# Poly(Amide-Acetals) and Poly(Ester-Acetals) from Polyol Acetals of Methyl (9(10)-Formylstearate: Preparation and Physical Characterization[1]

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## ABSTRACT

Condensation polymers were prepared from the pentaerythritol acetal of methyl 9(10)-formylstearate by reaction with diamines and with ethylene glycol. The glycerol acetal was self-condensed to a poly(ester-acetal) and also copolymerized with caprolactam. A novel step growth, addition polymerization was carried out with ethylene bis[9(10)-methoxymethylenestearate] and pentaerythritol. Physical and spectral (infrared and nuclear magnetic resonance) properties of the various products were determined. In general, the long $C_8$-$C_9$ side chains in the polymers of the pentaerythritol acetal of methyl 9(10)-formylstearate reduced crystallinity to such a degree that, unlike polymers from methyl azelaaldehydate pentaerythritol acetal, they were soluble in the more ordinary solvents, e.g., chloroform and tetrahydrofuran.

## INTRODUCTION

When reviewed 5-10 years ago, the literature was sparse on polyspiroketals, polyspiroacetals, and on polyspiroacetals containing a second type of functionality in the polymer chain, e.g., poly(ester-acetals) (1,2). Today, such polymers are being reported with greater frequency, mainly in patents concerned with such applications as unsaturated polyester resins (3); engineering thermoplastics, films, and fibers (4-6); electrical insulating varnish (7); polyurethane coatings (8); and printing ink binders (9). Potential applications have been reported also for various bifunctional spiroacetal compounds, e.g., spiroacetal diamines as crosslinking agents for epoxy resins (10-12) and sulfur-containing spiroacetals as stabilizers for polyethylene (13).

Characteristically, polyspiroacetals crosslink at high temperatures in the presence of a catalyst (1,14,15). Advantage has been taken of this property for such potential uses as bonded, transparent glass coatings (16) and bonded, polar stationary phases for gas liquid chromatgraphy (GLC) (17,18). Polyspiroacetals have been crosslinked also through free hydroxyl groups when dipentaerythritol is present in the polymer, and such systems have been used as thermosetting aqueous dispersions for coatings and wire enamels (19-24).

Much of the patent literature on polyspiroacetals is based on derivatives from pentaerythritol acetal of acrolein (e.g., 25-28), whereas previous work at the Northern Laboratory has been conducted on acetals of methyl azelaaldehydate (MAZ). Now, methyl 9(10)-formylstearate (MFS) has become available by a selective hydroformylation procedure and its acetals have structural properties different from those of acrolein or MAZ (29,30). Because the $C_8$ or $C_9$ alkyl side chain in MFS was expected to have a considerable effect on polymer crystallinity, solubility, and other properties, we investigated the preparation and properties of poly(ester-acetals) and poly(amide-acetals) from pentaerythritol and glycerol acetals of this aldehyde ester (Figs. 1 and 2). Further, we investigated a novel solution polymerization based on either a bis(enol ether) or a bis(dimethyl acetal) that produces a poly(ester-acetal) or poly (amide-acetal) with the same type of repeating structural unit.

## EXPERIMENTAL PROCEDURES

Methods of preparing MFS; its pentaerythritol acetal (MFSPA); its dimethyl acetal (MFSDMA); and the enol ether, methyl 9(10)-methoxymethylenestearate, (MFSMEE) were published earlier (29-31). For this investigation, MFSPA was prepared from previously distilled MFSDMA by the transacetalation procedure, but crude MFSPA was purified on a column of neutral alumina as reported earlier

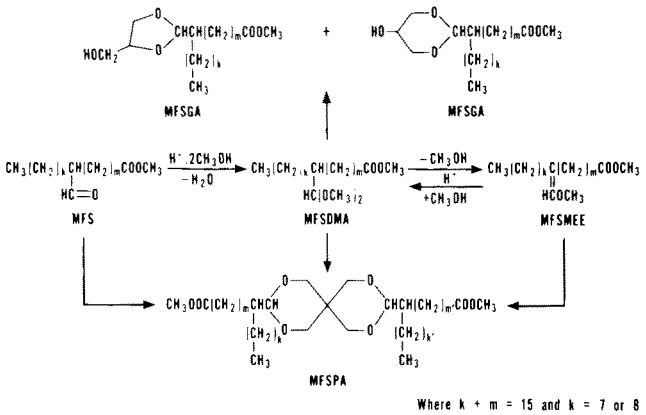


FIG. 1. Ester acetals and enol ether from methyl 9(10)-formylstearate (MFS); MFSDMA is the dimethyl acetal of MFS; MFSGA, the glycerol acetal; MFSMEE, the enol ether of MFSDMA; and MFSPA, the pentaerythritol acetal.

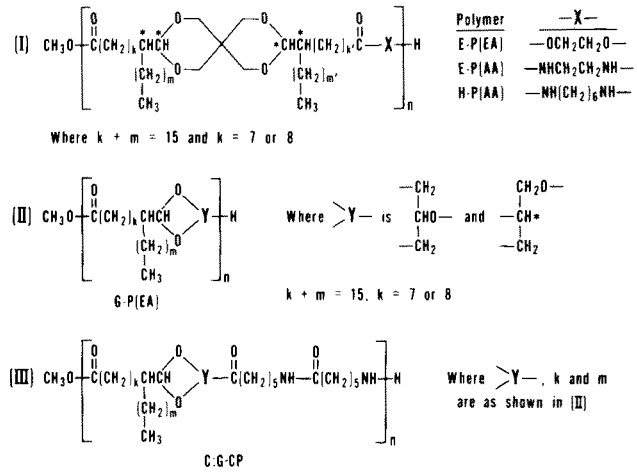


FIG. 2. Polymer structures: (I) Poly(ester-acetal) or poly(amide-acetal) from polycondensation of the pentaerythritol acetal of methyl 9(10)-formylstearate with glycol or diamine; (II) poly(ester-acetal) from self-condensation of the glycerol acetal of methyl 9(10)-formylstearate; and (III) poly(ester-amide-acetal) copolymer (C:G-CP) from polycondensation of caprolactam-MFSGA (2:1 molar ratio). Asterisks indicate chiral carbons. E = Ethylene, H = hexamethylene, G = glycerol.

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(31) with the acetalation or enol ether procedure. Pentaerythritol (mp 258-260 C), ethylene glycol (chromatoquality), ϵ-caprolactam (mp 68-70 C), ethylenediamine (98-100%), hexamethylenediamine (mp 39-41 C; 96.8% by titration), *p*-toluenesulfonic acid monohydrate (mp 104-106 C), and calcium oxide (reagent, powder) were purchased from Matheson, Coleman & Bell (Norwood, OH). The glycerol (analyzed; Fisher Scientific Co., Pittsburgh, PA) was distilled before use, and potassium acid sulfate was fused and pulverized. Neutral alumina (Fisher Scientific) was freshly activated before use.

### Analytical Methods

Chromatographic and thermal methods previously described for MFS and its acetal derivatives (31), except the glycerol acetal (MFSGA), were followed where applicable for polymeric products. For GLC of MFSGA, a 10-50 mg sample was treated for 5 min at room temperature with 0.5 ml of bis(trimethylsilyl)trifluoroacetamide. Conditions for GLC of silylated MFSGA were the same as for other MFS acetals, except temperature programming of the column of JXR (a methyl silicone packing) was 150-300 C at 10 C/min and injection port temperature was 290 C. Silylated MFSGA had a 12.8 min retention as compared to 9.5 min for MFSDMA. Conditions for thermomechanical analysis (TMA) with a Du Pont 940 module were penetration mode, 5.0 g probe loading, 5 C/min heating rate, and 0.02 mv/in. sensitivity. Samples (ca. 3 mm diameter, 1 mm thick) were cooled in liquid nitrogen and heated in air. Nuclear magnetic resonance (NMR) spectra were made by a Varian HA-100 instrument with tetramethylsilane as internal reference; infrared (IR) absorption spectra were recorded with a Perkin-Elmer Model 621 grating spectrophotometer. Number-average mol wts ($\bar{M}_n$) were determined by vapor pressure osmometry on chloroform solutions.

### Methyl 9(10)-Formylstearate Glycerol Acetal, MFSGA

MFSGA was prepared from MFSDMA (99+% by GLC), 37.3 g (0.100 mole), by transacetalation (32) with glycerol, 9.7 g (0.105 mole), and with sulfuric acid (0.04 ml) as catalyst. Reaction conditions were 110-114 C at 15 mm for 5 hr. The clear, colorless liquid product weighed 38.5 g.

Analysis calculated for $C_{23}H_{44}O_5$: C, 68.96; H, 11.07. Found: C, 68.72; H, 10.83. Calculated mol wt: 400.6 Found: 418.5.

By TMA: softened (melted) at -74.8 C. Analysis (GLC): 98% MFSGA, 2% MFSDMA. IR (neat): 3650-3140 $cm^{-1}$ (associated OH stretch, medium), 1740 $cm^{-1}$ (ester C=O, strong) and a series of medium intensity bands at 1235 $cm^{-1}$, 1192 $cm^{-1}$, 1160-1145 $cm^{-1}$ (strongest), 1115-1102 $cm^{-1}$, 1038 $cm^{-1}$, and 978 $cm^{-1}$ (weakest) for C-O-C stretching of the acetal and ester groups. NMR ($CDCl_3$): δ 0.86 t (terminal $CH_3$), δ 1.28 br s ($CH_2$ chain), δ 2.26 t ($CH_2$-C(=O)-), δ 3.60 s (-C(=O)-O-$CH_3$), δ 4.8 d (O-CH-O).

### Ethylene bis[9(10)-Methoxymethylenestearate], E-B(MMS)

MFSMEE, 16.0 g (0.047 mole), was transesterified with 1.47 g (0.024 mole) of ethylene glycol in the presence of sodium methoxide, 0.06 g. The reaction mixture was heated at 100-115 C and 70 mm for 10 hr. It was cooled and stirred and was neutralized with acetic acid. Then it was dissolved in $CH_2Cl_2$, washed 3 times, dried, and filtered. Solvent removal left a clear, pale yellow residue, which was redissolved in 20 ml hexane, stirred with 1.5 g activated charcoal, and transferred to a chromatographic column containing 19 g of neutral alumina (80-200 mesh). After slight nitrogen pressure was applied, effluent was collected. The column was washed with 40 ml of hexane. When solvent was removed from the collected effluent and washings, a clear, colorless liquid was left. Thin layer chromatography (TLC) showed only trace impurities.

Analysis calculated for $C_{42}H_{78}O_6$: C, 74.29; H, 11.58. Found: C, 74.14; H, 11.76.

IR and NMR spectra were consistent with the expected structure. IR (neat): 1740 $cm^{-1}$ (ester C=O), 1675 $cm^{-1}$ (C=C of enol ether) and a series of bands at 1200 $cm^{-1}$, 1155 $cm^{-1}$, 1135 $cm^{-1}$ (strongest), and 1099 $cm^{-1}$ (weakest) from ester and ether C-O-C stretching. NMR ($CDCl_3$): δ 5.69 s (>C=C$\underline{H}$OCH$_3$); δ 4.22 s (-C(=O)-O$\underline{CH_2}$-$\underline{CH_2}$-O-C(=O)-); δ 3.63 s [$\underline{CH_3}$O-C(=O)-(impurity)]; δ 3.45 s ($\underline{CH_3}$OCH=C<); and δ 2.29 t (-$\underline{CH_2}$C(=O)-O-).

### Ethylene N,N′-bis[9(10)-Dimethoxymethylstearamide], E-B(DSAM)

MFSDMA, 37.4 g (0.100 mole), and sodium methoxide, 0.35 g, were added to a polymer pressure bottle (Lab Glass, Inc., Vineland, NJ) previously flushed with dry nitrogen. A stirring bar was added, and the bottle was sealed with a Neoprene gasket and pressure cap, which contained 2 holes for injection. The bottle was evacuated to 160 mm via a syringe needle. Ethylenediamine, 3.05 g (0.100 equivalent), was injected. The polymer bottle, shielded by a metal grid, was heated in an oil bath, and the reaction mixture was stirred magnetically. The bath temperature was maintained for 8 hr at 190-205 C. After the bottle was cooled, 0.35 ml of acetic acid was injected, and the yellow solution was stirred for 10 min. The mixture was transferred to a separatory funnel with 50 ml each of water and methylene chloride. Saturated sodium chloride was added to aid phase separation after shaking the mixture. The organic phase was washed 3 times, dried, and then filtered through 40 g of neutral alumina. Solvent was removed to get 29.5 g of yellow wax. IR (neat): 3292 $cm^{-1}$ (amide NH, medium), 3090 $cm^{-1}$ (amide NH, weak), 1741 $cm^{-1}$ (ester C=O impurity, weak), 1637 $cm^{-1}$ (amide I, strong), 1555 $cm^{-1}$ (amide II, medium), 1240 $cm^{-1}$ (secondary amide bending-stretching, medium to weak) and a series of bands at 1188 $cm^{-1}$, 1112 $cm^{-1}$ (strongest), 1073 $cm^{-1}$, 1054 $cm^{-1}$, and 961 $cm^{-1}$ from C-O-C stretching.

### Ethylene Poly(ester-acetal), E-P(EA)

*Method A:* MFSPA, 10.0 g (0.0133 mole), ethylene glycol, 1.66 g (0.0266 mole), and calcium oxide, 0.3 g, were heated in a nitrogen atmosphere at 190-200 C (Woods metal bath temperature) and at atmospheric pressure for 2 hr. Then the pressure was reduced, and polymerization was continued as follows: 175-185 C (190-200 C bath temperature)/70 mm, 1 hr; 185-200 C (200-220 C)/30 mm, 1 hr; 205-210 C (220-230 C)/6-2 mm, 1 hr; and 205 C (230 C)/0.25 mm, 1.5 hr. The crude polymer was dissolved in hot chloroform and filtered (a few small particles of gelled polymer collected on the filter). The clear, colorless filtrate was concentrated, and this syrupy concentrate was added dropwise to a liter of cold vigorously stirred methanol. The cloudy methanol was decanted and filtered, and the gummy precipitate was washed, dissolved in chloroform, and transferred to a resin flask. Solvent was removed initially on a rotary evaporator and ultimately in a vacuum oven to get a colorless, transparent gum [Table I: E-P(EA); $\bar{M}_n$ 7160]. IR (neat): 3600-3100 $cm^{-1}$ (-OH end group, medium-weak), 1738 $cm^{-1}$ (ester C=O, strong) and a series of bands at 1242 $cm^{-1}$, 1197 $cm^{-1}$, 1162 $cm^{-1}$ (strongest), 1088 $cm^{-1}$, 1042 $cm^{-1}$, 1025 $cm^{-1}$, 988 $cm^{-1}$, 950 $cm^{-1}$, and 913 $cm^{-1}$ characteristic for C-O-C stretching of acetal and ester groups. NMR ($CDCl_3$): δ 4.23 s (-$\underline{CH_2}$O-C(=O)-) and 2.28 t (-CH$_2$$\underline{CH_2}$-C(=O)-).

TABLE I

Condensation Polymers from Methyl 9(10)-Formylstearate Pentaerythritol or Glycerol Acetals

| Polymer[a] | Empirical formula | Structure[b] | $\overline{M}_n$[c] | n[d] | Carbon (%) | | Hydrogen (%) | | Nitrogen (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calculated | Found | Calculated | Found | Calculated | Found |
| E-P(EA) | $CH_3O[C_{45}H_{82}O_8]_nH$ | I | 7,160 | 9.49 | 71.86 | 70.92 | 11.02 | 10.97 | --- | --- |
| E-P(AA) | $CH_3O[C_{45}H_{84}O_6N_2]_nH$ | I | 6,200 | 8.23 | 71.96 | 70.87 | 11.31 | 10.75 | 3.72 | 3.55 |
| | | | 7,170 | 9.52 | 71.99 | 70.78 | 11.31 | 10.94 | 3.72 | 3.55 |
| | | | 11,630 | 15.48 | 72.03 | 71.52 | 11.31 | 11.23 | 3.73 | 3.86 |
| H-P(AA) | $CH_3O[C_{49}H_{92}O_6N_2]_nH$ | I | 7,160 | 8.85 | 72.92 | 72.34 | 11.52 | 11.42 | 3.46 | 3.26 |
| | | | 10,200 | 12.60 | 72.96 | 72.72 | 11.52 | 11.72 | 3.47 | 3.31 |
| G-P(EA) | $CH_3O[C_{22}H_{40}O_4]_nH$ | II | 1,470 | 3.90 | 70.95 | 70.99 | 10.98 | 11.06 | --- | --- |
| C:G-CP | $CH_3O[C_{34}H_{62}O_6N_2]_nH$ | III | 2,340 | 3.88 | 68.22 | 68.03 | 10.54 | 10.80 | 4.65 | 4.15 |

[a]E = Ethylene, H = hexamethylene, G = glycerol, C = caprolactam, P(EA) = poly(ester-acetal), P(AA) = poly(amide-acetal), CP = copolymer. For example, E-P(EA) = ethylene poly(ester-acetal).

[b]As shown in Figure 2.

[c]$\overline{M}_n$ = Number-average mol wt.

[d]n = Degree of polymerization or number of repeating units (cf. Fig. 1).

*Method B:* Pentaerythritol, 1.00 g (0.00736 mole), and $KHSO_4$, 0.1 g, were added to 15 ml of dioxane in a 3-necked flask fitted with a nitrogen capillary, dropping funnel, and a distillation head. A nitrogen atmosphere was maintained, and a solution of E-B(MMS), 5.00 g (0.00736 mole), in 10 ml of dioxane was added to the funnel. The pentaerythritol-dioxane mixture was heated until dioxane was refluxing before the E-B(MMS) solution was added slowly (ca. 0.5 hr). Refluxing was continued 6 hr with intermittent distillation during the last 3.5 hr. The reaction solution was decanted and filtered; collected catalyst was washed with a little chloroform. The clear, colorless filtrate was shaken with potassium carbonate, refiltered, and concentrated. The concentrate was added dropwise to a liter of vigorously stirred, cold methanol to get a white precipitate. After the methanol was decanted and filtered, the precipitate was washed several times with methanol. Then the precipitate was dissolved and transferred with ether to an evaporating dish. Solvent was removed ultimately in vacuo at 100 C to get 4.4 g of highly viscous colorless liquid.

Analysis calculated for $CH_3O[C_{45}H_{82}O_8]_nH$ (for n = 3.7; $M_n$ = 3430): C, 71.58; H, 11.01. Found: C, 71.92; H, 11.12. Except for the absence of an -OH band at 3600-3100 $cm^{-1}$ and the presence of a shoulder at 730 $cm^{-1}$ on the band at 720 $cm^{-1}$, the IR spectrum was identical to that of E-P(EA) from method A (Table I). The NMR spectrum was also identical except for a small resonance at δ 3.63(s) for the $\underline{CH_3}O\text{-}\overset{O}{\overset{\|}{C}}$- end group.

### Ethylene Poly(amide-acetal), E-P(AA)

*Method A:* MFSPA, 30.2 g (0.0401 mole), ethylenediamine, 2.69 g (0.0448 mole), and CaO, 0.05 g, were added to a stainless steel rocker type autoclave previously flushed with nitrogen. The autoclave was sealed and heated to 190 C for 3 hr. A clear, yellow prepolymer was transferred to a resin flask by 4 repetitive extractions with hot $CHCl_3$ (ca. 200 ml total). Solvent was removed on a rotary evaporator, and polymerization was continued in the resin flask, fitted with a nitrogen capillary, as follows: 190 C (bath temperature)/70 mm, 1 hr; 190-220 C/4 mm, 2 hr; and 240-250 C/0.05 mm, 5 hr. Crude polymer was dissolved in hot chloroform and filtered. The clear filtrate was concentrated and then precipitated in 1500 ml of cold methanol as previously described. The brown, sticky precipitate was redissolved with chloroform for transfer to a Teflon coated evaporating dish. Ultimately, when solvent was removed at 120 C/0.2 mm, a light tan resin resulted [Table I: E-P(AA); $M_n$ 6200] which weighed 23.1 g. IR (neat): 3285 $cm^{-1}$ (amide NH; medium), 3065 $cm^{-1}$ (amide NH, weak), 1738 $cm^{-1}$ (ester C=O end group, moderately weak), 1638 $cm^{-1}$ (amide I, moderately strong), 1542 $cm^{-1}$ (amide II, medium), 1240 $cm^{-1}$ (secondary amide bending stretching, moderately weak), and a band series at 1195 $cm^{-1}$, 1160 $cm^{-1}$ (strongest), 1118 $cm^{-1}$ (shoulder), 1085 $cm^{-1}$, 1040 $cm^{-1}$, 1022 $cm^{-1}$, 983 $cm^{-1}$, 948 $cm^{-1}$, and 910 $cm^{-1}$ (weakest), due to C-O-C stretching of acetal and ester groups. NMR ($CDCl_3$): δ 6.70-6.30 br s ($-\underline{NH}\text{-}\overset{O}{\overset{\|}{C}}$=O); δ 3.40-3.30 br s ($-\underline{CH_2}\text{-NH-}\overset{O}{\overset{\|}{C}}$=O); and δ 2.15 t ($-CH_2\underline{CH_2}\text{-}\overset{O}{\overset{\|}{C}}\text{-NH-}$).

Additional alcohol- and water-soluble fractions were recovered as follows: 1.8 g of precipitate from addition of methanol concentrate to 500 ml of water and 3.6 g of residue from evaporation of the aqueous filtrate. IR (neat) revealed no structural differences in these fractions other than variations in relative intensities of amide and ester bands.

Various polymerization conditions gave polymers with different $\overline{M}_n$ (Table I). For example, E-P(AA) with $\overline{M}_n$ = 11,630 was obtained by essentially the same procedure; except after precondensation of 10.0 g MFSPA, 1.10 g ethylenediamine, and 0.03 g CaO, the prepolymer was filtered, 0.03 g additional CaO was added, and polymerization was continued in a resin flask at: 190-200 C (bath temperature)/90 mm, 1 hr; 200-225 C/25-13 mm, 2 hr; and 230-245 C/0.1 mm, 3 hr.

*Method B:* Pentaerythritol, 0.919 g (0.00645 mole); dioxane, 15 ml; and *p*-toluenesulfonic acid monohydrate, 0.104 g, were added to a flask equipped with nitrogen capillary, dropping funnel, and distillation head. The funnel contained E-B(DSAM), 5.00 g (0.00645 mole) in ca. 10 ml of 1:1 dioxane:toluene. A nitrogen atmosphere was maintained, and the flask was heated to reflux the solvent; then the solution in the funnel was added dropwise. After 15 min when addition was finished and pentaerythritol had completely dissolved, the funnel was replaced with a thermometer. The reaction was continued for 5 hr with intermittent distillation; pot temperature gradually increased from 98 to 105 C as vapor temperature climbed to 97 C. Sodium acetate, 0.11 g, in a milliliter of water was added and stirred 5 min. The mixture was filtered, and solvent was removed. The residue dissolved in chloroform was precipitated in cold methanol; the insoluble fraction, 0.7 g, had an IR spectrum like that of E-P(AA) polymer in Table I. An alcohol-soluble fraction, 4.4 g, was recovered from the methanol filtrate.

TABLE II

Thermal Characterization of Methyl 9(10)-Formylstearate Pentaerythritol and Glycerol Acetals and Polymers

| Monomer[a] or polymer[a] | $\bar{M}_n$[b] | Glass transition[c] | | Melting transition[c] | | Thermogravimetry[d] | | |
|---|---|---|---|---|---|---|---|---|
| | | DTA, C | TMA, C | DTA, C | TMA, C | $T_i$, C | $T_{10}$, C | $\frac{\Delta W}{\Delta T}$, $\frac{mg}{C} \times 10^2$ |
| E-P(EA) | 7,160 | --- | --- | --- | -34 | 280 | 396 | -10.3 |
| E-P(EA) | 3,430 | --- | --- | --- | -40 | 260 | 356 | -6.3 |
| E-P(AA) | 11,630 | --- | 4 | 48 | 44 | 316 | 401 | -11.7 |
| | 7,170 | -12 | -14 | 56 | 44 | 316 | 403 | -14.0 |
| | 6,200 | -2 | -8 | 47 | 42 | 314 | 406 | -10.0 |
| H-P(AA) | 10,200 | -8 | -13 | 43 | 47 | 350 | 416 | -10.3 |
| | 7,160 | -6 | -14 | 50 | 44 | 334 | 415 | -18.0 |
| G-P(EA) | 1,470 | --- | --- | --- | -53 | 210 | 321 | -11.3 |
| C:G-CP | 2,340 | --- | -34 | --- | 58 | 233 | 358 | -6.6 |
| MAZGA | --- | --- | --- | --- | --- | 117 | 157 | -7.8 |
| MAZPA | --- | --- | --- | --- | --- | 183 | 244 | -8.0 |
| MFSGA | --- | --- | --- | --- | --- | 173 | 244 | -6.0, -1.8 |
| MFSPA | --- | --- | --- | --- | --- | 163 | 263 | -4.0 |

[a]E = Ethylene, H = hexamethylene, G = glycerol, C = caprolactam, P(EA) = poly(ester acetal), P(AA) = poly(amide-acetal), CP = copolymer. For example, E-P(EA) = ethylene poly(ester-acetal). MAZGA = Glycerol acetal of methyl azelaaldehydate (MAZ) and MAZPA = pentaerythritol acetal of MAZ (Figs. 1 and 2 and Table I). MFSGA = Glycerol acetal of methyl 9(10)-formylstearate (MFS) and MFSPA = pentaerythritol acetal of MFS.

[b]$\bar{M}_n$ = Number-average mol wt.

[c]DTA = Differential thermal analysis; TMA = thermomechanical analysis.

[d]$T_i$ = Temperatures at initial wt loss ($N_2$), $T_{10}$ = temperature at 10% wt loss ($N_2$), and $\Delta W/\Delta T$ = linear decomposition rate (cf. Fig. 3). Heating rate: 5 C/min.

### Hexamethylene Poly(amide-acetal), H-P(AA)

Polycondensation of MFSPA, 10.1 g (0.0134 mole), with hexamethylenediamine, 1.69 g (0.0141 mole), in the presence of CaO, 0.03 g, was achieved with the following reaction conditions: 185-195 C (200 C bath temperature)/atmospheric pressure ($N_2$), 1 hr; 200-225 C (210-235 C)/100-15 mm, 3 hr; 200-225 C (225-240 C)/1.0 mm, 1 hr; 225-255 C (240-270 C)/1.0-0.1 mm, 1 hr; and 250 C (270 C)/0.1-0.03 mm, 1.5 hr. Crude polymer was dissolved with $CHCl_3$, filtered, and concentrated. Dropwise addition of concentrate to 750 ml of cold, stirred methanol gave a yellow, sticky precipitate, which was washed and then redissolved for transfer to a smaller container. When solvent was removed in vacuo (ultimately, 225 C/0.1 mm), light yellow H-P(AA) of $\bar{M}_n$ 10,200 resulted (Table I). IR (neat): 3285 $cm^{-1}$ (amide NH, medium), 3075 $cm^{-1}$ (amide NH, weak), 1740 $cm^{-1}$ (ester C=O end group, weak), 1640 $cm^{-1}$ (amide I, strong), 1545 $cm^{-1}$ (amide II, medium), 1240 $cm^{-1}$ (secondary amide bending-stretching, moderately weak) and a series at 1197 $cm^{-1}$, 1162 $cm^{-1}$ (strongest), 1118 $cm^{-1}$, 1085 $cm^{-1}$, 1040 $cm^{-1}$, 1023 $cm^{-1}$, 985 $cm^{-1}$, 948 $cm^{-1}$, and 910 $cm^{-1}$ (weakest) for C-O-C stretching due to acetal and ester groups. NMR ($CDCl_3$): δ 5.60-5.90 br s (-NH-C(=O)-); δ 3.20-3.30 (-$CH_2$-NH-C(=O)-); and δ 2.15 t (-NH-C(=O)-$CH_2$-$CH_2$-$CH_2$-). Varying polymerization conditions also gave an H-P(AA) with $\bar{M}_n$ = 7160 (Table I).

### Glycerol Poly(ester-acetal), G-P(EA)

MFSGA, 5.00 g (0.0125 mole), and CaO, 0.05 g, were added to a distilling flask fitted with a nitrogen capillary. Conditions during polymerization were 240-285 C (bath temperature)/40-32 mm, 4 hr; 285 C/0.05 mm, 1 hr. The distillate, collected in a dry ice trap, weighed 0.4 g (98%). The crude polymer was dissolved with $CHCl_3$ and filtered. Removal of solvent on a rotary evaporator left 4.6 g of light yellow, very viscous liquid [G-P(EA), Table I]. IR (neat): 3660-3160 $cm^{-1}$ (associated OH stretching, weak), 1740 $cm^{-1}$ (ester C=O, strong) and a series of bands of medium intensity at 1235 $cm^{-1}$, 1148 $cm^{-1}$ (strongest), 1110 $cm^{-1}$, 1040 $cm^{-1}$, 1010 $cm^{-1}$, and 975 $cm^{-1}$ (weakest) from C-O-C stretching (acetal and ester groups). NMR ($CDCl_3$): δ 2.32 m ($CH_2$-C(=O)-); δ 3.62 s (C(=O)-O-$CH_3$); δ 4.1 m ($CH_2$-O-); δ 4.79 d, J = 3 Hz (-O-CH-O-); and δ 4.86 d, J = 3 Hz (-O-CH-O-).

### Caprolactam-MFSGA (2:1) Copolymer, C:G-CP

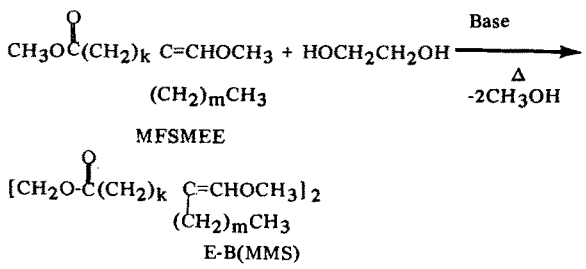
MFSGA, 4.00 g (0.010 mole), was copolymerized with ϵ-caprolactam, 2.26 g (0.020 mole), in a distillation flask fitted with a nitrogen capillary; 6-aminohexanoic acid, 0.1 g, was added for catalysis. Polymerization conditions were 255-264 C (bath temperature)/atmospheric pressure ($N_2$), 13.5 hr; then after cooling to 120 C, bath temperature was gradually increased to 230 C as the flask was evacuated to 0.03 mm during a 2-hr interval. The crude polymer dissolved in chloroform was filtered. Solvent removal left 6.2 g of resin (Table I, C:G-CP). IR (neat): 3290 $cm^{-1}$ (amide NH, moderately strong), 3060 $cm^{-1}$ (amide NH, weak), 1735 $cm^{-1}$ (ester C=O, moderately strong), 1635 $cm^{-1}$ (amide I, strong), 1540 $cm^{-1}$ (amide II, moderately strong), 1260 $cm^{-1}$ (secondary amide bending-stretching, medium), and a series of C-O-C stretching modes at 1230 $cm^{-1}$, 1198 $cm^{-1}$, 1155 $cm^{-1}$ (strongest), 1115-1102 $cm^{-1}$, and 970 $cm^{-1}$ (weakest) for acetal and ester groups. Three unidentified weak bands, possibly from deformation and skeletal modes of the secondary amide, were also observed at 685 $cm^{-1}$, 575 $cm^{-1}$, and 518 $cm^{-1}$. NMR ($CDCl_3$): δ 2.2 ($CH_2$-C(=O)); δ 3.2 ($CH_2$-N-); δ 3.62 (C(=O)-O-$CH_3$); δ 4.1 ($CH_2$-O-); and δ 4.8 (-O-CH-O-).

## RESULTS

### Monomer Preparation

Although the preparation and characterization of MFSPA have been reported earlier (31), those for MFSGA,

E-B(MMS), and E-B(DSAM) have not. MFSGA, like MFSPA, was prepared by transacetalation of distilled MFSDMA. Previous experience indicated that addition of an alcohol to enol ether MFSMEE was a more efficient route to the higher acetals of MFS than either direct acetalation of MFS or transacetalation of MFSDMA (31). Consequently, bis(enol ether) E-B(MMS) was prepared by transesterification of MFSMEE with ethylene glycol:




(I)

where k + m = 15 and k = 7 or 8

In a similar manner, the ethylene bis(acetal amide) E-B(DSAM) was prepared by base catalyzed condensation of MFSDMA with ethylenediamine.

Analyses of MSFPA, E-B(MMS), and E-B(DSAM) were limited to qualitative TLC and spectroscopy (IR and NMR); however, MFSGA was silylated and then analyzed semi-quantitatively by GLC. Purities of the monomers by these methods were deemed adequate for their polymerization. In addition, microanalyses, mol wts, and spectra were all consistent with proposed structures.

Like MFSPA, pure MFSGA is a highly viscous, colorless, and transparent liquid; E-B(MMS) is a colorless, transparent fluid, but E-B(DSAM) is a yellow wax. The NMR spectrum of E-B(MMS) is similar to that of MFSMEE (31) except carbomethoxy resonance at δ 3.63 is absent, and there is a singlet at δ 4.22 corresponding to the 4 protons of the ethylene glycol moiety. Thermal stabilities of these monomers, as determined by thermogravimetry, are compared in Table II.

### Polymer Preparation

High temperature polycondensations of MFSPA with ethylene glycol or ethylenediamine produced a linear poly(ester-acetal) or poly(amide-acetal), respectively [Fig. 2-I; Table I, E-P(EA) or E-P(AA)]. Similarly, polycondensation with hexamethylenediamine instead of ethylenediamine produced H-P(AA) of Table I. These polymers all have the spiroacetal group (-CH  CH-) in the main chain, together with the respective ester or amide group, and a $C_8$ or $C_9$ alkyl side chain alpha to the acetal group. All these condensation polymerizations were catalyzed with <0.5% calcium oxide, since previous experience showed that higher percentages result in dark, high ash polymers containing considerable amounts of associated carboxylate (33). Different mol wts in Table I may be attributed to slightly different polymerization conditions and times and also to differences in purity or composition of starting materials; however, no effort was made to study and control these variables. Different polymerization conditions yielded E-P(AA) of $\overline{M}_n$ 6200 to 11,630 (Table I). For characterization purposes, polymers with higher mol wts were desired; consequently, the spiroacetal polymers were all precipitated in methanol. Lower mol wt fractions were recovered from the methanol but were not characterized other than by IR, which indicated only a higher proportion of end groups than observed for the methanol-insoluble fractions. It was expeditious to precondense the low boiling (bp 117 C) ethylenediamine with MFSPA in an autoclave at 190 C and endogenous pressure. Although prepolymerization in an autoclave was not necessary with hexamethylenediamine and ethylene glycol, initial polymerization with ethylene glycol was performed with a 2:1 mole ratio of glycol to MFSPA at atmospheric pressure. Also, a lower polymerization temperature (<230 C) and less time used for polyamide polymerizations appeared necessary for the polyester to avoid gelation.

In an alternate, novel method of polymerization, bis(enol ether) E-B(MMS) was polymerized by a step growth addition of pentaerythritol in acidic, refluxing dioxane to produce an E-P(EA) with an $\overline{M}_n$ of 3400 after precipitation. E-P(AA) was likewise prepared by an alternate polymerization method in which the bis(dimethyl acetal) E-B(DSAM) was added to an acidic, refluxing solution of pentaerythritol. However, polymerization with E-B(DSAM) was of the condensation type and proceeded via transacetalation; the yield of polymer was much lower by this method. The IR absorption spectra of these 2 polymers from solution polymerization were identical with the respective spectra of E-P(EA) or E-P(AA) polymers by conventional polycondensation, method A, except that absorptions assigned to respective end groups, such as methyl ester, enol ether, or hydroxyl, were absent or relatively much weaker. The physical state and appearance of these alternate polymers were also similar to their respective condensation polymers, but mol wts were lower.

Because of its hydroxyl group, MFSGA, unlike MFSPA, could be self-condensed to a homopolymer. Thus, polycondensation of MFSGA gave homopolymer G-P(EA) with the analysis given in Table I. IR and NMR spectra were consistent with the structure in Figure 2-II. MFSGA was also copolymerized with caprolactam in a 1:2 molar ratio (C:G-CP), Table I; Fig. 2-III). Unlike previous polymerizations, this one was catalyzed with 6-aminohexanoic acid. C:G-CP has 3 functional groups in the main chain, i.e., cyclic acetal, ester, and amide groups. These glycerol acetal polymers were prepared specifically for evaluation as bonded stationary phases for gas chromatography. Higher mol wts were not desired; hence, the MFSGA polymers were not precipitated, and mol wts were lower than those of the spiroacetals. Further, GLC indicated that MFSGA monomer contained ca. 2% MFSDMA impurity, which would act as a chain stopper.

### Polymer Characterization

All the poly(amide-acetals), including C:G-CP, were tough either yellow or tan resins, which exhibited some resiliency; as thin films the polyamides were transparent, but as thicker materials they were translucent. Unlike H-P(AA), E-P(AA) was slightly tacky to touch and was lower melting (Table II). The poly(ester-acetals), on the other hand, were colorless or nearly so. E-P(EA) from polycondensation was a transparent gum; E-P(EA) by addition polymerization, however, was translucent and more fluid ($M_n$ >6000 vs. $\overline{M}_n$ 3430, respectively). G-P(EA) was also a transparent, highly viscous liquid.

Unlike the polyspiroacetals from methyl azelaaldehydate (MAZ), those derived from MFS, even the polyamides, were readily soluble in ordinary solvents, such as chloroform and tetrahydrofuran (16-18).

All the polyesters had melting points well below room temperature, and their glass transitions could not be determined by differential thermal analysis (DTA) or TMA (Table II). The polyamides had melting transitions in the range 43-56 C and glass transitions in the range +4 to -14 C. Small differences in transition temperatures for specific polymers, as determined by DTA vs. TMA, are attributed to different thermal histories associated with each sample and method. These transition endotherms were difficult to determine because they were broad, shallow, and sensitive to previous thermal history.

As expected, the spiroacetal polyamides showed good

thermal stability in a nitrogen atmosphere and, according to thermogravimetry, were superior to the polyesters and the copolymer (Table II). Figure 3 shows typical thermograms for both monomers and polymers and gives decomposition rates, as well for the linear positions of the curves. As expected, an increase in thermal stability is observed with increased chain length of the diamine. The inferior stability of glycerol acetals is not surprising because the presence of hydroxyl groups is known to accelerate thermal decomposition of polyethers (34). Surprisingly, the glycerol acetal of MFS appeared more stable than that of MAZ; apparently degradation of the MFS spiroacetal, in particular, is retarded. Possibly, crosslinking is occurring at a greater rate, and degradation is less than with the MAZ acetal.

In addition to the analyses and characterizations in Tables I and II, these polymers were characterized spectroscopically. Although characteristic functional group absorptions or resonances are listed under Experimental Procedures, some additional observations concerning the NMR spectra can be given. The polymer spectra have several features in common. Terminal methyl group absorption appears at $\delta$ 0.88(t); the large methylene chain resonance, at $\delta$ 1.25(br s); and triplet absorption pattern typical of methylenes $\alpha$ to the carboxy carbonyl, at $\delta$ 2.15 in the polyamides and at $\delta$ 2.30 in the polyesters. Difference in chemical shifts of the $\alpha$-methylenes is caused by the difference in electronegativity of oxygen and nitrogen. The resonance absorption of the spiroacetal protons is similar for all the spiro compounds and analogous to that observed for MFSPA (31). The polyamides exhibit resonance in the region $\delta$ 3.30-$\delta$ 3.40 attributed to the methylene protons $\alpha$ to nitrogen; the polyesters exhibit absorption at $\delta$ 4.24 due to the methylene protons adjacent to oxygen.

Even though the NMR spectra of MFSGA and G-P(EA) are quite similar, the most noteworthy feature of both is a pair of overlapping doublets at $\delta$ 4.74 and $\delta$ 4.84, J = 3 Hz for MFSGA and $\delta$ 4.79 and $\delta$ 4.86, J = 3 Hz for G-P(EA). These signals are attributed to the acetal proton in a 5-membered ring, which is coupled to only one adjacent proton. A 5-membered ring is indicated by the shift of the doublets (15,31,35). The appearance of 2 overlapping doublets indicates that 2 different isomers of the dioxolanyl acetal may be present. The dioxanyl acetal resonance is probably also present, but resonances of other protons in the $\delta$ 4.2-$\delta$ 4.4 region make this assignment uncertain. The signal of the hydroxyl proton is also too obscure to observe.

### Chromatographic Stationary Phases

Spiroacetal polymers of MFS have been evaluated previously as bonded stationary phases for GLC (18); polyamide phases were more polar than those of polyesters but still not so polar as those of MAZ polyesters (17). A bonded stationary phase of C:G-CP, a poly(amide-ester-acetal), was prepared to determine its polarity. A 20% by wt coating of C:G-CP on 45/60 mesh Chromosorb P(AW) was crosslinked in a 4 ft X 1/8 in. stainless steel column as reported earlier (18). When programmed from 100 to 220 C at 6 C/min with a 45 cc/min flow of He, this column separated well and with good efficiency a mixture of nonpolar to polar compounds. However, this phase was not so polar as that of the homopolymers. For comparison (cf. Table II; ref. 18), the mixture composition and retention indices determined for the stationary phase of C:G-CP were 2-pentanone (681), hexanal (801), heptanal (911), 1-hexanol (1032), 1-heptanol (1138), dimethyl glutarate (1195), nonanal dimethyl acetal (1252), 1-nonanol (1352), 1-decanol (1452), butyl nonanoate (1475), hexadecane (1610), and methyl azelaaldehydate (1711).

## DISCUSSION

The amorphous nature of MFS polymers can be attributed not only to the disorder or entropy effects resulting from $C_8$ and $C_9$ alkyl side chains in the repeating unit, but also to the isomeric complexity of the acetal groups. Preparation of MFS by selective hydroformylation (29) gives 2 positional isomers each with an asymmetric carbon atom, i.e., 4 stereoisomers. Acetalation of MFS with glycerol produces 5- and 6-membered ring isomers, i.e., 1,3-dioxolanyl and 1,3-dioxanyl, and their *cis* and *trans* isomers, as well as another asymmetric carbon. When individual isomers of similar MAZGA polymers were investigated (35,36), each ring isomer influenced the polymer crystallinity differently.

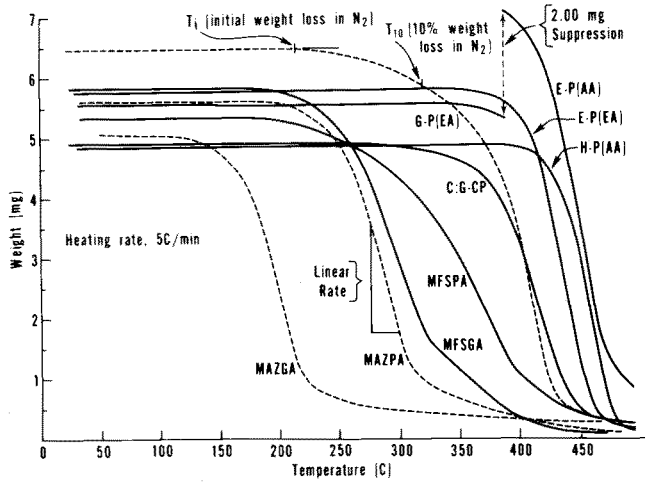



FIG. 3. Typical thermogravimetric curves for monomers and polymers cited in Table II. E = Ethylene, H = hexamethylene, G = glycerol, C = caprolactam, P(EA) = ethylene poly(ester-acetal). MAZGA = Glycerol acetal of methyl azelaaldehydate (MAZ) and MAZPA = pentaerythritol acetal of MAZ (Figs. 1 and 2 and Table I). MFSGA = Glycerol acetal of methyl 9(10)-formylstearate (MFS) and MFSPA = pentaerythritol acetal of MFS.

There is another significant structural difference between MAZ and MFS acetals, e.g., the MFS acetal structure contains an adjacent tertiary hydrogen ($R_1R_2CH$-CH$\langle$O-O-) which the MAZ acetal (R-$CH_2$CH$\langle$O-O-) does not have. This structural difference may account for different chemical properties, such as crosslinking reactivity and thermal stability. Their crosslinking reactivity and bonding to various substrates will be the subject of another paper.

With regard to their transparent, low melting, and amorphous nature, the poly(amide-acetals) of MFS resemble the polyamide of 9(10)-aminomethyloctadecanoic acid (37). This acid, derived by reductive alkylation of ammonia with MFS, confers its transparency and elastomeric property on copolymers with caprolactam or $\omega$-amino acids.

The preparation of spiroacetal monomers and polymers is facilitated by the addition of polyols to MFSMEE and its bis(enol ether) derivatives, such as E-B(MMS), rather than by acetalation or transacetalation procedures, as shown by the better yield of E-P(EA) vs. E-P(AA) in the alternate polymerizations (method B). Polymerization of the bis(enol ether) E-B(MMS) with pentaerythritol (a step growth, addition mechanism) must involve both addition and end group reactions. After addition of hydroxymethyl groups to enol ether double bonds, another hydroxymethyl group undergoes intra-acetalation with the methoxy acetal group and cyclization to stable spiroacetal. A process is now being developed to prepare pure MFSMEE and provide a better monomer for such polymers.

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