Synthesis, characterization, and application of nanoporous materials based on silicon- or halogen-containing spiroketal and spirothioketal polymers

Hamada Hamada ABDEL-RAZIK

Chemistry Department, Faculty of Science, Mansoura University,
New Damietta 34517, EGYPT
e-mail: hamada600@yahoo.co.uk

Organic microporous materials based on silicon-containing spiroketal and spirothioketal polymers were synthesized via a 1,3-dioxol-forming polymerization reaction between 1,1a,4,4a,5,5a,8,8a-octahydro-2,3,6,7-tetra(trimethylsilyl)-9,10-anthraquinone and different types of polyol or polythiol. These silicon-containing polymers were subjected to bromination to yield bromine-containing polymers. The structures of the prepared polymers were confirmed by NMR spectroscopy and molecular mass measurements. Nitrogen adsorption/desorption isotherms of the prepared polymers showed that a large amount of nitrogen was adsorbed at low relative pressure, indicating microporosity. These polymers have BET surface areas in the range of 505-830 $m^2 g^{-1}$. These polymers were determined to be useful for pervaporation separation of phenol/water mixtures.

Key Words: Tetra(trimethylsilyl)-9,10-anthraquinone, spiroketal polymers, nanoporous materials, pervaporation separation.

Introduction

The study of materials that possess voids of molecular dimensions is an area of nanoscience with technological applications. Microporous materials are defined as solids that contain interconnected pores less than 2 nm.[1] The preparation of phthalocyanine-based microporous network polymers from spirocyclic monomers has been reported.[2] Double aromatic nucleophilic substitution offers a general reaction for the preparation of polymers

of intrinsic microporosity from appropriate hydroxylated aromatic monomers and fluorinated (or chlorinated) aromatic monomers.[3] A polymer membrane with intrinsic microporosity was tested for the removal of organic compounds from aqueous solution by pervaporation.[4] The diaminomaleonitrile-functionalized polystyrene graft membrane was determined to be useful for pervaporation separation of phenol/water mixtures.[5] Ultra-high free-volume poly(1-trimethylsilyl-1-propyne) was studied and used for membrane applications.[6−8] In this context, organic microporous materials based on silicon- or bromine-containing spiroketal and spirothioketal polymers were synthesized and studied for use in pervaporation separation.
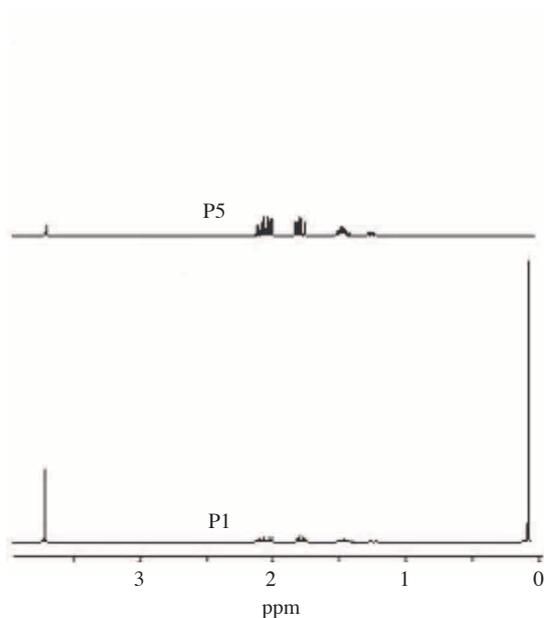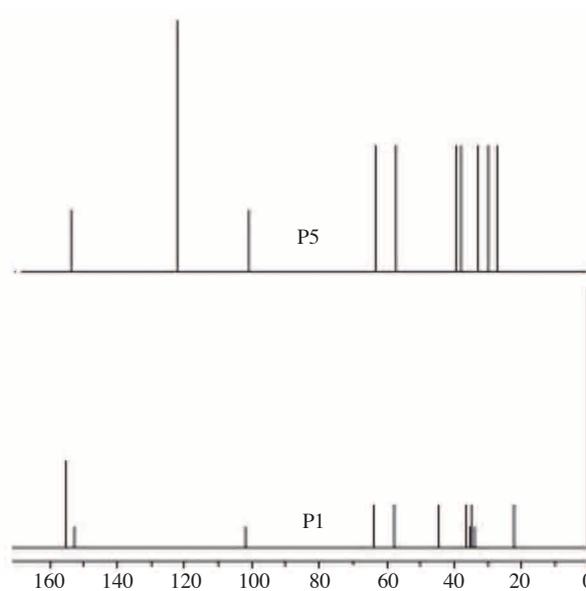

Figure 1. ^{1}H NMR spectra of P1 and P5.

Figure 2. ^{13}C NMR spectra of P1 and P5.

Experimental

Characterization

^{1}H-NMR and ^{13}C-NMR spectra were obtained with the use of a Varian Gemini 200 instrument at 200 MHz and 50.3 MHz, respectively. Molecular mass (number average [Mn], weight average [Mw]) was determined by gel permeation chromatography (GPC) (Polymer Laboratories, PL-GPC 20) using dilute polymer solutions (10 mg 5 mL^{-1}) in THF at room temperature at the rate of 1 mL min^{-1}. BET multi-point calculations derived from low-temperature (77 K) nitrogen adsorption/desorption isotherms were made using a Coulter SA 3100 surface analyzer. Samples were degassed for 1 day at 70 °C under high vacuum prior to analysis.

Preparation of membranes

The dried polymers were dissolved in THF. The membranes were made by pouring 20 mL of 4% (wt/vol) polymer/THF solution onto a clean and smooth glass plate, and then the solvent was allowed to evaporate at 60 °C for 3 days.

Pervaporation separation

Pervaporation separation[9] is a membrane process in which the feed is a liquid mixture and a vacuum is applied to the opposite side of the membrane to remove permeate as a vapor, which is then condensed and collected. Phenol/water mixtures (0.2, 0.4, and 0.6 wt % phenol) were used as feed solutions. The feed-side was maintained at 25 °C. The pressure at the downstream side was maintained at ~ 1 mmHg by means of a vacuum pump. The feed and the permeate compositions were analyzed by measuring their refractive indexes at 25 °C.

Preparation of silicon-containing spiroketal polymers (P1, P3) by reaction of compound 1 with polyol (2a, 3a)[10]

A mixture of 0.01 mol of polyol (**2a**, 1.36 g or **3a**, 1.96 g) derivative, 0.01 mol of **1** (5.0477 g), and 0.1 g of p-toluenesulfonic acid (as a catalyst) was heated under reflux with stirring in 100 mL of benzene for 3 h. The mixture was cooled to room temperature and allowed to stand overnight. The precipitate was collected by filtration, washed several times with ethanol, and air dried. The polymer was soluble in chloroform, toluene, and THF. For **P1**, ^{1}H-NMR (CDCl$_3$): 2.10, 1.96, 1.46 (CH); 2.04, 1.79, 1.49, 1.24, 3.72 (CH$_2$); 0.08 (CH$_3$). ^{13}C-NMR (CDCl$_3$): 44.6, 36.4 (CH), 64.1, 57.7, 35.3, 34.7, 22.3 (CH$_2$), 155.3, 152.9, 101.9, 33.9 (C), 0.6 (CH$_3$).

Preparation of silicon-containing spirothioketal polymers (P2, P4) by reaction of compound 1 with polythiol (2b, 3b)[10]

A mixture of 0.01 mol of polythiol derivative (**2b**, 2.001 g or **3b**, 2.601 g), 0.01 mol of **1** (5.0477 g), and 4 g of purified dioxane was cooled in an ice bath, and hydrogen chloride gas was introduced. As the mixture warmed to room temperature a polymeric spirothioketal precipitated, which was collected by filtration, washed with ethanol, and air dried. The polymer was soluble in chloroform, toluene, and THF.

Preparation of bromine-containing spiroketal polymers P5-P8

A mixture of 0.25 mmol of polymer **P1-P4** and 0.50 mmol of pyridine was dissolved in THF (75 mL). The mixture was cooled in an ice bath. Then, 1 mmol of bromine was added and the solution was stirred for 3 h at room temperature. The mixture was diluted with ether, washed with saturated Na$_2$S$_2$O$_3$ and saturated NaHCO$_3$, and dried using MgSO$_4$. Evaporation gave a white solid. The polymer was soluble in chloroform and THF. For **P5**, ^{1}H-NMR (CDCl$_3$): 2.09, 1.97, 1.46 (CH); 2.05, 1.78, 1.49, 1.25, 3.73 (CH$_2$). ^{13}C-NMR (CDCl$_3$): 44.6, 36.4 (CH), 64.1, 57.7, 35.3, 34.7, 22.3 (CH$_2$), 155.3, 152.9, 101.9, 33.9 (C).

Results and discussion

1,1a,4,4a,5,5a,8,8a-Octahydro-2,3,6,7-tetra(trimethylsilyl)-9,10-anthraquinone (**1**) was prepared through a Diels-Alder reaction between 2,3-bis(trimethylsilyl)buta-1,3-diene and benzoquinone in benzene at 60 °C in the presence of quinol, as previously described.[11,12] Compound **1** reacted with **2a** (pentaerythritol) to yield silicon-containing spiroketal polymer **P1**. Upon the treatment of **1** with **2b** (pentaerythritol tetrathiol), silicon-

containing spirothioketal polymer **P2** was produced. The same procedure for the preparation of **P1** and **P2** was applied to produce the polymers **P3** and **P4** via the reaction of **1** with polyol **3a** and polythiol **3b**, respectively (Scheme 1, see Experimental). The synthesized polymers **P1-P4** were subjected to bromination to yield bromine-containing polymers **P5-P8** (Scheme 2, see Experimental).

Scheme 1

Scheme 2
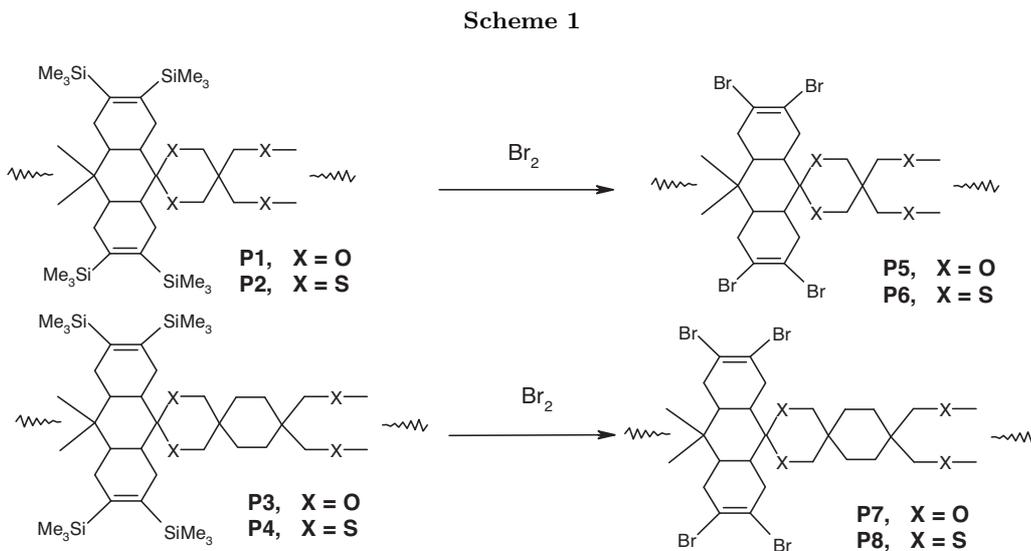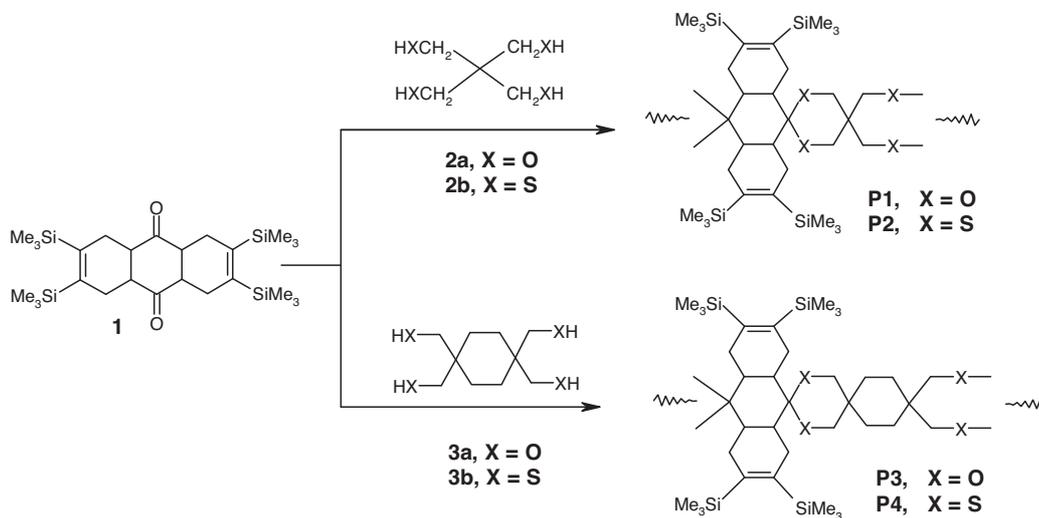
The ^{1}H-NMR spectra of silicon-containing polymer **P1** and bromine-containing polymer **P5** had the same peaks, with very little change in the chemical shift values; however, there was an extra peak at 0.08 ppm assigned to the methyl protons in **P1** (Figure 1). Additionally, ^{13}C-NMR spectra, which gave the same characteristic chemical shifts of the carbon atoms in **P1** and **P5**, revealed an extra peak at 0.6 assigned to the methyl carbon in **P1** (Figure 2).

Molecular masses of the synthesized polymers (Table) were of high molecular mass, which confirms the efficiency of the 1,3-dioxol-forming polymerization reaction. The high molar mass and good solubility of these

polymers allow conventional solution-based polymer processing techniques.

The ability to introduce highly polar functional groups without compromising microporosity is an important feature of the porous polymers and will allow, with greater permeability, the further design of selective polymers for separation techniques.

The spirocenter (i.e. a single tetrahedral carbon atom shared by 2 rings) provides a nonlinear shape and prevents close packing of the chains, giving an amorphous structure. The needed rigidity of these polymers is attributed to the fused rings. The lack of rotational freedom along the polymer back-bone ensures that the macromolecules cannot rearrange their conformation to collapse the open structure of the material. The bulky trimethylsilyl groups in silicon-containing polymers **P1-P4** cause the polymer chains to twist. These twisted, inflexible polymer chains trap a considerable amount of excess free volume elements, which are connected to give a micropore structure.[13]

Table. Yield, melting point, number average molecular masses (Mn), weight average molecular masses (Mw), and BET surface area of the prepared polymers.

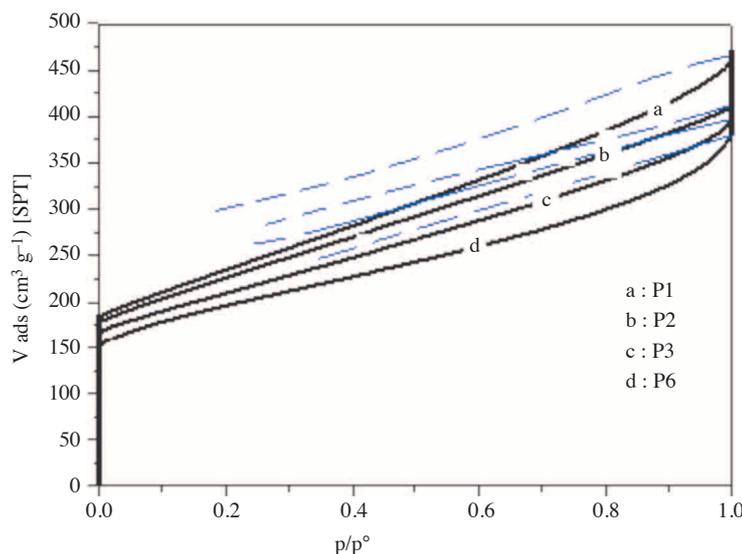| Sample	Yield (%)	mp (°C)	Mn (g mol^{-1})	Mw (g mol^{-1})	Surface area (m^{2}g^{-1})
P1	88	177-179	42,480	170,820	830
P2	93	168-169	38,130	160,970	826
P3	87	154-155	38,860	154,350	823
P4	91	130-131	40,730	158,630	818
P5	86	139-140	39,300	155,470	535
P6	84	144-145	38,260	161,730	505
P7	79	163-164	37,445	156,340	508
P8	83	127-128	36,260	144,290	522

Figure 3. Nitrogen adsorption/desorption isotherms for silicon-containing polymers P1-P4 (i.e. the volume of nitrogen adsobed versus relative pressure). The dotted line is the desorption plot.

Nitrogen adsorption/desorption isotherms of the silicon-containing polymers (Figure 3) show that a large amount of nitrogen was adsorbed at low relative pressure, indicating microporosity. The BET surface areas in the range of 505 to 830 $m^2 g^{-1}$ can be calculated from the isotherms (Figures 3 and 4).
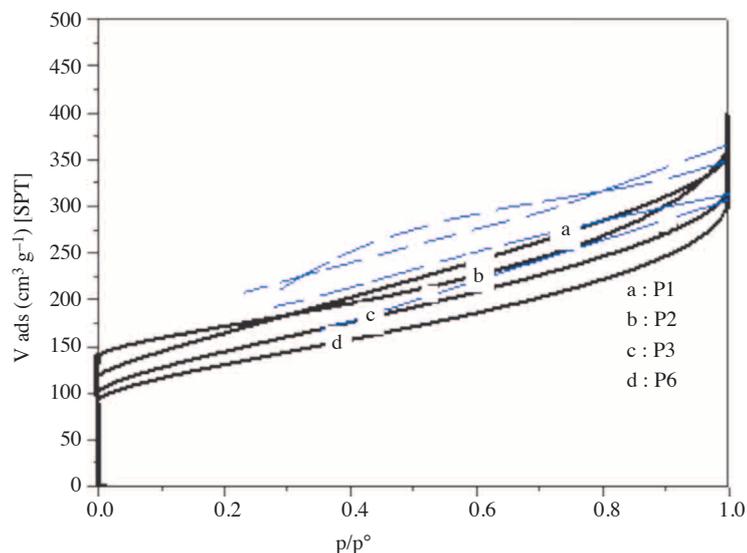

Figure 4. Nitrogen adsorption/desorption isotherms for halogen-containing polymers P5-P8 (i.e. the volume of nitrogen adsobed versus relative pressure). The dotted line is the desorption plot.
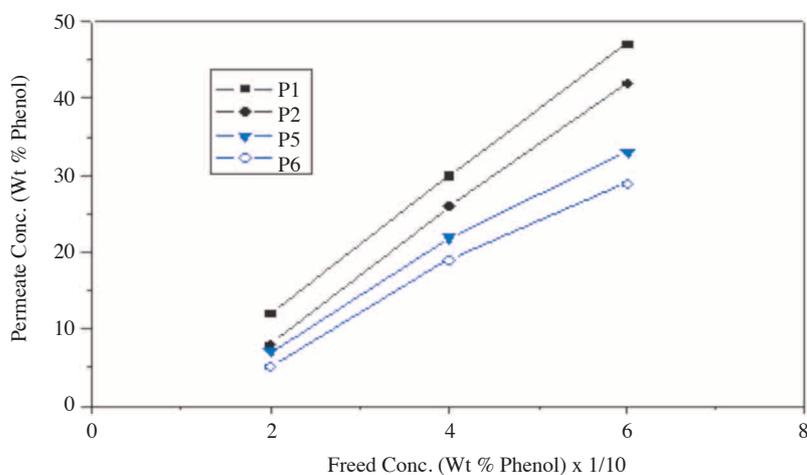

Figure 5. Pervaporation-based separation of phenol from aqueous solution using a memberane derived from silicon containing (P1,P2) and halogen containing (P5,P6) polymers.

Potential application of the microporous polymer membrane

Pervaporation-based separation of phenol from aqueous solution using a membrane derived from the prepared silicon-containing polymers and their corresponding halogen-containing polymers at 25 °C is illustrated in

Figures 5 and 6. In the case of silicon-containing polymer **P1** the permeate was enriched in the organic component (e.g. a feed of 0.6 wt % phenol in water gave a permeate of 47 wt % phenol, which demonstrates that the membrane is selective for organic compounds over water). Figures 5 and 6 show that there was high separation efficiency for membranes derived from silicon-containing polymers, indicating high microporosity, as compared with halogen-containing polymers. This separation process is of environmental importance, as phenols are common contaminants in wastewater streams from industrial processes. In this case the transport mechanism, such as sorption onto pore walls, in addition to surface diffusion occurs and a large, strongly adsorbing species can inhibit transport of a smaller molecule with weaker interactions.[14]
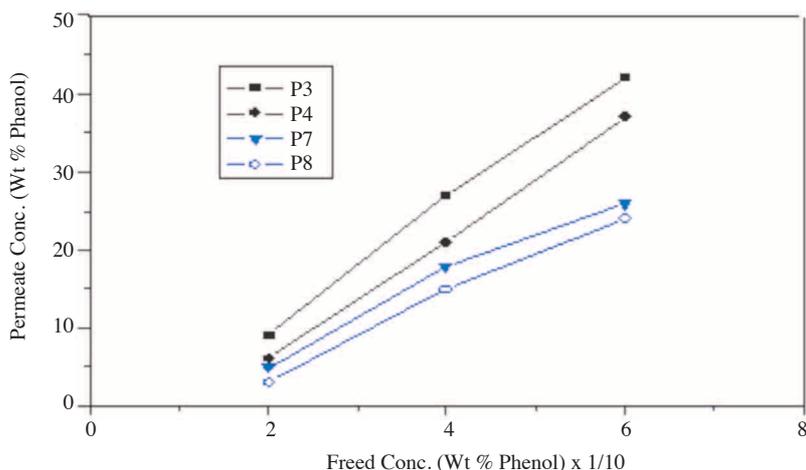

Figure 6. Pervaporation-based separation of phenol from aqueous solution using a memberane derived from silicon containing (P3,P4) and halogen containing (P7,P8) polymers.

References

1. Schth, F.; Sing, K.; Weitkamp, J. *In Handbook of Porous Solids*; Eds.: Schth, F.; Sing, K.; Weitkamp, J.; Wiley-VCH, Berlin, *Vol. 1-5*, 2002.

2. McKeown, N. B.; Budd, P. M.; Msayib, K. J.; Ghanem, B. S.; Kingston, H. J.; Tattershall, C. E.; Makhseed, S.; Reynolds, K. J.; Fritsch, D. *Chem.Eur. J.* **2005**, *11*, 2610-2620.

3. Budd, P. M.; Ghanem, B. S.; Msayib, K. J.; McKeown, N. B.; Tattershall, C. E. *J. Mater. Chem.* **2003**, *13*, 2721-2726.

4. Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D. *Adv. Mater.* **2004**, *16*, 456-459.

5. Abdel-Razik, H. H. *Chem. Pap.* **2008**, *62 (4)*, 404-409.

6. Yu, A.; Yampolskii, Y.; Shantarovich, V. P.; Nemser S. M.; Plate, N. A. *J. Membr. Sci.* **1997**, *126*, 123-132.

7. Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473-7475.

8. Nagai, K.; Masuda, T.; Nakagawa, T.; Freeman, B. D.; Pinnau, I. *Prog. Polym. Sci.* **2001**, *26*, 721-795.

9. Khayet, M.; Nasef, M. M.; Mengual, J. I. *J. Membr. Sci.* **2005**, *263*, 77-95.

10. Sandler, S. R.; Karo, W. *Polymer syntheses*; Academic press Inc., London, *Vol. 2*, 196, **1977**.

11. Garrat, A.; Tsotins, A. *Tetrahedron Lett.* **1986**, *27*, 2761-2762.

12. Batt, D. G.; Ganem, B. *Tetrahedron Lett.* **1978**, *19*, 3323-3324.

13. Srinivasan, R.; Auvil, S. R.; Burban, P. M. *J. Membr. Sci.* **1994**, *86*, 67-86.

14. Pinnau, I.; Toy, L. G. *J. Membr. Sci.* **1996**, *109*, 125-133.