPPO]≡c (mol/L)	[PPO]≡p (mol/L)	[ClSO$_3$H]≡a (mol/L)	I[b] (L/mol)
Run 1								
$-\infty$	50	0	0	0	0	0.4000	0.2660[c]	
-0	50	0	0.698	0.0887	0.0355	0.3645	0	
0	75	25	0.698	0.0887	0.0177	0.1823	0.2000	0
15	75	25	1.014	0.1324	0.0265	0.1735	0.1913	0.2513
30	75	25	1.339	0.1800	0.0360	0.1640	0.1817	0.5540
45	75	25	1.546	0.2117	0.0423	0.1577	0.1754	0.7748
60	75	25	1.786	0.2500	0.0500	0.1500	0.1677	1.0652
120	75	25	2.422	0.3605	0.0721	0.1279	0.1456	2.0860
Run 2								
$-\infty$	50	0	0	0	0	0.4000	0.2660[d]	
-0	50	0	0.477	0.0595	0.0238	0.3762	0	
0	75	25	0.477	0.0595	0.0119	0.1881	0.2000	0
15	75	25	0.888	0.1147	0.0229	0.1771	0.1890	0.3112
30	75	25	1.170	0.1549	0.0310	0.1690	0.1809	0.5625
45	75	25	1.449	0.1967	0.0393	0.1607	0.1726	0.8497
60	75	25	1.703	0.2366	0.0473	0.1527	0.1646	1.1520
120	75	25	2.415	0.3579	0.0716	0.1284	0.1403	2.2921

[a] Mol SO$_3$H/mol repeating unit (conversion).
[b] $I \equiv (a_0 - p_0)^{-1} \cdot \ln(ap_0/a_0p) = kt$ from integrating $dc/dt = kpa$.
[c] Neutralization of CHCl$_3$; 0.2305 mol/L, sulfonation of PPO; 0.0355 mol/L.
[d] Neutralization of CHCl$_3$; 0.2422 mol/L, sulfonation of PPO; 0.0238 mol/L.
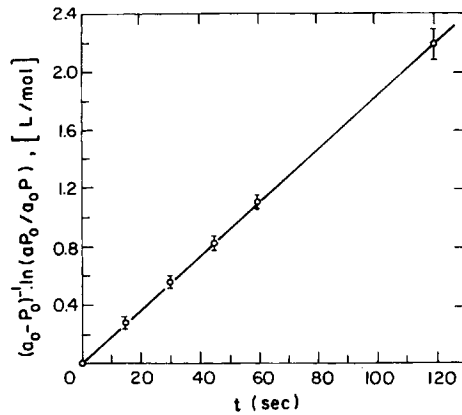
Fig. 5. Result of kinetic analysis for the sulfonation of poly(phenylene oxide) at 20°C.

tution by sulfonation. There was no difference between the hydrogen and sodium forms of sulfonated polymer.

CONCLUSIONS

The molecular weight of PPO and degree of polymerization were found to be proportional to the catalyst concentration at a fixed ligand ratio. The sulfonation rate of PPO was proportional to the concentration of the phenylene repeating unit and concentration of chlorosulfonic acid.
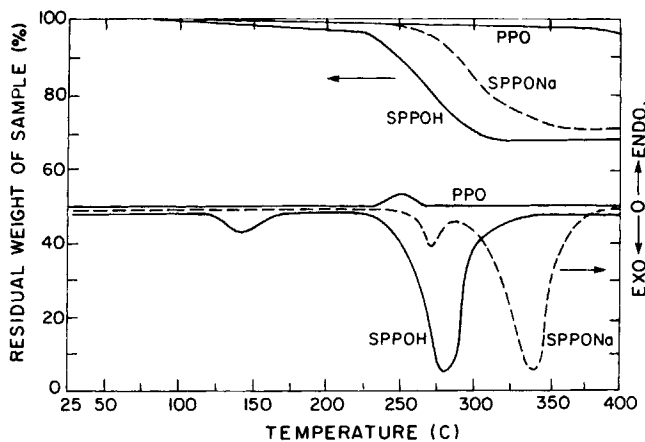
Fig. 6. Thermogravimetry and differential scanning calorimetry of poly(phenylene oxide) and sulfonated polymers in helium atmosphere.
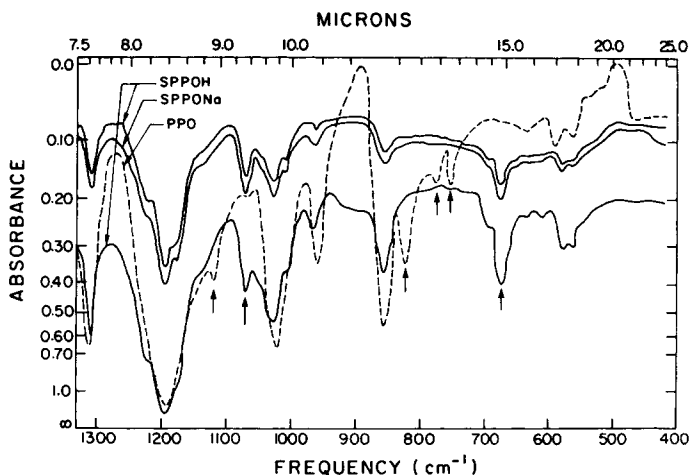
Fig. 7.   Infrared spectra of poly(phenylene oxide) and sulfonated polymers.

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