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Notes

Some Aspects of Highly Cross-Linked Polymers: Condensation Product of Carbon Tetrabromide and Biphenol

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In recent years reactive polymers have emerged as new important materials because of their various important end uses such as ion exchangers,[1-4] selective metal chelating agents,[5,6] adsorbents[7,8] for trace analysis of organic volatile compounds, selective[9,10] and stereoselective reagents, catalysts, and many others. Some of these reactive polymers are macroporous, selective macromolecules with built-in reactive functionalities. The macroporosity and its dimensional stability are introduced by means of controlled three-dimensional cross-linking, which also provides the maximum possible accessibility of the reactive functional groups to any chemical environment. With proper design of the polymeric cross-link network, it may be possible to synthesize new polymers having characteristics very similar to those of the crystalline aluminosilicates and their phosphorous and boron analogues, commonly known as molecular sieve systems.

These crystalline aluminosilicates and their B or P analogues have two important properties that make them indispensable in modern chemical technology. First, their very regular and well-defined porosity offers sieve action at the molecular level, thus making them useful as selective adsorbents, hence the name molecular sieve. Second, they have protons, which can be exchanged with metal ions. The second characteristic has been successfully reproduced in organic cation-exchange resins, but the molecular sieve action, as yet, has not been simulated in organic polymers.

In this paper we present the synthesis and characteristics of the highly cross-linked condensate of CBr_4 and 4,4′-biphenol with a specific aim to simulate molecular sieve action in the polymer. Possible variations in the reactions and the probable properties and applications envisaged with these product polymers are also highlighted.

Experimental Section

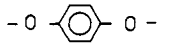
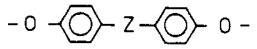
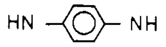
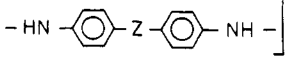
CBr_4 (Riedel de Haen, 99.5%), 4-4′-biphenol (Buffalo Color Chem. Corp., USA), and nitrobenzene (AnalaR, BDH, UK) were used for synthesis. All other chemicals and reagents used were of analytical grade and were subjected to purification before use.

Polymer Synthesis. Condensations between CBr_4 and dry sodium biphenolate in a stoichiometric proportion of 1:2, respectively, were carried out under pressure under a nitrogen atmosphere using nitrobenzene as the reaction medium. The hard black lump of the condensation product was crushed in a mortar and subjected to repeated extraction first with refluxing ethanol and then with refluxing water. Finally it was dried in a vacuum oven.

Characterization. Chemical identity of the polymer was ascertained by IR spectra and elemental analysis. It was characterized with respect to surface area (BET method), crystallinity (X-ray diffractometer, DORN-I, USSR), porosity and pore-size distribution (mercury porosimetry), and thermal stability (DTA, Stanton Redcroft).

Table I
Some Representative Combinations of X, Y, R, and M

X = -Cl, -Br, -I M = C, Si, Sn

R =	Y =
 	Li, Na, K
 	H
$-C\equiv C-$ $-C\equiv C-C\equiv C-$	Ag, Cu Na, K

Z =
nil, O, S
CO, SO
SO_2, CH_2

Results and Discussion

Polymer Synthesis. Condensation between CBr_4 and dry sodium biphenolate was carried out according to the equation

$$nCBr_4 + 2nNaOC_6H_4C_6H_4ONa \xrightarrow{-4nNaBr} -[OC_6H_4C_6H_4O\overset{|}{\underset{|}{C}}OC_6H_4C_6H_4O]_n- \quad (1)$$

Many variations in the above reaction are possible which may be represented by a generalized equation

$$nMX_4 + 2nYRY \xrightarrow{-4nXY} -[R\overset{|}{\underset{|}{M}}R]_n- \qquad (2)$$

where X stands for any active leaving group like Cl, Br, I, etc. Y is an active atom like H, Na, K, Ag, etc., and R may be a rigid moiety derived from biphenols, diamines, diacetylenes etc., with or without any active functionalities which are unreactive to either X or Y. M represents a tetravalent atom like C, Si, Sn, etc.

Several combinations of different X, Y, or R are shown in Table I.

The reactions of CBr_4 and sodium biphenolate were tried in solid-phase vacuum fusion at 300–350 °C, in refluxing nitrobenzene under atmospheric pressure, and in nitrobenzene medium at 150–250 °C under nitrogen pressure. The best results were obtained in high-pressure synthesis. The optimum conditions were 215 °C, 11 MPa of cold nitrogen, 8 h, and a stoichiometric ratio of the reactants. The corresponding yield was 58% (theory).

The reaction as such is very sluggish as evidenced by poor yield both in the vacuum fusion and in the liquid-phase reaction in nitrobenzene at normal pressure. Both pressure and temperature appeared to have critical roles on the product yield and quality. The critical temperature is about 215 °C. Below this critical temperature the yield is substantially low, presumably because of the limited solubility of sodium bisphenolate in nitrobenzene and/or deposition of the insoluble condensation products on the

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solid biphenolate particles. Above this optimum temperature the product is liable to be decomposed or may enter into unknown chemical reaction with the solvent itself, leading to lower yield or undesired carbonaceous product of indefinite composition.

The critical pressure is about 11 MPa of cold nitrogen. Below this critical pressure the yield was low, indicating that the reaction is favored by higher pressure. Above this critical pressure, the reaction possibly proceeds on very small nuclei of the condensate, the growth of which is restricted only at the surface. The other possibility is a very fast nucleation rate at the beginning of the reaction which offers only a limited supply of the mobile reactants for the growth of the nuclei. Both these possibilities would entail with products of low degree of condensation and are apparently reflected in the poor yield of only 58%.

The observed little improvement in yield with increase in time of reaction is explained on the basis of slow surface reaction on the nuclei and depleted concentration of the reactant due to fast nucleation.

Probable Characteristics of the Polymers. The polymers as would be obtained by reaction 2 are expected to have several unique characteristics. Structurally these polymers would be analogues of diamond in which the C–C bonds (in diamond) are enlarged considerably to rigid M–R–M linkages. This is likely to impart a very highly ordered arrangement of the constituent atoms (which are not generally attainable in known organic polymers), leading to several interesting properties. They would be crystalline, and hard, insoluble even in the most powerful solvents, and resistant to attack even by very reactive reagents. They would offer enhanced thermal stability and would be characterized by a regular and well-defined pore size distribution. Another important property likely to be exhibited by them is action as organic molecular sieves, which is known so far only with inorganic silicates, phosphates, and borates. The inner cavity of the perfect tetrahedral configuration in diamond, though regular and uniform, is too small to accommodate even small molecules or atoms because of a very short C–C single bond length of only 0.154 nm. Because of a considerably increased distance of separation between two M atoms (from MX_4) due to the insertion of the R group, the tetrahedra in the polymer would be voluminous enough to accommodate small molecules like H_2O, NO, NO_2, NH_3, SO_2, CO_2, etc. Larger molecules, however, could not be entrapped. Because of this specific size-exclusion characteristic, these polymers would behave as molecular sieves.

Applications. These highly cross-linked polymers with a predetermined size of the built-in cavities and having reactive functionalities, when deposited on inert supports, would provide column materials for chromatography. These materials are of particular interest to combat air pollution by detecting and estimating organic volatile compounds which are potential health hazards and which are present in air at a parts-per-million level. Some of these micropollutants are HCN, CH_3CHO, CH_3CN, H_2S, SO_2, NO_2, etc. The environment of the tetrahedral cavity in the polymers can be suitably modified by the presence of such groups as O, S, S=O, O=S=O, NH, C=O, C≡C, C=C, etc., in R to offer highly selective adsorption. The size of the tetrahedral cavity can also be enlarged or reduced by proper choice of R.

Further, by the use of disilver (or dicopper) tetraacetylide, it may be possible to synthesize a rigid polymeric analogue of diamond with a localized but labile π-electron cloud within the enlarged tetrahedral cavity. It may be possible also to intercalate such a network with small and highly electropositive metal atoms like Li, Na, etc. This would combine such properties as hardness with desirable semiconducting-to-conducting properties which are totally absent in diamond. In effect, a nonmetallic metal can be synthesized.

Table II
Porosity, Pore Size Distribution, and Surface Area of Biphenol-CBr_4 Condensate

surface area	8.7 m^2/g
true volume	0.3176 cm^3/g
pore volume	0.7572 cm^3/g
porosity	70.4 $cm^3/100\ cm^3$

pore radii, nm	vol %	pore radii, nm	vol %
0.4–6.0	50.4	30–40	2.1
6–10	3.6	40–50	1.5
10–20	5.8	50–75 000	33.1
20–30	3.5		

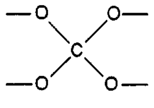
Polymer Characterization. The product polymer was a black, hard solid which was difficult to ground and was insoluble in any sovlent, including concentrated H_2SO_4. Elemental analyses showed the presence of bromine but only in a trace amount. C (79.03%) and H (4.06%) contents agreed well with the calculated values of 79.59 and 3.92%, respectively. IR spectra obtained in a KBr pellet indicated the presence of C–O–C (alkyl–aromatic) with characteristic absorption at 1310 cm^{-1}.

Pore-Size Distribution and Surface Area. The porosity, pore-size distribution, and surface area of the powdered polymer are presented in Table II. The data show that the polymer is more than 70% porous and is in conformity with the predictions made earlier. Further, about 67% of the total porosity is contributed by the pores of narrower dimension, indicating predominant contribution of intraparticle pores. With the assumption of a regular tetrahedral network of the polymer and with a calculated length of 1.08 nm for $COC_6H_4C_6H_4OC$, the predicted pore radius for the tetrahedral cavity is about 0.535 nm. It is heartening to note from the data in Table II that the largest contribution of more than 50% of the total porosity is made by a pore radius of 0.4–6.0 nm, which is again about 75% of the total intraparticle porosity.

Surface area of the polymer, however, is low, only 8.7 m^2/g. A probable explanation for such a low value of surface area is that the flat biphenylene group in biphenol prohibits entry of adsorbent N_2 molecules into the tetrahedral cavity for adsorption or that the adsorption of N_2 at low temperature is very much diffusionally hindered, leading to very slow equilibration and hence an apparently low value of equilibrium adsorption.

Thermal Stability. A representative DTA thermogram of the polymer in air is illustrated in Figure 1. It will be apparent from the TG curve that the polymer retains a substantial amount of moisture, to the extent of about 15% of its weight, which is released before 110 °C. In conformity with the behavior of highly cross-linked polymers, no T_g could be detected in the thermogram. Both DTG and DTA curves indicate a continuous exothermic decomposition of the polymer starting right from 100 °C. However, the decomposition is rather slow upto about 285 °C. Beyond this temperature, the decomposition is very rapid and runs in a nearly explosive manner with a highly exothermic peak at a temperature of about 410 °C.

This unexpectedly poor thermal stability of the polymer perhaps owes its origin to the presence of



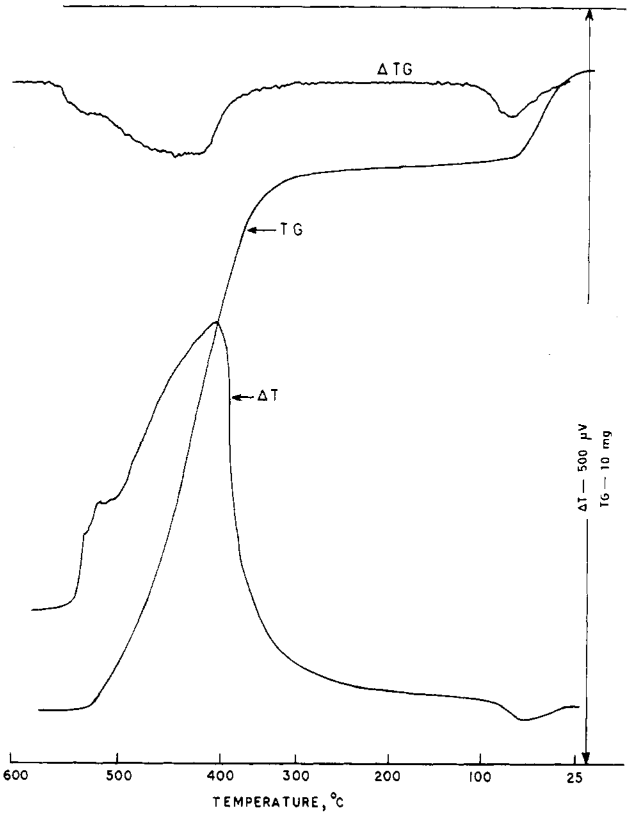


Figure 1. Thermograms of biphenol–CBr_4 condensate.

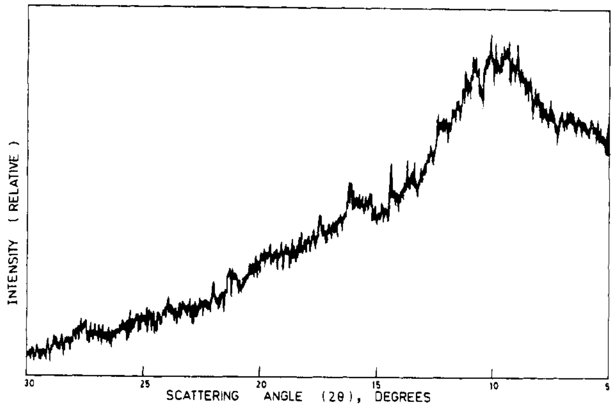


Figure 2. X-ray diffractogram of biphenol–CBr_4 condensate.

groups which, due to four electronegative oxygen atoms, are susceptible to facile oxidative degradation.

X-ray Diffraction. An X-ray diffractogram of the polymer was recorded with Mo Kα 0.071-nm radiation. A typical X-ray diffractograms is illustrated in Figure 2, which has the characteristics of amorphous materials. There are, however, some peaks of low intensity that are not well resolved.

The apparent absence of any well-defined peaks in the diffractogram may be attributed to either of two reasons. First, the polymer was itself obtained in an amorphous form. This is quite likely in view of the facts that the condensation may be incomplete in regard to the formation of closed tetrahedral network and that there may be rotation around the carbon–oxygen–aryl bonds, leading to a large deformation in the structure. The latter could have been minimized by prolonged annealing at a suitable temperature to bring about uniformity in the network. However, in view of the poor thermal stability of the polymer even at lower temperature, (vide thermal stability) no improvement in the diffractogram was observed.

Second, the regular uniform network might have led to a large unit cell dimension and hence to too low an angle of diffraction maximum to be identified in the diffractogram. With the assumption of a perfectly ordered diamond cubic structure of the polymer, a large distance of 1.08 nm for the C–R–C linkages, and a low Mo Kα radiation wavelength of 0.071 nm, the scattering angle (2θ) for the first-order diffraction for a diamond cubic lattice parameter of 2.488 nm works out to be only about 0.2°, which is too low to be detected in the diffractomgram.

It, therefore, remains unresolved, at least from the diffraction pattern, as to whether the polymer is really crystalline.

Concluding Remarks

The proposed scheme of synthesis of a highly cross-linked ordered polymer appears to be applicable in the case of condensation between CBr_4 and disodium biphenolate, although the optimum conditions and the mode of carrying out the reaction are subject to variation depending upon the physical characteristics and reactivity of the component reactants. In the case of CBr_4–biphenol condensate, many of the predicted properties like hardness, solubility characteristics, porosity, and pore size distribution have been attained. However, an ordered structure and high degree of crystallinity in the polymer could not been established unambiguously, and the prediction regarding thermal stability has been totally belied. It is expected that the ambiguity regarding an ordered structure and high degree of crystallinity of the cross-linked polymers can be resolved, and high thermal stability can be ensured by proper choice of the component reactants on the basis of their structures and reactivity. Further investigation in this direction is in progress.

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Registry No. (4,4′-$HOC_6H_4C_6H_4OH{\cdot}2Na$)($CBr_4$) (copolymer), 106989-10-0.

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Scattering from Polyelectrolyte Solutions

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Benmouna et al.[1] have proposed a model for the scattering intensity from a dilute solution of charged macro-

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