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OPEN PORE POLYURETHANE -
A NEW SEPARATION MEDIUM

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Jefferson and Salyer disclosed a unique polyurethane where the mixing of separate solutions of polyurethane precursors, comprised of a polyaryl-polyalkylene polyisocyanate and a polyol, would react and form a precipitate of open pore polyurethane at ambient temperatures.^{1,2} The polymer structure is comprised of agglomerated spherical particles, five to ten microns in diameter, rather than containing interconnected struts left from blown dodecahedral cells as are found in foam products. The material has a high degree of interstitial porosity. The density of the material can be altered by varying the reaction conditions and starting materials to produce a polymer of from 0.1 to 0.5 gram per cubic centimeter. The material is compressible, and for compressions of less than 20%, complete recovery will occur. A variety of interstitial pore sizes can be obtained by varying reaction conditions. Pore sizes ordinarily are <10 microns, which is considerably smaller than the finest foam cells known.

Ross and Jefferson took advantage of the unique characteristics of this polymeric material and made in situ formed chromatographic columns³. The open pore polyurethane (OPP) provides a chromatographic medium or

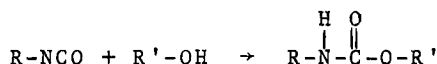
support that readily fills the chromatographic column and adheres tightly to the column wall of most column materials. The adherence of the material to the column considerably reduced channeling effects which are experienced with particulate-type chromatographic supports. OPP provides a medium of controllable density, porosity, and surface characteristics that can be optimized for a specific application. The material is chemically inert to most solvents and can readily be used as a liquid chromatographic support. The very low viscosity of a mixture of the precursor materials facilitates the filling of very complex column configurations of both small diameter (<1 mm I.D.) and large preparative type columns. The polyurethane product has excellent gas flow permeability properties. Stationary phases may be added to this support by incorporating the liquid phase in the precursor chemicals or by adding the stationary phase after the support is formed.⁴ Permanently bonded stationary phases can be added quantitatively by permitting functional groups of the stationary phase to react to the desired number of functional groups exposed on the OPP. This is accomplished by providing excess -OH or -NCO groups by altering the ratio of the two starting chemicals.⁵

Porous polymers have been described and used for chromatographic separations by several researchers in the last decade. Hollis reported the use of porous polyaromatic polymer beads synthesized from styrene with divinylbenzene as a crosslinker to separate gaseous mixtures⁶. Pretorius and Hahn have disclosed chromatographic columns utilizing particles of porous foam rubber⁷. Porous polyethylene was used for gas chromatography by Baum⁸. Foamed polyurethane was disclosed as a column packing material by Van Venrooy in 1967⁹.

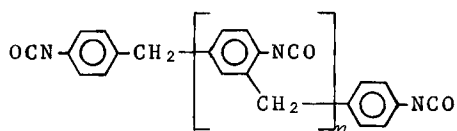
Crowley described the use of polyurethane cellular layers for inducing lateral flow and localized mixing of streams moving through a chromatographic column¹⁰. Schnecks and Bieber described the preparation of gas-solid chromatographic supports with various types of elastomeric and thermoplastic foams by in situ formation.¹¹

SYNTHESIS OF OPEN PORE POLYURETHANE

Polyurethanes are produced by step growth polymerization of polyisocyanates and polyols. The mode of propagation involves the addition of a hydroxy group to an isocyanate to yield a substituted amide ester of carbonic acid, i.e., polyurethane.

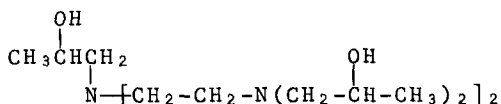


The isocyanate used to form polyurethane has the following general formula:



Two sources of isocyanate have been used in OPP studies: Kaiser Chemical's NCO-10 (manufacture of NCO-10 has been discontinued) and Mobay's Mondur MR. Both sources contain mixtures of 4,4'-diphenylmethane-diisocyanate with lesser amounts of tri-, tetra-, and penta-isocyanates. Special care in storage and handling of this reagent is critical because it reacts with moisture in air and in solvents. The material should be stored in a desiccator and dried continually by adding molecular sieves. The isocyanate should be weighed and diluted in the solvent just prior to use.

The polyol used in the reaction is a pentahydroxy compound resulting from the total oxypropylation of diethylenetriamine.



The tertiary amine backbone present in Union Carbide's LA 475 provides a self-contained catalyst for the polymerization reaction.¹²

The formation of OPP depends upon the relatively slow precipitation of a polyurethane from a quiescent, homogeneous, diluted mixture of the reactants. The following criteria must be considered for satisfactory polymer precipitation: the polyurethane product must be insoluble in the precursor organic solvent, the solvent must be inert to the reactants and product, and polymer formation must not be so rapid as to cause precipitation before quiescence is attained.

The rate of polymerization should be such that gelation occurs no sooner than five minutes. This is to provide adequate time to fill columns and will prevent shrinkage and a weakened structure as a result of precipitation occurring before the system has reached a quiescent state. Factors which influence the reaction time are the presence of catalysts (e.g., tertiary amines, metal compounds), the nature of the solvent, the concentration of reactants, the NCO/OH ratio of the system, and the temperature.¹² These factors can be adjusted to determine a favorable length of gelation time.

Various single or binary combinations of solvents can be used that meet the above requirements. Salyer et al.¹³ have suggested the use of solvent mixtures which have the same density as the polyurethane in order to

inhibit the settling or floating effects of the OPP during formation. Hileman et al. used a 60:40 volume percent toluene-carbon tetrachloride mixture. The solvent density of 1.17 g/ml matched the precipitate density.

A suggested mechanism for the formation of OPP is that the polyisocyanate and the polyol reactants interact to form liquid-soluble, short-chain polymers. As the polymerization proceeds, the chain lengths and molecular weights increase, until the polymeric material is no longer soluble and acquires gel-like properties, i.e., is semi-dispersed in a swollen phase. As further reactions at the ends of the polymer chains yield even higher molecular weight material, the material is precipitated in situ. The freshly formed surfaces have excellent cohesion so that aggregated spherical particles are formed in an interconnected matrix (see Figure 1). Adhesion occurs at the polymer-column wall interface. An open network of polymeric material is formed with the organic liquid trapped in the interstitial spaces. These spaces are irregular in shape and interconnected, resulting in a structure which is highly permeable.

The concentration of reacting solids in the mixture can be controlled by simply changing the amount of organic liquid present. The concentrations should range between 15 to 30% solids by weight. If the concentration is appreciably less than 15%, the matrix will be fragile. The resulting shrinkage will cause the polyurethane to pull away from the column walls. If more than 30% concentration is used, the OPP will tend to crack, opening up undesirable channels. The variation of concentrations is a means of changing the density and porosity, and hence the permeability of a chromatographic column.

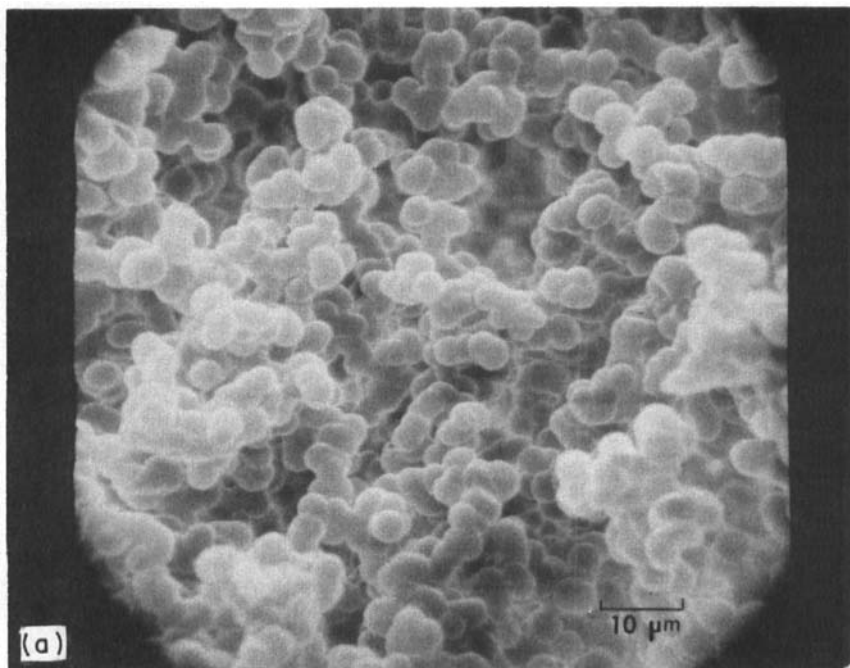


Figure 1a. Photomicrograph of Open Pore Polyurethane at X1100.

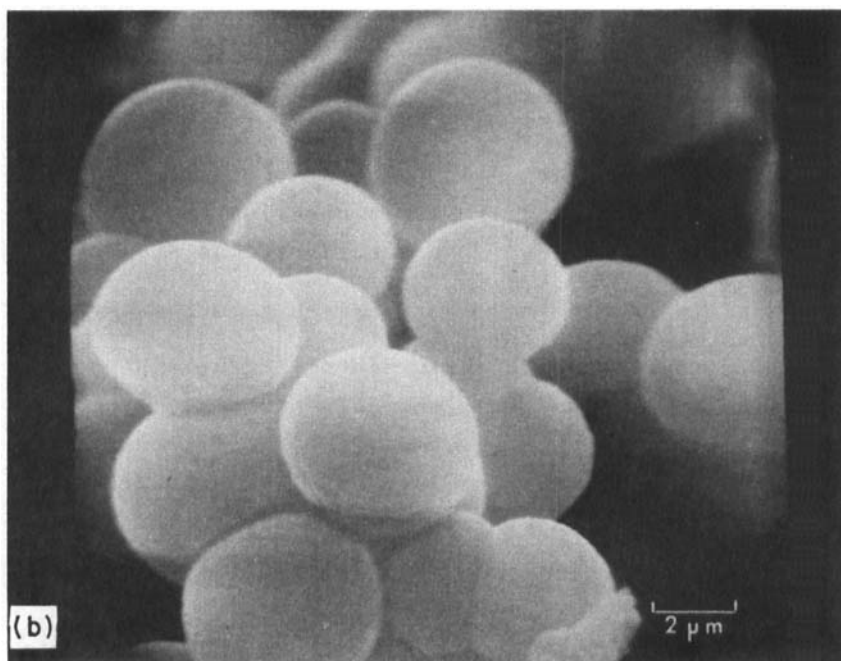


Figure 1b. Photomicrograph at X5500.

The reaction proceeds readily at ambient temperatures, and ordinarily gellation will begin in 10 to 20 minutes. Lower temperatures increase gel time and generally give less rigid structures. Higher temperatures increase the rate of the gelling process and may cause undesirable convection currents, which may weaken the structure by disrupting gel formation. Higher temperatures result in the formation of smaller spheres. After a brief reaction time (2-4 hours), the OPP is rigid, and the organic solvent can be removed by flushing with a neat solvent which removes any unreacted monomer. If a more dense matrix is desired, the column can be left undisturbed and polymerization will continue for several days.

Preparation of Columns

The in-situ formation of polyurethane from the polyisocyanate and the polyol is the result of a reaction which proceeds by the isocyanate reacting with the active hydrogen of the polyol. The isocyanate can also react with other active hydrogens such as amines, organic acids, glycols and particularly with water.¹² The isocyanate must be protected from water for two reasons. First, the isocyanate is destroyed and replaced by a reactive amine. Second, CO₂ is released causing voids in the polyurethane, which is very undesirable in a chromatographic system. The condition of the polyisocyanate can be checked by observing the infrared absorption at 3.0 microns (NH₂ stretch) and 6.02 microns (C=O stretch). Broad peaks at these wavelengths indicate that water has reacted with the isocyanate and it should be discarded.¹⁵

The columns are filled by forcing a mixture of stoichiometric amounts of the isocyanate solution and

the polyol solution into the column using a disposable plastic syringe. Care should be taken to expel any pockets of air that have been trapped. Bubble formation can result from degassing of the reactant solutions and the formation of CO_2 during the polymerization process. Columns should be rotated at ~ 5 rpm during polymerization for two reasons. First to prevent the settling of the polymer in a system where the polymer density is not equal to the solvent density. Secondly, it permit bubbles formed during the reaction to float to the ends of columns preventing the formation of large voids in the polymer. Bubble formation is not a problem in straight columns in the vertical position provided the top end remains open.⁵ Columns made of flexible material, e.g., copper, aluminum, or stainless steel may be filled and polymerized in the straight configuration and then bent into the desired shape before removing the solvent.

The column is then flushed with neat solvent to remove any unreacted monomer or the solvent can be removed by forcing it out with an inert gas. The column should then be heat conditioned to remove any residual solvent if preparing gas chromatographic column.

Gas Chromatographic Column Properties of Open Pore Polyurethane

The ideal solid support for gas chromatography should be highly permeable to gas flow, exhibit a large surface to permit retention of a large volume of liquid phase as a thin film and be mechanically strong. More conventional supports that are mechanically strong do not usually have high liquid phase capacity. Many conventional supports are not ordinarily good supports for gas-liquid chromatography and also good for gas-solid chromatography.

Open pore polyurethane is a unique structure that is remarkably uniform, has a high permeability due to large interstitial porosity, but with pore sizes usually $<10\text{ }\mu\text{m}$, and has a very high liquid phase loading capacity. It can also be used for gas-liquid and certain specialized gas-solid chromatographic separations. The polymeric structure is mechanically strong, withstanding 20% compressibility without damage to the particles. Many of its properties can be varied by changing the reaction conditions. The in situ formation of this material is of significant merit.

Table I is a comparison of the permeability, porosity, and density for various polyurethane and Chromosorb W columns. The OPP columns prepared and evaluated by Hileman¹⁵ were designated by their theoretical densities. This number and the observed densities

TABLE I

PERMEABILITY, POROSITY, AND DENSITY FOR
VARIOUS POLYURETHANE AND CHROMOSORB W COLUMNS¹⁵

<u>Column Type</u>	<u>Permeability ($\text{cm}^2 \times 10^7$)</u>	<u>Porosity (%)</u>	<u>Density (gm/cc)</u>
Chromosorb W			
40/60	8.86	89.0	0.247
60/80	4.71	87.6	0.282
80/100	3.04	88.6	0.273
100/120	2.71	85.5	0.278
Polyurethane			
0.106	16.00*	90.0	0.104
0.130	6.28	88.2	0.126
0.154	2.92	87.0	0.153
0.178	1.14	85.5	0.172
0.198	1.05	84.5	0.190
0.219	0.66	81.3	0.219
0.243	0.44	75.8	0.234

*Serious channeling

are very close, indicating nearly quantitative polymerization. From Table I it can be observed that a permeability similar to that of finer mesh Chromosorb W is achieved at a polyurethane density of 0.154 gm/cc. Concentrations higher than this resulted in nearly impermeable columns, while lower concentrations resulted in high permeability but had serious channeling problems. In addition to exhibiting an acceptable permeability, Hileman¹⁵ found the 0.154 gm/cc density columns to be most efficient.

Thermal Stability

Thermogravimetric analysis (TGA) has been performed on OPP of the 0.154 gm/cc density. The OPP sample was exposed to a range of temperatures from ambient to 400°C. The TGA curve indicated that decomposition became noticeable at 200°C. Discoloration of the OPP was noticed at lower temperatures. The suggested sustained upper working temperature is around 160°C; however, operation as high as 180°C for shorter time periods will not cause rapid column degradation.

Gas-Solid Chromatography by OPP

Uncoated OPP ordinarily behaves as a gas-solid chromatographic column. Hileman found that a plot of H.E.T.P. versus flow indicated the H.E.T.P. remains constant above 150 ml/min. flow rate. Apparently the adsorption process occurs very rapidly on the polymer surface thus giving a very small C term in the van Deemter equation. This is not the case with a commercial polyvinyl polymer, Porapak Q (Waters Associates) where the normal van Deemter plot is obtained.¹⁵

Some unique separations are achieved on the uncoated OPP. Nonpolar compounds, e.g., hydrocarbons are

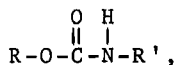
separated in the order of the boiling points on the uncoated polyurethane. Polar compounds that can hydrogen bond behave differently, i.e., they do not elute in the order of their boiling points, but probably elute in order of the acid strength of the available proton. Table II is a comparison of elution times of various polar compounds.

TABLE II

COMPARISON OF ELUTION TIMES OF VARIOUS POLAR COMPOUNDS¹⁵

<u>Compound Type</u>	<u>Relative Retention Time</u>	<u>Boiling Point (°C)</u>
(CH ₃) ₂ CHOH	1.0	82.5
CH ₃ CH ₂ OH	2.0	78.3
CH ₃ OH	9.6	64.5
CCl ₄	1.0	77
CHCl ₃	1.05	61
CH ₂ Cl ₂	1.6	40

The tertiary and secondary alcohols are eluted ahead of the primary alcohols even though this reverses the boiling point order. The structure of the OPP support contains amide ester linkages. This functional group,



contains several sites capable of acting as acceptors for available protons. The tertiary amine of the polyol could also act as a basic site. The tertiary and secondary alcohols contain electron-releasing methyl groups on the hydroxy-bearing carbon. This electron release would tend to distort the electron cloud around oxygen

in the direction of the hydrogen, making the hydrogen less positive, and thus, less able to interact with other electronegative atoms. As the methyl groups are removed from the hydroxy carbon, the stability of the hydrogen bonded complex increases, thus enhancing the interaction with the polyurethane and increasing the retention time.

Carbon tetrachloride, chloroform, and methylene chloride gave results similar to the alcohols. The proton is attached to a carbon but can hydrogen bond due to the presence of highly electronegative chlorines.¹⁵

The author has demonstrated that the uncoated OPP can achieve a remarkable separation of geometrical isomers of metal chelates because of its polar properties. The *cis* and *trans* isomers of tris(trifluoroacetylacetonato)chromium(III) $[\text{Cr}(\text{tfa})_3]$ chelate are completely resolved on the uncoated polyurethane^{14,16} (Figure 2).

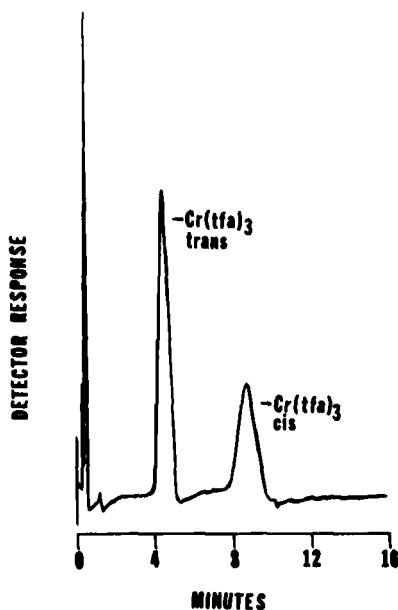


Figure 2. Gas chromatogram of chromium trifluoroacetylacetonate on uncoated OPP showing complete separation of geometrical isomers.

This complete separation has not been possible on other more conventional supports.

The complete separation of *cis* and *trans* isomers of $\text{Rh}(\text{tfa})_3$ was also completely resolved on OPP¹⁶ (Figure 3.)

The *cis* isomer has the trifluoromethyl groups of the unsymmetrical $\text{H}(\text{tfa})$ ligand in a facial arrangement on the octahedral chromium metal ion. This places the fluorines totally to one side of the complex, resulting in a high dipole moment. The *trans* isomer has a peripheral arrangement of fluorines about the central ion, thus giving a less polar compound. The difference in polarity results in the elution of the *trans* isomer in half the time of the polar *cis* isomer.

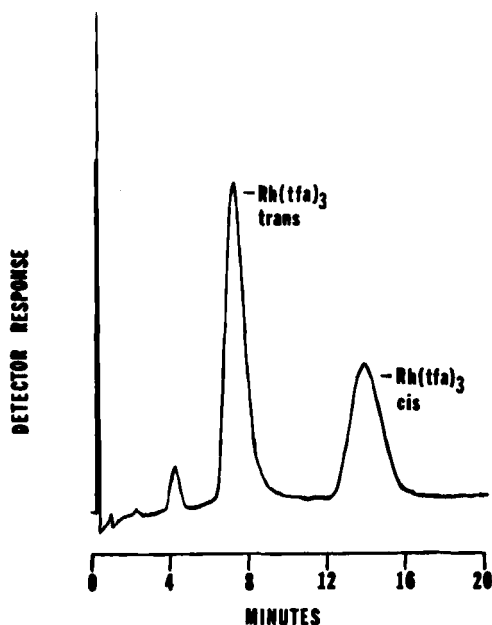


Figure 3. Gas chromatogram of rhodium trifluoroacetate on uncoated OPP, showing complete separation of geometrical isomers.

Kutal and Sievers have used the separation of the geometrical isomers of $\text{Cr}(\text{tfa})_3$ on OPP to perform rate and equilibrium studies of *cis-trans* isomerization of $\text{Cr}(\text{tfa})_3$ in the gas phase.¹⁷ The separation was accomplished on a 16-inch glass column and was complete in 10 minutes with no evidence of isomerization occurring on the OPP support.

Gas-Liquid Chromatography

Stationary phases can be added to the OPP by incorporation into the precursor solutions or by addition as a solute onto the formed material. The gas-solid properties are covered and the material now takes on the characteristics of a gas-liquid substrate. Since a solution rather than an adsorption process is occurring, the isotherm is linear over a wide range of sample sizes, resulting in more symmetrical peaks and constant retention times for a wide range of sample loading. The theoretical plate number and resolution improves for certain compounds. Liquid phases which are included in situ with the reactants provided for a good distribution of stationary phase. Consequently, the C term of the van Deemter equation is minimized, with resulting high plate numbers. Further evidence that the highly polar uncoated polyurethane is masked by the liquid phase (DC 550) is illustrated in Figure 4, where four metal chelates, $\text{Be}(\text{tfa})_2$, $\text{Al}(\text{tfa})_3$, $\text{Cr}(\text{tfa})_3$ and $\text{Rh}(\text{tfa})_3$, are all separated but the *cis-trans* isomers of the $\text{Cr}(\text{tfa})_3$ and $\text{Rh}(\text{tfa})_3$ are not resolved.^{4,14} The alcohols elute in order of their respective boiling points on OPP coated with Carbowax, indicating the covering of the polar sites of the polyurethane.

Normal hydrocarbons are well resolved on either coated or uncoated polyurethane. Relatively high boil-

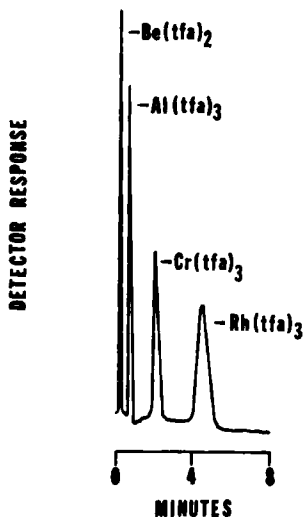


Figure 4. Gas chromatogram of metal trifluoroacetylacetonates on OPP with DC 550 liquid phase.

ing n-hydrocarbons elute readily at low column temperatures on the uncoated support. Figure 5 shows the separation of C_6 - C_{16} n-aliphatic hydrocarbons at maximum column temperature of 120°C on an uncoated column. (Hexadecane boils at 237°C .) The effects of a liquid phase, 10% DC 550 (Dow Corning), is shown in Figure 6 where C_6 - C_9 n-aliphatic compounds were separated using a column temperature of 120°C .³

Liquid Chromatography

Ross and Jefferson¹⁸ first reported the use of OPP as a liquid-solid chromatographic support in 1970. These investigators separated three metal chelates in an OPP column at ambient pressures. Copper(II), cobalt(II) and cobalt(III) heptafluorodimethyloctanedionates were resolved using a benzene carrier.

Lynn et al.¹⁹ have recently described their work on the use of OPP as a support in high resolution - low

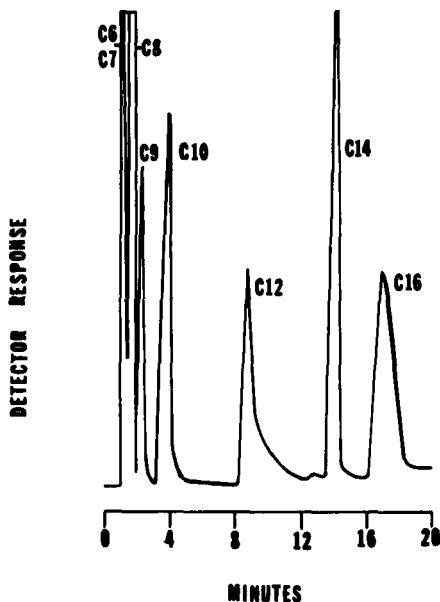


Figure 5. Gas chromatogram of a hydrocarbon mixture on uncoated open pore polyurethane.

pressure liquid chromatography. These investigators found that the chemical and physical stability of OPP, coupled with the ability to change porosity and functionality and its uniform sphere size, make it a near ideal support for liquid chromatography. Their major objective was to determine if selective LC packing materials could be made by altering the quantity of the starting monomers and the stoichiometry of the addition polymerization. The mechanical properties of OPP have made it possible to inject samples directly on the column material without any syringe needle blocking. The gel particles are both cohesive and adhesive to the column walls. No column inlet filter is needed and outlet filters are not required to prevent detector cell blockage from the support material. This is an important advantage eliminating porous filters which contribute to band spreading.

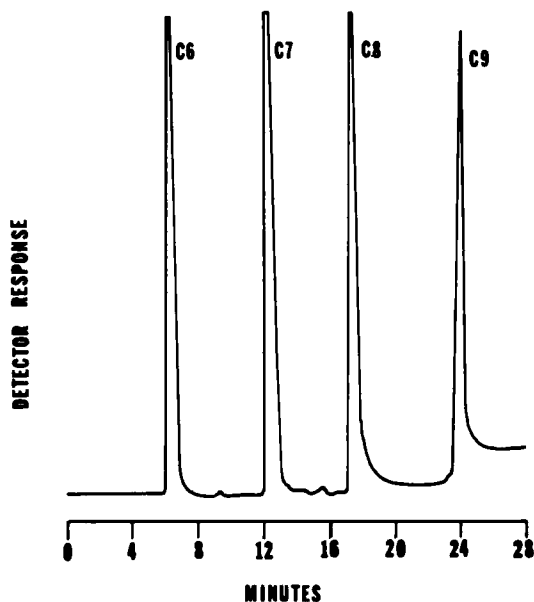


Figure 6. Gas chromatogram of a hydrocarbon mixture on a DC 550 incorporated OPP column.

Pressure tests indicate that the mechanical integrity is stable up to pressures of 1500 psi. However, it would be unusual to encounter pressures this high with OPP because of its high permeability. At typical high speed liquid chromatography flow rates, the column inlet pressure would be ~ 100 psi. The requirement of expensive high pressure pumps is eliminated for high speed liquid chromatography.

Various ratios of NCO/OH were evaluated from 3:1 to 1:3. Useful gels were formed over this range. Figure 7 is a separation of dichloroanilines by liquid chromatography on OPP using a NCO/OH ratio of 1.0 to 1.5. Measurements on the 2,6-dichloroaniline peak indicate an efficiency of 1085 theoretical plates per meter with an inlet pressure of only 70 psi and a flow rate of 0.25 ml/min. Figure 8 shows the separation of acetone

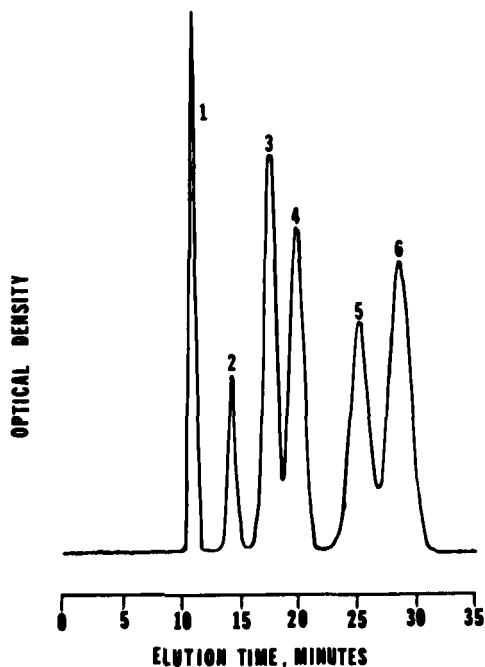


Figure 7. Liquid chromatogram of the separation of dichloroanilines. (1) Benzene, (2) 2,6-dichloroaniline, (3) 2,4-dichloroaniline, (4) 2,3-dichloroaniline, (5) 3,5-dichloroaniline, and (6) 3,4-dichloroaniline.

and o-aminophenol showing 4050 and 750 theoretical plates, respectively.

The polyurethane columns have a wide dynamic loading range in contrast to the silica and alumina type adsorbents for liquid chromatography. Lynn et al. have shown that a column of 2 mm diameter and 1 meter length will take up to 50 μg of 2,4-dichloroaniline before the peak broadens, and even larger sample sizes do not decrease peak symmetry, indicating a more liquid-liquid partitioning type of chromatography.¹⁹

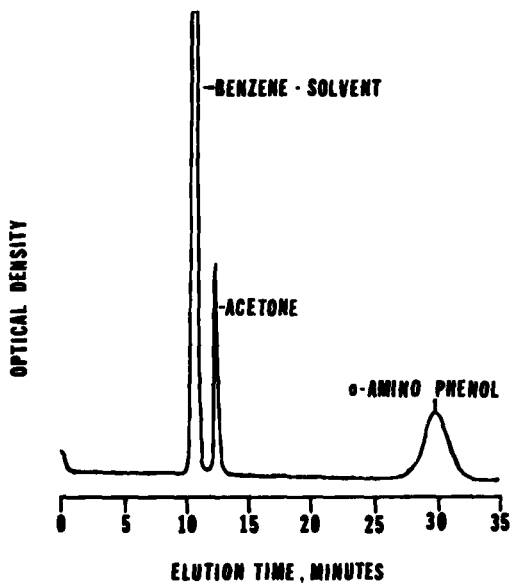


Figure 8. Liquid chromatogram of separation of acetone and o-amino phenol on OPP.

CONCLUSION

The future of OPP as a separation medium appears encouraging. Much research is still needed to determine its full potential. Analabs, Inc., New Haven, Conn., is performing research and is licensed to produce the material for chromatographic separations. There are many possible conditions for synthesis, each of which alters the physical properties of the finished product. Synthesis conditions can be varied to alter porosity, permeability, particle size, and exposed functional groups, i.e., excess -NCO or -OH chemical moieties. Another advantage of this material is that rapid filling of columns of very complex configurations can be achieved. Along with the unique physical properties,

selective chemical alterations of the polymer bead surface hold the most potential utility of OPP which should open the way for the production of a large variety of unique separation materials.

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