Poly(amide-acetals) and Poly(ester-acetals) from 9(10)-Formylstearic Acid as Stationary Phases for Gas Chromatography[1]

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ABSTRACT

Diesters from the reaction product of methyl 9(10)-formylstearate with pentaerythritol were condensed with diols and diamines to produce the respective linear poly(ester-acetals) and poly(amide-acetals). Like those derived from methyl azelaaldehydate, these polymers have latent crosslinking sites at the acetal bond and, when crosslinked on an acidic diatomaceous support, form useful stationary phases bonded to the support surface for gas chromatography. Unlike that derived from methyl azelaaldehydate, the linear poly(amide-acetal) from methyl 9(10)-formylstearate is soluble in solvents, so that column packings are more easily prepared and advantage can be taken of the more polar nature of the poly(amide-acetal). The stationary phases derived from the formylstearate have a continuous operating range from at least -60 C to 190-220 C with no detectable amount of phase bleed. Bleeding gradually increases, but the packings are still useful in dual column, compensated systems to 290 C. The poly(amide-acetal) derived from formylstearate has intermediate polarity, whereas the poly(ester-acetal) counterpart is relatively nonpolar. Polarity of the poly(ester-acetal) was greatly increased, whereas that of the poly(amide-acetal) was slightly lowered by adding dimethyl 1,4-cyclohexanedicarboxylate as a comonomer. Compounds of widely different polarities were separated with good resolution and adequate efficiency on these packings during programed or isothermal gas chromatography.

INTRODUCTION

Pentaerythritol acetals of alkyl formylalkanoates, like methyl azelaaldehydate (1) and methyl 9(10)-formylstearate (2), are diesters that can be converted to linear polymers by reaction with diols or diamines. Such polymers have latent crosslinking capabilities at the acetal linkage and become insoluble, infusible gels after crosslinking (3,4). Further, the crosslinked polymer becomes bonded to glass surfaces through participation of the surface silanol groups during crosslinking. Davison and Moore (5) took advantage of this property to prepare stationary phases bonded to a support for gas chromatography (GC). Their first trial with a poly(ester-acetal) from methyl azelaaldehydate produced a stable, useful column, but they were unable to repeat their results. Later work showed that the support must be one which was calcined without a flux and which had an acidic surface (6,7). One poly(ester-acetal) that gave exceptionally good, continuous behavior as a stationary phase from -60 to 290 C was a copolymer of methyl azelaaldehydate pentaerythritol acetal and 1,4-cyclohexanedicarboxylate with diethylene glycol. Poly(amide-acetals) should provide packings with desirably greater polarity, but those from methyl azelaaldehydate were too insoluble, and column packings from these polymers were not feasible.

More recently, we have prepared and characterized chromatographic stationary phases from certain poly(amide-acetals) and poly(ester-acetals) derived from methyl 9(10)-formylstearate pentaerythritol acetal (MFSPEA). Since both types of polymers from MFSPEA are readily soluble, column packings were easily prepared.

EXPERIMENTAL PROCEDURES

Materials

Starting polymers were condensation products of pentaerythritol acetals of methyl 9(10)-formylstearate (2) with ethylene glycol, ethylene and hexamethylene diamines (R.A. Awl, unpublished). All polymers had a molecular weight of 7100 as determined by vapor-phase osmometry.

TABLE I

Comparison of Some Physical Properties of Linear and Crosslinked, Bonded Stationary Phases

		Thermogravimetric analyses				Column bleed,[e] mv	
MFSPEA polymer type[a]	Polymer state	Break temperature,[b] C	Weight loss[c] at 300 C, %	Loading,[d] wt%	Chloroform solubles, wt%	Initial response, C	At 280 C, mv
EG	Linear	240	10.1	25.4	24.8	---	---
EG	Crosslinked	305	0.0	22.0	0.4	205	0.168
DMC/DEG	Linear	199	30.9	19.4	19.2	---	---
DMC/DEG	Crosslinked	270	7.5	16.0	1.2	193	---
ED	Linear	250	2.4	18.2	18.6	---	---
ED	Crosslinked	347	0.0	14.8	1.0	220	0.065
HMD	Linear	227	5.6	22.4	22.0	---	---
HMD	Crosslinked	334	0.0	19.2	0.5	227	0.066
DMC/HMD	Linear	299	0.8	21.7	20.1	---	---
DMC/HMD	Crosslinked	324	0.0	10.2	0.4	196	0.076

[a] MFSPEA = methyl 9(10)-formylstearate pentaerythritol acetal; EG = ethylene glycol; DMC = dimethyl 1,4-cyclohexanedicarboxylate copolymer; DEG = diethylene glycol; ED = ethylene diamine; HMD = hexamethylene diamine.

[b] Temperature at which packing begins to lose weight.

[c] Percentage of organic coating lost.

[d] Determined by total weight loss at 500 C.

[e] For 1 mv full scale recorder response and an attenuation of 1.

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TABLE II

Gas Chromatographic Characteristics for Crosslinked, Bonded Poly(ester-acetal)

Item	Stationary phase				
	EG	DMC/DEG	ED	HMD	DMC/HMD
ΔI[a] relative to squalane for					
Benzene	99	142	108	106	90
1-Butanol	60	152	180	196	186
2-Pentanone	32	128	86	95	96
Nitropropane	162	224	210	208	206
Pyridine	50[b]	156	119	122	97
2-Methyl-2-pentanol	46	119	122	134	125
1-Iodobutane	65	123	97	90	76
2-Octyne	56	99	65	59	43
1,4-Dioxan	81	171	108	104	88
cis-Hydrindan	19	75	60	65	30
		Mixture A. Programed			
Retention indices[c] for					
2-Pentanone	760	861	796	782	570
Hexanal	865	978	911	905	898
Heptanal	978	1088	1012	1015	1001
Hexanol	994	1137	1100	1146	1150
Heptanol	1097	1228	1201	1248	1251
Dimethyl glutarate	1220	1381	1285	1318	1300
Nonanal dimethyl acetal	1598	1759	1321	1339	1334
Nonanol	1298	1438	1415	1459	1452
Decanol	1401	1532	1518	1560	1549
Butyl nonanoate	1526	1609	1564	1585	1599
Hexadecane	1574	1735	1600	1611	1646
Methyl azelaaldehydate	1638	1848	1666	1701	1757
Methyl tetradecanoate	1755	1961	1804	1827	1855
		Mixture B. Isothermal			
Benzene	740	846	755	776	759
1,4-Dioxan	794	922	826	837	821
Nitropropane	851	949	906	932	912
Pyridine	888[b]	1007	933	965	943
cis-Hydrindan	1046	1100	1064	1092	1024
N(HETP)[d] for					
Dodecane[e]	760(0.16)	851(0.14)	900(0.14)	540(0.23)	625(0.19)
Methyl hexanoate[f]	560(0.22)	1286(0.10)	650(0.19)	410(0.30)	357(0.34)
1-Nonanol[e]	680(0.18)	1012(0.12)	1070(0.12)	790(0.16)	821(0.15)

[a] Retention indices determined according to McReynolds (9), but at 100 C instead of 120 C. At 120 C, the standards eluted too rapidly from the crosslinked, polymeric stationary phases. Only a slight change in retention index results from a 20 C temperature change (10).

[b] Peak tailed.

[c] Retention indices according to Kovats (13,14). The programed runs were made at 100-220 C at 6 C/min and 45 cc/min of helium flow. The isothermal runs were made at 100 C and 45 cc/min of helium flow.

[d] N = number of theoretical plates; HETP = height equivalent to a theoretical plate (cm) for a column 4 ft x 2 mm ID (12).

[e] Gas chromatographic conditions: 140 C isothermal, 30 cc/min flow of helium.

[f] Gas chromatographic conditions: 100 C isothermal, 30 cc/min flow of helium.

Described by glycol or diamine, the polymers had these melting points: ethylene glycol, liquid; ethylene diamine, 56 C; and hexamethylene diamine, 42 C. A copoly(ester-acetal), mol wt 1941, of 10% methyl 9(10)-formylstearate 40% reagent-grade dimethyl 1,4-cyclohexanedicarboxylate (DMC) and 50% diethylene glycol was prepared according to Neff et al. (7). A copoly(amide-acetal), differential thermal analysis mp 295 C, of 10% methyl 9(10)-formylstearate, 40% DMC and 50% hexamethylene diamine was also prepared. The monomer mixture was heated at 182-185 C under atmospheric pressure for 1.5 hr and then at 0.01 mm Hg. The highly viscous material was heated from 155 to 250 C for 1 hr, then from 252 to 258 C for 4-1/2 hr. The GC support was Johns-Manville Chromosorb P, acid-washed, 45/60 mesh, and when slurried in water, the pH of the solution was 6.50. Chloroform, trifluoroethanol and *p*-toluenesulfonic acid were commercially available, reagent-grade materials used as received.

Packing Preparation

Preparation of the packing from poly(amide-acetal) made with hexamethylene diamine will serve as an example except for the copoly(amide-acetal) packing preparation. The polymer (1.0 g, 25% of support weight) was dissolved in 250 ml chloroform at reflux under dry nitrogen. To the solution at room temperature was added *p*-toluenesulfonic acid (0.015 g in 2 ml absolute ethanol) as the crosslinking catalyst. The support (4.0 g of Chromosorb P) was then added to the solution with swirling to ensure uniform mixing. The solvent was removed in a rotary evaporator at reduced pressure and with gradually increasing temperature to 80 C. The packing (2 g) was loaded into a stainless steel column (122 cm long, 2 mm ID) by the usual procedure. Crosslinking and conditioning of the sorbent were carried out in the column at 270 C for 16 hr with a helium flow of 13 cc/min, after a preliminary heating from 100 C at a rate of 2 C/min.

The copoly(amide-acetal) (1.0 g) was dissolved in 250 ml trifluoroethanol at reflux under dry nitrogen. To the solution at room temperature was added *p*-toluenesulfonic acid (0.05 g in 2 ml trifluoroethanol) as the crosslinking catalyst. The rest of the procedure is the same as for the hexamethylene diamine poly(amide-acetal), except that a temperature of 300 C was maintained during crosslinking and conditioning.

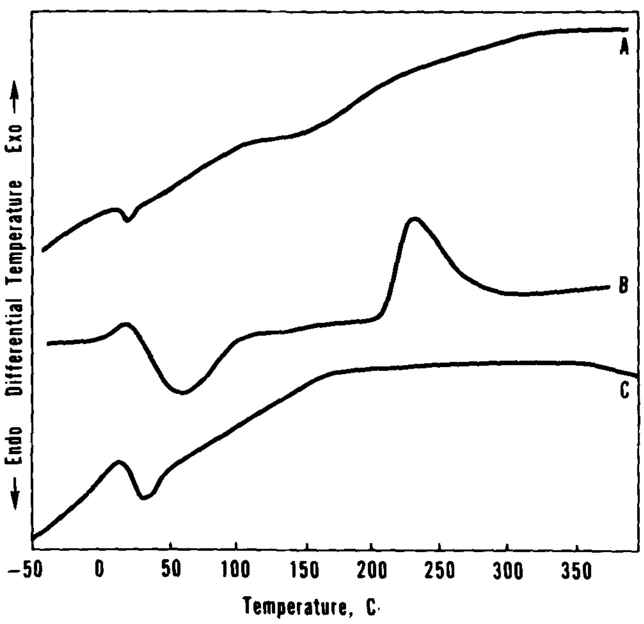

FIG. 1. Differential thermal analyses (DTA) of (A) uncoated acid-washed Chromosorb P, 45/60 mesh; (B) noncrosslinked ethylene diamine-methyl formylstearate pentaerythritol acetal coated on support A; and (C) the same polymer crosslinked on support A. DTA conditions are: dynamic nitrogen atmosphere, ca. 20 mg loaded into aluminum sample pan, empty aluminum sample pan as reference, 10 C/min rate, ΔT axis or sensitivity at 0.008 mv/in. and T axis at 50 C/in. Support A was heated first above 100 C to remove water and then cooled to starting temperature.

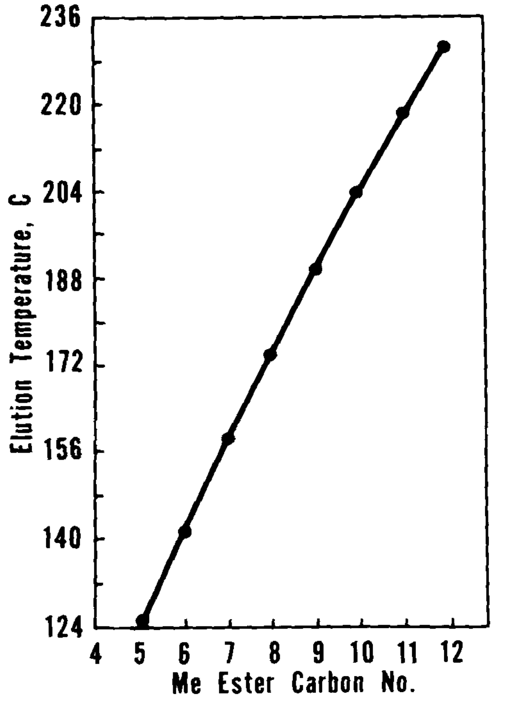

FIG. 2. Methyl esters on crosslinked-ethylene-diamine-methyl 9(10)-formylstearate-pentaerythritol-acetal packing (elution temperature vs. carbon number). Gas chromatography conditions are temperature programing from 100 C at 8 C/min with 30 cc/min helium flow.

Apparatus and Methods

Differential thermal analyses (DTA) were run with a DuPont Model 900350 calorimeter cell attached to the Model 900 Analyzer. Thermogravimetric analyses (TGA) were performed on the DuPont Model 950 instrument. Thermal stabilities, column loadings and break temperatures (initial weight loss) were determined by TGA with a sample size of 5-6 mg, 40 cc/min nitrogen purge, 10 C/min heating rate to 800 C, temperature axis at 100 C/in., weight axis at 1.0 mg/in. (Table I). Another indication of thermal stability was the amount of phase bleeding as indicated by chromatographic base-line stability. DTA showed the absence of phase transitions, such as melting points, for the crosslinked polymeric coatings. Degree of crosslinking was determined by refluxing the column packing (0.5 g) in 50 ml chloroform for 1 hr, filtering, washing the packing six times with chloroform and air-drying to constant weight to determine weight loss (Table I). Trifluoroethanol was used for the copoly(amide-acetal). Since not more than 5% of any one of the crosslinked polymers could be extracted, crosslinking and bonding to the support were almost complete.

GC data were developed with a Hewlett-Packard F&M Model 810 chromatograph equipped with hydrogen flame detectors and operated with an injection port temperature of 250 C and a detector temperature of 300 C. GC data for low temperature work were obtained with a series 7400 Packard dual column chromatograph equipped with hydrogen flame detectors and Model 804 oven. The injection temperature was 110 C and detector temperature 120 C. All GC columns were 122 cm x 2 mm ID stainless steel.

Peak resolution was calculated for a number of homologous compound pairs, including decane/dodecane 5.5:7.2, tetradecane/hexadecane 5.2:6.3, methyl hexanoate/heptanoate 2.4:4.5, methyl undecanoate/dodecanoate 2.8:3.3, 1-pentanol/1-heptanol 5.8:7.6, 1-heptanol/1-octanol 2.6:3.8 and 1-nonanol/1-decanol 2.5:3.1. The peak resolution was calculated as 2 x (distance between apexes)/(width of peak base no. 1 + width of peak base no. 2) (11). A value of 1.5 corresponds to 99.7% resolution. GC conditions included temperature programing from 100 to 235 C at 8 C/min and 30 cc/min flow of helium.

RESULTS AND DISCUSSION

Crosslinked polymeric stationary phases for GC were prepared from MFSPEA with ethylene glycol, ethylene diamine and hexamethylene diamine. A copoly(ester-acetal) of MFSPEA, DMC and diethylene glycol and a copoly(amide-acetal) of MFSPEA, DMC and hexamethylene diamine were also prepared. The chloroform-soluble starting poly(amide-acetals) and poly(ester-acetals) as well as the trifluoroethanol-soluble copoly(amide-acetal) for these crosslinked phases were easily coated onto acid-washed Chromosorb P (Johns-Manville) to produce a free-flowing packing. After crosslinking-conditioning in column, the packing was ready for analytical work.

The degree of stationary-phase crosslinking was examined by TGA, by refluxing the packing in solvent and by DTA (Table I). TGA of the crosslinked polymeric packings shows that thermal stability, as represented by packing weight loss and break temperature, is much higher than for noncrosslinked material. The packings were refluxed in solvent for 1 hr followed by thorough washing. Almost all noncrosslinked stationary phases were extracted, whereas little weight loss occurred for crosslinked phases (Table I).

Except for decomposition (indicated by an endothermic shift) at 330 C, which corresponds to the TGA weight loss beginning at 347 C, DTA of the crosslinked-ethylene-diamine stationary phase (Fig. 1) produced a curve similar to the uncoated support. However the noncrosslinked-ethylene-diamine stationary phase had a broad melting endotherm at 26-110 C with what appears to be decomposition beginning at 216 C corresponding to the TGA break temperature of 250 C. DTA curves of the same type were obtained for the hexamethylene and ethylene glycol polymers, as well as for the copolymers. DTA of diethylene glycol succinate packing produced a similar trace with correlation for the known melting and decomposition

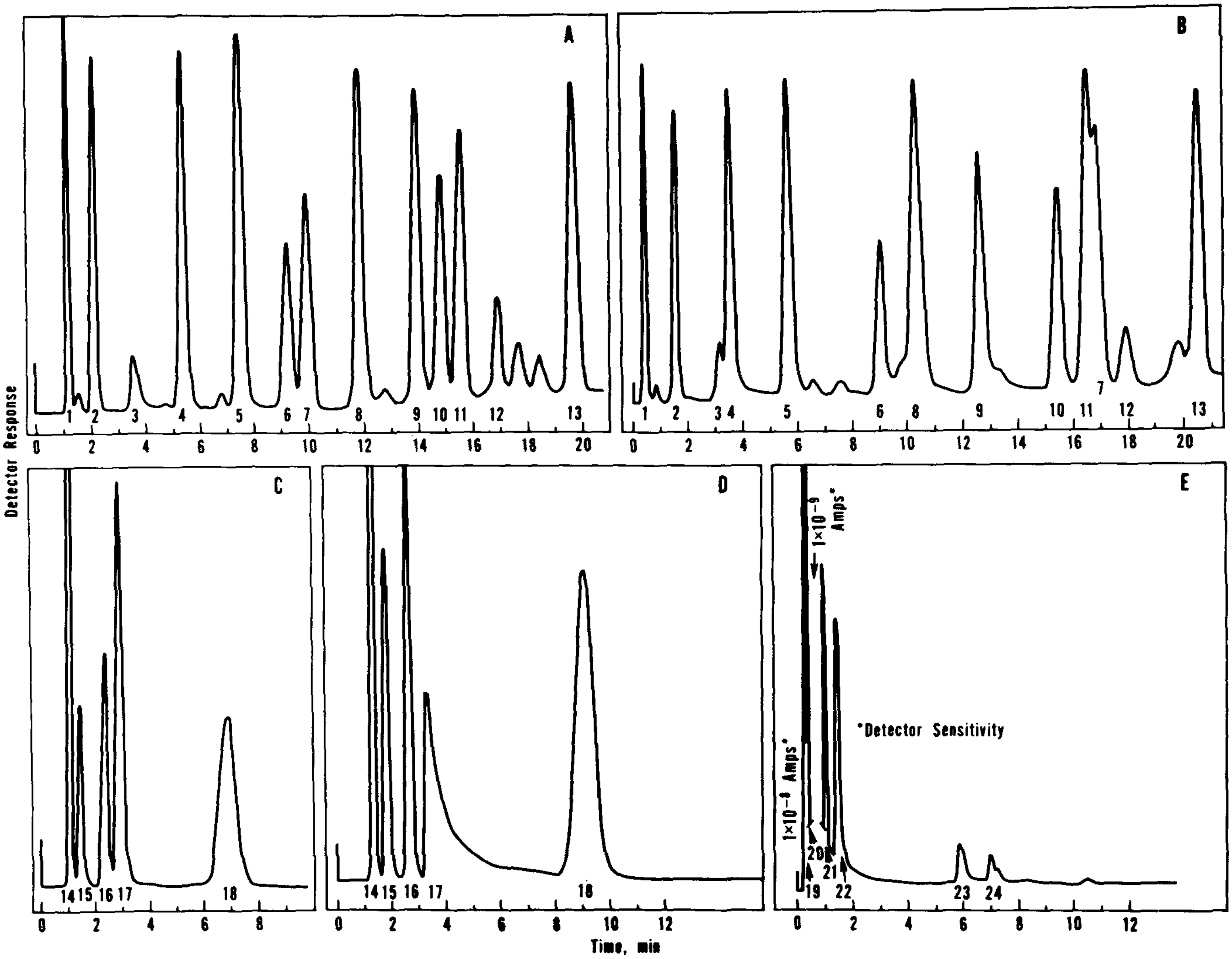

FIG. 3. Chromatograms on crosslinked-stationary-phase packings. Gas chromatography conditions are: temperature program conditions 100-220 C at 6 C/min and isothermal conditions at 100 C, all with 45 cc/min helium flow. Temperature programing (Fig. 3A) and isothermal conditions (Fig. 3C) on crosslinked-ethylene-diamine/methyl 9(10)-formylstearate-pentaerythritol-acetal phase. Temperature programing (Fig. 3B) and isothermal conditions (Fig. 3D) on crosslinked-ethylene-glycol/methyl 9(10)-formylstearate-pentaerythritol-acetal phase. 1, 2-Pentanone; 2, hexanal; 3, heptanal; 4, 1-hexanol; 5, 1-heptanol; 6, dimethyl glutarate; 7, nonanal dimethyl acetal; 8, 1-nonanol; 9, 1-decanol; 10, butyl nonanoate; 11, *n*-hexadecane; 12, methyl azelaaldehydate; 13, methyl tetradecanoate; 14, benzene; 15, 1,4-dioxane; 16, 1-nitropropane; 17, pyridine; and 18, *cis*-hydrindane. Natural gas (Fig. 3E) on crosslinked-40%-dimethyl 1,4-cyclohexanedicarboxylate/50% diethylene-glycol/10%-methyl-9(10)-formylstearate-pentaerythritol-acetal phase. Gas chromatographic conditions were -60 C for 2 min then 5 C/min temperature programing and 40 cc/min helium flow. 19, Methane; 20, ethane; 21, propane; 22, butane; 23, pentane; 24, hexane.

temperatures. All these data indicate that after exposure to crosslinking conditioning in a column, the polymeric coatings derived from MFSPEA are crosslinked. Since polyester and polyamides utilizing methyl azelaaldehydate pentaerythritol acetal produce infusible and insoluble coatings bonded on glass (1), the poly(amide-acetals) and poly(ester-acetals) from MFSPEA are believed also to bond to the support surface via silanol groups.

The DTA trace (Fig. 1) for crosslinked-ethylene-diamine poly(amide-acetal) (starting polymer mp 56.4 C) shows no endo- or exotherms attributed to the coating itself from -50 C to 330 C. Elution data (Fig. 2) for methyl esters on the ethylene diamine poly(amide-acetal) stationary phase under programed temperature conditions also show no discontinuity, which, if present, would indicate a phase transition. Elution data plots were similar for crosslinked-hexamethylene-diamine and crosslinked ethylene-glycol stationary phases. These data indicate that the crosslinked stationary phases are solids from at least -50 C to as high as the decomposition temperature.

The lower temperature GC limit for both crosslinked poly(amide-acetals) and poly(ester-acetals) appears to be at least -60 C where natural gas was chromatographed. Figure 3E shows this separation on crosslinked 10% MFSPEA/40% DMC and 50% diethylene-glycol stationary phase. DTA curves, which were operated to -50 C, showed neither melting nor softening transitions.

Stationary phase stability was measured by TGA and recorder base-line shift with a flame ionization detector. TGA gave gross thermal-stability data and was useful for determining packing loading. However recorder base-line stability from flame ionization detection of column bleed (Table I) was more sensitive than TGA and showed packing bleed between 190 and 220 C, gradually increasing up to 290 C. Hence single column application is possible to at least 190-220 C. TGA showed that the poly(ester-acetal) phase had a potential upper temperature limit of 300 C, except 270 C for the diethylene glycol DMC phase; for the poly(amide-acetals) the upper limit was ca. 325 C. Dual column operation was demonstrated from ca. 190 to 290 C for both poly(ester-acetals) and poly(amide-acetals). However packing life is shortened at these high temperatures.

The capacity ratios for the crosslinked ethylene-glycol poly(ester-acetal) and ethylene-diamine and hexamethylene-diamine poly(amide-acetals) were 19:1, 17:1 and 11:1, respectively. These values were determined for *n*-decane under 100 C, 50 cc/min helium and 0.1 μl sample GC conditions. Should the packing capacity ratio be reduced to one-half of the original value (8), the column should be discarded.

Polarity data determined from McReynolds' constants for the MFSPEA polymers are given in Table II in which various other phases are compared. These sorbents are less polar than the methyl azelaaldehydate poly(ester-acetal). Unlike the methyl azelaaldehydate polymer (7), the methyl 9(10)-formylstearate polymers showed no separation of C_{18} saturated and unsaturated fatty esters. The poly(amide-acetals) are of intermediate polarity since they are close to OV-11 and dilauryl phthalate polarities. The ethylene glycol poly(ester-acetal) is relatively nonpolar since it is similar to OV-3 polarity. However addition of DMC to the poly(ester-acetal) to form a copolymer of 10% MFSPEA, 40% DMC and 50% diethylene glycol greatly increased the crosslinked-stationary phase polarity at the expense of reduced thermal stability. Addition of DMC to the poly-(amide-acetal) to form a copolymer of 10% MFSPEA, 40% DMC and 50% hexamethylene diamine reduced the thermal stability and produced only a slight polarity change.

Resolution data show that the poly(amide-acetal and poly(ester-acetal) packings produce excellent separation for homologous normal hydrocarbons and for consecutive compounds of homologous normal esters and alcohols.

Efficiency data (Table II) show that these sorbents have adequate efficiency for hydrocarbons, alcohol and esters.

Resolution with adequate efficiency was obtained for rather complex mixtures on the crosslinked-ethylenediamine-methyl-9(10)-formylstearate-pentaerythritol packing under programed (Fig. 3A) and isothermal conditions (Fig. 3C). The hexamethylene-diamine packing produced similar resolution for the same mixtures, whereas the ethylene glycol/MFSPEA poly(ester-acetal) had somewhat poorer resolution with tailing of the pyridine peak (Figs. 3B and 3D).

Retention data are given in Table II for the analysis of these mixtures on all five sorbents. The poly(ester-acetals) show some changes in retention position compared to the same compounds on poly(amide acetals).

Crosslinked polymers and copolymers from the condensation products of ethylene diamine, hexamethylene diamine, ethylene glycol and dimethyl 1,4-cyclohexanedicarboxylate with MFSPEA produce solid stationary phases that are useful over a wide temperature range and that are good for compounds of varying polarities. Such sorbents not only avoid the problems of freezing, viscosity and bleed of liquid phases (15), but also have higher thermal stability than liquid phases bonded to supports (16). Unlike crosslinked polystyrene beads, our crosslinked polymers are recommended for compounds above carbon number six (17), and they avoid the long retention times and tailing for polar compounds on adsorbents such as silica gel.

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