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Note

Improvements in gas chromatographic columns formed by *in situ* polymerization

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The preparation of chromatographic columns formed by *in situ* polymerization to produce an open-pore polyurethane (OPP) has been described previously by several workers[1–3]. One advantage of using such columns is that they can be prepared in any configuration and in a variety of lengths and diameters with little difficulty. Analyses using uncoated polymer exhibited gas–solid chromatographic behavior, whereas those performed on polymer coated with a suitable stationary phase showed typical gas–liquid behavior. Two limitations have hampered the general use of these columns: pronounced peak tailing for polar molecules and low temperature stability of the polymer. In this note we report improvements in both of these problem areas.

With regard to the problem of tailing peaks we report that a column prepared using a ratio of hydroxyl to isocyanate functional groups of approximately 2:1 gives good gas chromatographic separations of, and symmetrical peaks for, polar compounds including alcohols. That the ratio of the monomers could be varied to a considerable extent while still producing usable polymers has already been reported[4,5] in connection with liquid chromatographic applications. In this work we have demonstrated that changing the ratio of OH to NCO functional groups results in improved characteristics for gas chromatography.

The maximum temperature at which columns of the kind described by Hileman *et al.*[2] can be used is approximately 165°, which severely limits their applicability. Above 165° the polymer begins to undergo thermal decomposition. The temperature stability problem is important in that many analyses are performed in the range 150–225°. In the present study we have developed a new polymer system that can be used effectively in this higher temperature range.

EXPERIMENTAL

Materials

The polyol LA-475, a mixture of pentahydroxy compounds obtained from the oxypropylation of diethylenetriamine, was kindly provided by Union Carbide (New York, N.Y., U.S.A.). Mondur MR, a mixture of *p,p'*-diphenylmethane diisocyanate

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with lesser amounts of tri-, tetra- and pentaisocyantes, was kindly provided by Mobay (Pittsburgh, Pa., U.S.A.). Epon 1001, an epoxide-terminated polyol based on bisphenol A, manufactured by Shell Chemical Co., was purchased from Analabs (North Haven, Conn., U.S.A.). Samples of methyl Fenac and methyl 2,4-D were obtained from W. Davidson of Brehm Labs., Wright State University (Dayton, Ohio, U.S.A.).

Methods

Following the procedure reported previously[2], columns having a functional group ratio (OH:NCO) of nearly 2:1 were prepared using LA-475 (3.00 g, 0.0254 equiv.) dissolved in carbon tetrachloride–toluene (10 ml, 40:60 by volume) and Mondur MR (1.53 g, 0.0116 equiv.) dissolved in an equal amount of solvent. These columns were used directly without coating to obtain the separations described later.

Columns with higher thermal stability are produced by reacting Epon 1001 with Mondur MR in weight ratios (Epon:Mondur) ranging from 3.0:1.0 to 0.8:1.0. These correspond to OH:NCO ratios ranging from 1.1:1.0 to 1.0:3.0. In a typical preparation, Mondur MR (1.2 g, 0.0090 equiv.) was dissolved in acetone (8 ml) dried over molecular sieves. The solution was mixed rapidly with Epon 1001 (2.4 g, 0.0067 equiv.) and triethylamine catalyst (10 drops) dissolved in acetone (11 ml). The solution was injected into a 1.2 m × 6 mm O.D. coiled glass column capped with rubber tubing and screw clamps. The column was rotated slowly for about 30 min, periodically loosening the screw clamps to release bubbles of vapor that had migrated to the ends of the column. The source of the bubbles was believed to be due to both dissolved air in the solutions and the reaction of RNCO with trace amounts of moisture, producing carbon dioxide. The column was then left stationary for 1 day. When the clamps were removed, dry nitrogen was used to force out the solvent, and the column was conditioned at 210° for 1 day with a slow flow of dry nitrogen.

If a stationary liquid phase was desired, it was added prior to the conditioning. Typically, Carbowax 20M (0.8 g) dissolved in chloroform (12 ml) was forced into the column and allowed to stand for 5 h. The solution was then expelled and the column was conditioned at 210°. The expelled solution was collected, the chloroform was evaporated and the Carbowax residue was weighed to determine by difference the amount coating the column. Comparison of the Carbowax retained on the column with the weight of the polyurethane polymer indicates that approximately 10% loading was achieved. The thermal stability of the polymers was measured using a DuPont Model 951 thermogravimetric analyzer. A Varian Model 1440 gas chromatograph with a flame-ionization detector was used for all chromatographic analyses.

RESULTS AND DISCUSSION

The apparent decrease in polarity of the 2:1 LA-475–Mondur MR polymer as compared to the 1:1 formulation of Hileman *et al.*[2] is evident from the Rohrschneider constants for the two columns given in Table I. Although the values for the 1:1 column are not reliable because of broad peaks and severe tailing, they are reproducible and presumably reflect the highly polar character of the solid. Although Rohrschneider constants are normally used for characterizing liquid phases, they are used here as a rough indication of the affinity of the polymeric column for various compounds.

Fig. 1 shows the symmetrical peaks obtained in the analysis of alcohols on a

TABLE I

ROHRSCHNEIDER CONSTANTS FOR POLYURETHANE COLUMNS

The chemical probes used were x = benzene, y = ethanol, z = 2-butanone, v = nitromethane and s = pyridine.

Column	x	y	z	v	s
1:1 LA-475–Mondur MR	5.06	10.98	7.59	10.90	10.35
2:1 LA-475–Mondur MR	2.88	5.66	4.19	6.08	5.55

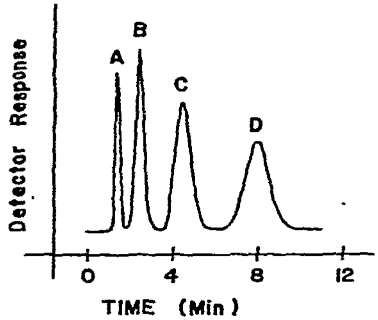
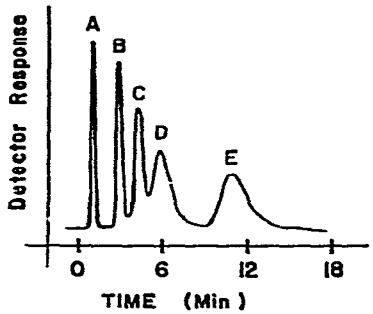


Fig. 1. Chromatogram of alcohols on 2:1 LA-475–Mondur MR column. Peaks: A = ethanol; B = *n*-propanol; C = *n*-butanol; D = *n*-pentanol. Column dimensions, 1.2 m × 4 mm I.D.; flow-rate, 60 ml/min; detector temperature, 200°; injector temperature, 150°; column temperature, 120°; 0.5-μl injection.

2:1 column. Separations of a series of normal 2-alkanones and the ethyl esters of a series of normal carboxylic acids were also readily achieved.

The 1:1 Mondur MR–LA-475 polymer system described by Hileman *et al.*[2] underwent apparent thermal decomposition beginning at 200°, according to thermogravimetric analysis (TGA) conducted under nitrogen[6], whereas the polymer prepared from Mondur MR–Epon 1001 in a 1:2 weight ratio (NCO:OH = 1.3:1) shows only a 0.6% weight loss at 250° and a 2% loss at 300°, after which rapid decomposition ensues. Polymer containing a greater proportion of Mondur MR shows even higher temperature stability. To gather evidence of column stability under conditions of actual use we placed a column (Epon 1001:Mondur MR = 1:2, by weight) coated with approximately 10% Carbowax 20M in the chromatograph at 225° for 72 h. No darkening of the column was observed and the performance of the column was only slightly changed. Thus, the column containing the polymer of Mondur MR and Epon 1001 coated with Carbowax 20M can be used at temperatures substantially above those possible with the Mondur MR and LA-475 system. Polyurethanes are not usually very thermally stable so it is particularly noteworthy that the polymer with Epon 1001 has such good thermal stability.

Some results obtained with Carbowax-coated Epon columns are shown in Figs. 2 and 3. Both of the separations were made at column temperatures that exceed the upper temperature limitations of all previously reported polyurethane columns. The fact that menthone is eluted significantly earlier than isophorone agrees with results that were obtained on a series of methyl-substituted cyclohexanones, which showed that the molecules with more hindered carbonyl groups are eluted more quickly than



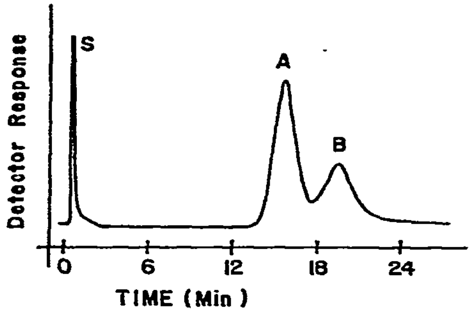


Fig. 2. Chromatogram of ketones separated on a column coated with Carbowax 20M on a polymer formed from Epon 1001 and Mondur MR in a 2:1 weight ratio. Peaks: A = 3-methyl-2-butanone; B = cyclopentanone; C = cyclohexanone; D = menthone; E = isophorone. Column dimensions, 1.2 m × 4 mm I.D.; helium flow-rate, 27 ml/min; detector temperature, 270°; injector temperature, 200°; column temperature, 175°.

Fig. 3. Chromatogram of herbicides on the column specified in Fig. 2. Peaks: S = diethyl ether; A = methyl Fenac; B = methyl 2,4-D. Helium flow-rate, 75 ml/min; detector temperature, 270°; injector temperature, 230°; column temperature, 220°.

those with less hindered carbonyl groups. Fig. 3 indicates the moderately difficult separation of the related herbicides methyl 2,4-D (methyl 2,4-dichlorophenoxyacetate) and methyl Fenac (methyl 2,3,6-trichlorophenylacetate).

We are continuing to explore the Epons and related monomers in the synthesis of polymers with higher temperature stabilities and greater separating efficiencies for both liquid and gas chromatographic applications.

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