Structure, Properties, and Cross-linking Reactions of Poly(ester acetals)

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ABSTRACT: Diester and hydroxy ester monomers containing internal five-, six-, and seven-member acetal rings were prepared and converted into linear polyesters, copolyesters, and copolyamides. The polymers so obtained were characterized for glass temperature, crystallinity, melting point and ring structure. The poly(ester acetals) served as prepolymers for thermosetting polymers cross-linked by ring opening, acetal-interchange reactions with acid catalysts and catalyst-promoter combinations. The effects of acetal ring size, temperature, catalyst and promoter on rate and degree of cross-linking were evaluated.

The work described in this paper is part of a research program, which originated in the Northern Regional Research Laboratory, on the preparation and evaluation of a new family of thermosetting polyesters.[2] These polymers derive their second stage, cross-linking reactivity from the presence of cyclic acetal units in the main chain backbone because such units can be transformed into intermolecular primary bonds by ring-opening polymerization and copolymerization reactions, as discussed in an earlier publication.[2b]

In previously described investigations,[2] particular attention was given to the poly(ester acetals) obtained from monomers prepared by the reaction of methyl azelaaldehydate dimethyl acetal (I) with either pentaerythritol or glycerol. The monomer obtained from the former is a diester containing two six-membered acetal rings (1,3-dioxane units) in a spiro configuration, while the monomer from glycerol is a physical mixture of two ω-hydroxy esters, one with an internal five-membered acetal ring (dioxolane unit) and the other with an internal six-membered acetal ring. Polyesters and copolyesters of the pentaerythritol-based diester monomer were effectively cross-linked with a variety of acidic and metal oxide, acetate and carbonate catalysts in those investigations, but quite high temperatures in the range of 250–270° were required for this purpose.[2b-d] The present investigation was concerned primarily with evaluating the effect of ring size in the internal cyclic acetal units on both the physical properties of the prepolymers and their ease of cross-linking and, secondarily, on evaluating catalyst-promoter combinations for the latter purpose.

Monomers

In all, four different ω-hydroxy ester monomers and three different diester monomers, containing either five-, six- or seven-membered acetal rings, were synthesized from the reaction of I with triols and tetrols, respectively. The precursors involved in these monomer preparations and the designations or abbreviations to be used in this paper for the resulting ester acetal monomers are collected in Table I for ease of reference. All of these monomers were capable of existing as mixtures of *cis–trans* isomers, but only the GA monomer (see Table I for abbreviations) could exist in two different ring forms. Fortunately for quantitative characterization of the latter, the high-resolution nmr spectra of these compounds revealed that the chemical shifts of the acetal protons were a function of ring size and differed characteristically for five- and six-membered cyclic acetal rings. In general, as shown by the data in Table II, the acetal proton in the five-membered dioxolane ring monomers could be found in the range of 285–295 cps downfield from tetramethylsilane (TMS), while the equivalent proton in the six-membered, dioxane-rang monomer resided at 260–275 cps.

All of the monomers in Table I, except one, were prepared from readily available polyols; the exception being the seven-membered, dioxepane-ring monomer for which there was no commercially available tetrol. Four different precursors were prepared and evaluated for conversion into this type of diester momomer; each was obtained by the hydrogenation of a tetracarboxylic dianhydride or its tetraester. The precursor finally chosen for extensive studies and for monomer development investigations was tetramethyl pyromellitate, which on reduction yielded 1,2,4,5-tetrakis(hydroxymethyl)benzene, and the latter was converted into its respective diester monomer, BTA, by reaction with I in the usual manner. The inability to obtain readily and inexpensively an appropriate precursor for a seven-membered ring acetal monomer was most unfortunate because polymers containing this structure were found to be considerably more reactive in ring-opening cross-linking reactions than those having either dioxolane or dioxane rings, and the potential utility of all of these polymers as thermosetting resins is greatly dependent upon their ease of cure. Attempts were also made to prepare amino ester monomers by reacting amino-polyols, such as 2-amino-2-methyl-1,3-propanediol,

(1) Work done in part at Fabric Research Laboratories, Dedham, Mass., under contract to the U. S. Department of Agriculture.

(2) (a) E. H. Pryde, D. J. Moore, H. M. Teeter, and J. C. Cowan, *J. Polym. Sci.*, **58**, 611 (1962); (b) E. H. Pryde, R. A. Awl, H. M. Teeter, and J. C. Cowan, *ibid.*, **59**, 1 (1962); (c) E. H. Pryde, U. S. Patent 3,183,215 (1965); (d) E. H. Pryde, U. S. Patent 3,223,683 (1965); (e) W. R. Miller, E. H. Pryde, and J. C. Cowan, *J. Polym. Sci., Part B*, **3**, 131 (1965); (f) *Chem. Eng. News*, 38 (Dec 26, 1966); (g) R. W. Lenz, R. A. Awl, W. R. Miller, and E. H. Pryde, *J. Polym. Sci., Part A-1*, in press.

TABLE I

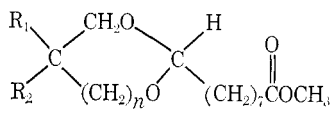
MONOMER PREPARATION AND DESIGNATION

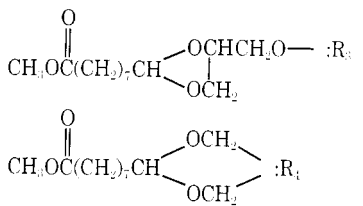
Monomer type	Acetal ring unit	Polyol precursor	Monomer designation
ω-Hydroxy ester	Dioxolane	1,2,6-Hexanetriol	HTA
	Dioxolane or 1,3-dioxane	Glycerol	GA
	1,3-Dioxane	2-Hydroxymethyl-2-methyl-1,3-propanediol[a,b,e]	HMA
	1,3-Dioxane	2-Hydroxymethyl-2-ethyl-1,3-propanediol	HEA
Diester	Dioxolane	Diglycerol	DGA
	1,3-Dioxane	Pentaerythritol[b,c,e]	PEA
	Dioxepane	1,2,4,5-Tetrakis(hydroxymethyl)benzene[d,e]	BTA

[a] For the preparation of related compounds, see W. E. Conrad, B. D. Gesner, L. A. Levasseur, R. F. Murphy, and H. M. Conrad, *J. Org. Chem.*, **26**, 3571 (1961). [b] For the preparation of related compounds, see R. M. Lukes, *ibid.*, **26**, 2515 (1961). [c] For the preparation of related compounds, see J. B. Clements and L. M. Rice, *ibid.*, **24**, 1958 (1959). [d] For the preparation of other dioxepanes, see D. B. Pattison, *ibid.*, **22**, 662 (1957). [e] For the preparation of similar compounds, see C. S. Rondestvedt, Jr., *ibid.*, **26**, 2247 (1961).

TABLE II

CHEMICAL SHIFT VALUES FOR ω-HYDROXY ESTER AND DIESTER ACETAL MONOMERS





Cylic acetal monomer	R_1	R_2	n	Chemical shift of acetal protons, cps
GA–dioxane form	OH	H	1	274
GA–dioxolane form	CH_2OH	H	0	294
DGA	R_3	H	0	285
HMA	CH_2OH	CH_3	1	264
PEA	—— R_4 ——		1	268

with I, but instead of the desired products only fused ring oxazolidine compounds were obtained.[3]

The most surprising finding in the investigation of monomer stereochemistry was the observation of apparent geometric isomers of the spiroacetal monomer, PEA. Early observations on this monomer by mnr analysis indicated that, when PEA was purified by crystallization instead of distillation, two triplet peaks were observed in the acetal proton region of the nmr spectrum, instead of only one triplet as expected for a compound free of geometric isomers. This and other observations based on tlc analysis and melting point behavior (*i.e.*, multiple melting peaks by differential scanning calorimetry) suggested the presence of a minor geometric isomer in some samples of the monomer. However, subsequent attempts to isolate this minor isomer by careful molecular distillation were unsuccessful. A possible structure of this isomer is one in which one of the spiro rings of the chair–chair conformation[4a] contains the heptamethylene carbomethoxy group in an axial position, but this conformation would presumably invert readily to the more stable equatorial form on mild thermal treatment. Indeed mild refluxing under acidic conditions of a monomer sample having a low melting peak at 53° by dsc analysis essentially eliminated this component on subsequent crystallization leaving only the high melting peak at 63°.

The nmr spectrum of the HMA monomer contained two singlet peaks attributable to the methyl group at the 5 position of the 1,3-dioxane ring. These two peaks were found at approximately 41 and 68 cps downfield from TMS, generally in the ratio of 5–10:1 for the area under the higher field peak relative to that of the lower one. It has been reported that methyl groups in the 5 position of a 1,3-dioxane ring show the unusual behavior of having higher shift values in the equatorial position,[4b] so the spectrum for HMA indicates that the principal isomer is one with the ring methyl group equatorial. The hydroxymethyl group, therefore, is preferred in the axial position, possibly because it is stabilized in that position by hydrogen bonding to the ring oxygen atoms,[5] although alkyl groups in the 5 position of a 1,3-dioxane ring also seem to prefer the axial conformation.[6]

(3) J. S. Pierce, C. D. Lunsford, R. W. Raiford, Jr., J. L. Rush and D. W. Riley, *J. Amer. Chem. Soc.*, **73**, 2595 (1951). American Cyanamid Co., British Patent 564,509 (1944).

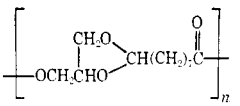
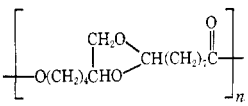
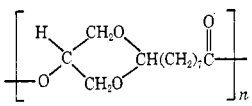
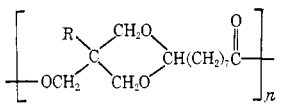
(4) (a) C. H. LeFevre, R. J. W. LeFevre, and M. R. Smith, *J. Chem. Soc.*, 16 (1958); (b) E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 682 (1968).

(5) N. Baggett, M. A. Bukhari, A. B. Foster, J. Lehmann, and J. M. Webber, *J. Chem. Soc.*, 4157 (1963).

(6) E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

TABLE III

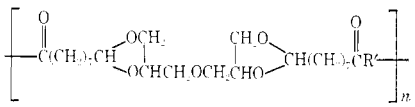
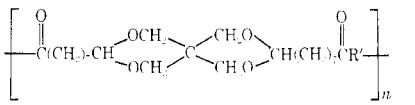
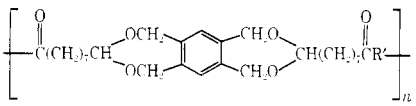
THERMAL PROPERTIES OF LINEAR POLYMERS FROM ω-HYDROXY ESTER MONOMERS[a]

Monomer designation[b]	Polymer repeating unit structure[b]	T_m, °C[c]	T_g, °C[d]
GA-5[e]		54	−35
HTA		23	−44
GA-6 *cis*[e]		122	2
GA-6 *trans*[e]		150	7
HMA (R = CH_3) HEA (R = C_2H_5)		81 Amorphous	−26

[a] Determined by differential thermal analysis and differential scanning calorimetry. [b] Monomer and polymer repeating units are mixtures of *cis* and *trans* isomers unless designated otherwise. [c] Melting point, taken as the peak temperature of melting endotherm in DTA or dsc curve. [d] Glass temperature, taken as the median temperature of the endothermic base-line shift in dta or dsc curve. [e] See ref 2g.

TABLE IV

MELTING POINTS OF LINEAR POLY(ESTER ACETALS) AND POLY(AMIDE ACETALS) FROM DIESTER MONOMERS[a]

Monomer designation[b]	Polymer repeating unit structure[b]	T_m, °C[c] R = OCH_2CH_2O	T_m, °C[c] R = $NH(CH_2)_6NH$
DGA		19	145
PEA		85	186
BTA		42[d]	243

[a] Determined by differential thermal analysis and differential scanning calorimetry. [b] Monomer and polymer repeating units are mixtures of *cis* and *trans* isomers. [c] Melting point, taken as the peak temperature of melting endotherm in dta or dsc curve. [d] T_g of this polymer is 78°; see footnote *d* in Table III.

Polymer Preparation and Characterization

Previous investigations[2g] on reactions of model compounds for the monomers and repeating units in the polymers established the appropriate conditions for carrying out polymerization reactions by ester interchange without ring-opening side reactions which could lead to cross-linking through acetal interchange. These conditions were applied successfully to essentially all polyesterification reactions used for preparing both homopolymers and copolymers. In general two sets of conditions were established; these were (1) the use of $Pb(OAc)_2 \cdot 3H_2O$ as catalyst at 190° for the preparation of low to moderate molecular weight, linear polyesters and (2) the use of CaO as catalyst at 250° and above for moderate to high molecular weights. With one exception, the two types of conditions could be used interchangeably to yield the same polymeric structures, that is, varying only in molecular weight. The one exception was the polymerization of GA monomer which yielded different products by the two different conditions as discussed in a previous publication.[2g]

Linear Homopolymers. Most of the linear poly(ester acetals) and poly(amide acetals) were crystalline, and a compilation of the melting points and glass temperatures, where available, of these homopolymers is given in Tables III and IV. In general, it appears that the *cis* and *trans* repeating units of these polymers can cocrystallize, and this behavior was also observed for most such monomer isomer mixtures.[7] One notable

(7) N. Baggett, J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *J. Chem. Soc.*, 2574 (1960).

exception to this generalization is the polymer from HEA in which the bulky ethyl group apparently induces sufficient steric hindrance to prevent cocrystallization of the geometric isomers.

As with monomer characterization, the best method for characterizing polymers according to acetal repeating unit stereochemistry was by high-resolution nmr spectroscopy. The five- and six-membered ring repeating units were again clearly distinguishable by the chemical shifts of their acetal protons, and in many polymers, the chemical shifts for the axial and equatorial substituents of *cis* and *trans* isomers, respectively, were also resolvable. One notable example of this type of analysis was the estimation of axial and equatorial ring methyl groups in the HMA polymer in the manner discussed above for this monomer.

One of the most interesting nmr spectra was that obtained for the DGA polyamide dissolved in phenol–tetrachloroethane solvent. Unlike most other spectra of either monomers or polymers, all of the peaks of the protons in the acetal ring appeared to be cleanly separated. Tentative assignment of these peaks placed the ring methylene protons as a doublet at 199 cps, the *exo*-methylene protons as a doublet at 214 cps, and the ring tertiary proton as a multiplet at 238 cps. This spectrum was obtained at 80° so that all peaks were probably shifted approximately 10 cps upfield from their normal positions at room temperature.

Linear Copolymers. Most attempts to prepare copolymers were by ester interchange polymerization reactions; hence, the successful preparation of copolymers of cyclic acetal monomers was confined primarily to the use of diester monomers and was not very practical with ω-hydroxy ester monomers. No difficulty was encountered in preparing copolymers of adequate molecular weight under the polymerization conditions described earlier, and a wide variety of compositions were obtained and characterized. Infrared spectroscopy proved to be a reliable method for estimating acetal unit content above the 5 mol % level as discussed in the Experimental Section, and all polymers were characterized with respect to crystallinity, melting point, and glass temperature.

The effect of comonomer composition on these properties is shown in Figure 1 for a typical example, the copolymers obtained from PEA and dimethyl adipate with ethylene glycol. The behavior shown in these curves, a minimum in the T_m curve and a bow-shaped T_g curve, is to be expected for random copolymers. As shown in this figure, the PEA copolymers retain some crystallinity throughout the composition range, which is also true for the BTA copolymers but may not hold for the DGA copolymers. The latter were not crystalline at room temperature, but this behavior might be attributable to a depression of the melting point rather than a lack of crystallizability in the copolymer. This characteristic of the DGA copolymer proved to be of considerable practical importance because the noncrystalline 25 and 50 mol % copolymers obtained from mixtures of this diester and dimethyl adipate with ethylene glycol exhibited the attractive properties of tackiness and pressure-sensitive adhesion.

Two series of copolymers were prepared to evaluate

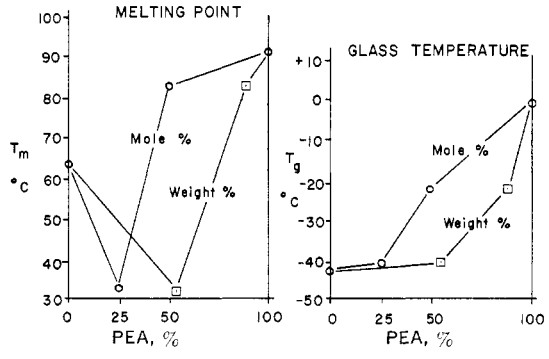


Figure 1. Thermal transitions of PEA copolymers.

the effects of small amounts of ester acetal repeating units on the crystalline properties of poly(ethylene terephthalate) and nylon 66. The melting points, recrystallization temperatures and relative degrees of crystallinity of these copolymers are collected in Table V. Significant depressions were observed in most of these properties even though the ester acetal monomer was present to the extent of only 5 mol %, which was the minimum amount considered necessary to effect cross-linking as discussed in the following section.

In subsequent applications studies, most interest was centered around copolyesters containing varying amounts of ethylene adipate and ethylene ester acetal units. In general, it was observed that most of these copolymers obeyed the following intrinsic viscosity–molecular weight relationship, $[\eta] = 1.2 \times 10^{-4} M^{0.9}$, as shown by representative data collected in Table VI.

Polymer Cross-linking

Solubility and gel swelling measurements were generally used to evaluate the degree of cross-linking quantitatively, although crystalline melting point and degree of crystallinity were found to be even more sensitive measures of the degree of cross-linking for some polymers.

The results of cross-linking studies on copolyesters of one five-membered (HTA), two six-membered (HMA and PEA) and one seven-membered (BTA) acetal ring monomers are collected in Figures 2–5, which represent, respectively, the effects of cross-

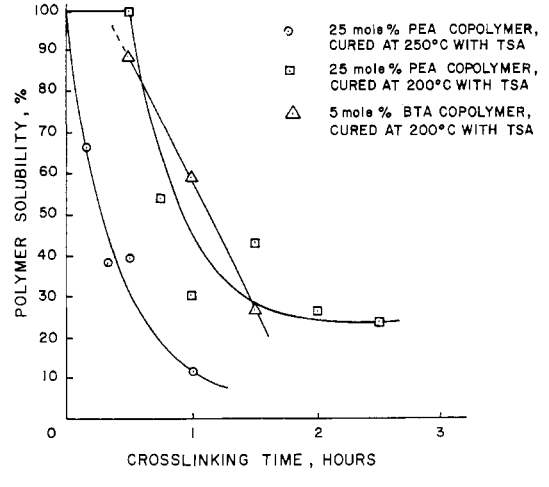


Figure 2. Effect of ester acetal comonomer and temperature on degree of cross-linking.

TABLE V

CRYSTALLINE PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE) AND NYLON 66 COPOLYMERS[a]

	PET copolymer			Nylon 66 copolymer		
Comonomer[b]	T_m, °C[c]	T_c, °C[d]	Relative degree of crystallinity[e]	T_m, °C[c]	T_c, °C[d]	Relative degree of crystallinity[e]
None	270	210	0.278	270	229	0.319
GA	263	195	0.245	261	220	0.275
HMA	241	193	0.275	264	217	0.397
PEA	248	187	0.260	255	214	0.296
DGA	255	192	0.264	259	217	0.312
BTA	245	158	0.254	259	213	0.335

[a] Determined by differential scanning calorimetry on a Perkin-Elmer DSC-1 instrument at heating and cooling rates of 10°/min. [b] Comonomer is present to the extent of 5 mol %. [c] Melting point, taken as the temperature at which the endothermic melting transition peak returns to the base line during the third melting–recrystallization cycle. [d] Crystallization temperature, taken as the temperature at the top of the exothermic recrystallization peak during the third melting–recrystallization cycle. [e] Degree of crystallinity is arbitrarily taken as the ratio of the area under the recrystallization peak during the third cycle to the weight of the sample.

linking conditions, copolymer composition and acetal monomer structure on the degree of cross-linking catalyzed by *p*-toluenesulfonic acid, TSA. Figure 2 presents a comparison of the course of the cross-linking reaction for two different types of acetal copolymers and for a single type of copolymer at two different

TABLE VI

INTRINSIC VISCOSITY–MOLECULAR WEIGHT DATA FOR COPOLYESTERS

Polymer[a]	$[\eta]$[b]	Mol wt[c]
P(EA)	0.201	4270
P(75 EA/25 GA)	0.224	3650
P(50 EA/50 HMA)	0.431	3600
P(75 EA/25 E-DGA)	0.204	4180
P(71 EA/29 E-PEA)	0.278	6060
P(45 EA/55 E-PEA)	0.292	7130
P(E-PEA)	0.170	4260

[a] Abbreviations: P(EA), poly(ethylene adipate); P(75 EA/25 GA), copolymer containing 75 mol % ethylene adipate units and 25 mol % GA units; P(75 EA/25 E-DGA), copolymer containing 75 mol % ethylene adipate units and 25 mol % ethylene–DGA diester units; P(E-PEA), homopolymer of ethylene glycol and PEA. [b] Intrinsic viscosity in benzene at 30°. [c] Number-average molecular weight determined by vapor pressure depression in benzene at 37° with Mechrolab Model 1301 A osmometer.

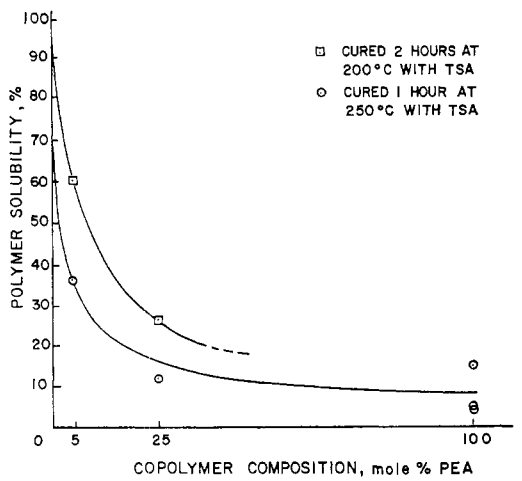


Figure 3. Effect of ester acetal content on degree of cross-linking.

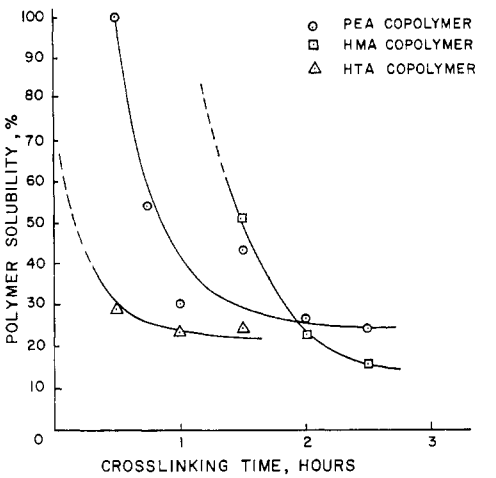


Figure 4. Relative reactivities of three ester acetal units in cross-linking reactions of 25:75 acetal–adipate copolyesters of ethylene glycol at 200°.

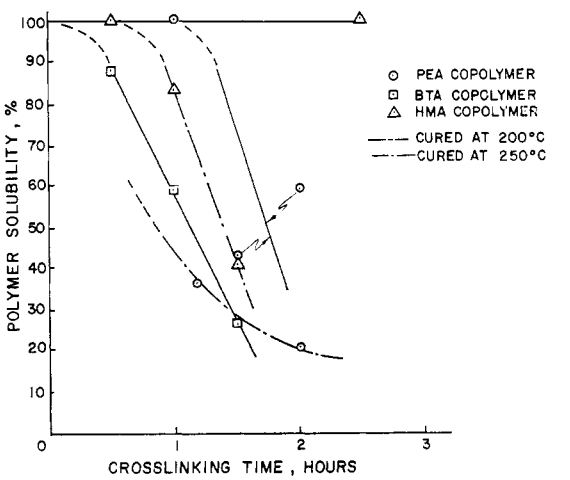


Figure 5. Relative reactivities of three ester acetal units in cross-linking reactions of 5:95 acetal–adipate copolyesters of ethylene glycol.

cross-linking temperatures. For the latter variable, the course of the cross-linking reaction appeared to undergo a simple shift in time scale with change in reaction temperature. However, for the two different types of acetal copolymers, differing both in amount and type of acetal comonomer, in Figure 2 the cross-linking reactions differed not only in absolute rate but apparently also in rate behavior. The copolymer containing 5 mol % BTA cross-linked at approximately the same rate as the 25 mol % PEA copolymer, indicating that the seven-membered cyclic acetal units in the former reacted at a much faster rate than the six-membered cyclic acetal units in the latter, apparently because of the relative ring stabilities of the two types of cyclic acetals.

Figure 3 reveals the effect of comonomer content on the degree of cross-linking for PEA copolymers alone. Solubility and swelling data indicated that density of cross-linking in the fully cured 25 mol % copolymer was not much less than that in the PEA homopolymer. The solubility plots in Figure 3 also reveal, as does swelling data, that copolymers containing as little as 5 mol % PEA could be partially cross-linked under relatively mild conditions with TSA catalyst.

Finally, Figures 4 and 5 present quantitative comparisons of the rates of cross-linking of poly(ethylene adipate) copolymers containing four different types of acetal comonomers at the 25 and 5 mol % levels, respectively. These curves clearly reveal that the order of reactivity of the four acetal monomers toward cross-linking reactions catalyzed by TSA was BTA > PEA > HMA. The position of HTA in this series is uncertain because, at the 25 mol % level in Figure 4, HTA appeared to be more reactive than PEA, but at the 5 mol % level, HTA copolymers did not cross-link at 250° for 2 hr and were only very slightly cross-linked at 275° for 1 hr.

As expected from ring stability considerations, therefore, the ease of cross-linking was found to be a function of ring size in the order seven- > five- > six-member ring,[8] but, unfortunately, the most reactive cyclic acetal unit, the dioxepane ring, was the least accessible as a monomer. On the other hand, although the ability of six-membered cyclic acetal units to undergo readily ring-opening cross-linking reactions was problematical at the start of this study (because dioxanes are known to be very reluctant to polymerize),[9] it was found possible to cross-link both HMA and PEA polymers at 200° without difficulty with a mild acid catalyst, TSA. Of these two six-membered acetal ring units, the PEA polymer was slightly more reactive, perhaps indicating a higher degree of steric strain in the spiro ring unit than in the isolated ring unit. On the other hand, mild protonic acid catalysts were found to be ineffective for cross-linking at temperatures below 200°, and an investigation of strong acids and catalyst-promoter combinations for this purpose was undertaken.

Catalyst-Promoter Combinations. The investigation of small ring compounds as possible promoters for the acid-catalyzed cross-linking of five- and six-membered acetal-ring polymers was suggested by the observation reported in the literature that small amounts of epoxides accelerate the cationic polymerization of both oxetanes and tetrahydrofurans.[10] Presumably the smaller ring compound, being a more reactive monomer to cationic ring-opening polymerization reactions, combines with the acid catalyst to form a reactive oxonium (or carbonium) ion, which initiates the polymerization of the larger ring compound.

Initially, the relative reactivities of these promoters were evaluated by their rate of homopolymerization with TSA, and some of the results of this study are collected at the top of Table VII. This study was followed, in turn, by an investigation of the relative ability of a variety of protonic and Lewis acid catalysts to initiate the cationic polymerization reactions of many of these promoters, with the results again collected in Table VII. Finally, the most promising combinations of catalyst and promoter were applied to cross-linking a 50 mol % PEA copolymer. In the earlier evaluations of this last type of reactivity, solubility measurements were applied to evaluate efficacy, but additional studies were carried out in an applications program in which surface hardness of metal coatings was chosen as the measure of degree of cross-linking. A summary of both types of results are collected on the bottom of Table VII.

When surface hardness was used as a measure of degree of cross-linking, an adequate level of this property was achieved for the 50 mol % PEA copolymer at 150° in a satisfactory period of time (3 hr) only with the strongest protonic acid catalysts evaluated (fluorosulfonic acid–SbF_5 complex) and then only with severe discoloration of the polymer. Consistent with the results of cross-linking studies on homopolymers, the conditions required to cross-link a comparable DGA copolymer were noticeably milder. It is interesting to note that the following conditions and catalysts achieved essentially the same degree of cross-linking (30 wt % solubles) with this DGA copolymer (see Table VII for abbreviations): (1) heat alone at 200° for 6 hr, (2) heat alone at 275° for 1 hr, (3) 1 mol % TSA catalyst at 100° for 16 hr, (4) 1 mol % TSA catalyst at 200° for 1 hr, (5) 1 mol % BFNE catalyst with 10 wt % EN promoter at 150° for 2 hr and (6) 1 mol % BFNE catalyst with 25 wt % EN promoter at 150° for 1 hr. In contrast to the results for condition 5, the comparable PEA copolymer cured to only 55 wt % solubles after 3 hr with this catalyst-promoter combination.

Experimental Section

General procedures for monomer and polymer synthesis are described in previous publications.[2] Collected below are examples which embody typical procedures for the preparation of ω-hydroxy ester and diester monomers and the conversion of these to homopolymers and copolymers.

HMA Monomer and Polymer. A mixture of 22.0 g (0.0944 mol) of methyl azelaaldehydate dimethyl acetal, I, 15.2 g (0.126 mol) of 2-hydroxymethyl-2-methyl-1,3-propanediol and 0.05 g of *p*-toluenesulfonic acid was stirred under water pump vacuum with nitrogen bubbling through for 6.5 hr. The mixture was heated gently, with the reac-

(8) R. W. Lenz, "The Organic Chemistry of Synthetic High Polymers," Interscience Publishers, New York, N. Y., 1967, p 532 ff; P. Watts, *J. Chem. Soc., B*, 543 (1968).

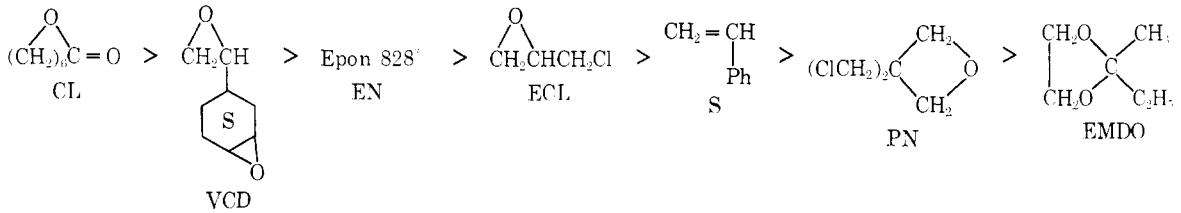
(9) J. Furukawa and T. Saegusa, "Polymerization of Aldehydes and Oxides," Interscience Publishers, New York, N. Y., 1963, p 237.

(10) See ref 9, p 431 ff; D. Sirus, *Makromol. Chem.*, **98**, 245 (1966).

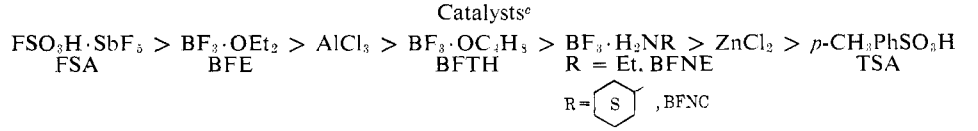
TABLE VII

RELATIVE REACTIVITY ORDERS

Promoters[b]



Catalysts[c]



Cross-linking activity

(1) Solubility and swelling studies on 50% PEA copolymer cross-linked at 150°

FSA > BFE—EN > BFNE—EN > BFNE—VCD > TSA

(2) Hardness studies on 50% PEA copolymer films cross-linked at 150°

FSA > TSA > BFTH > BFNE—EN > BFNC—EN

[a] Shell Chemical Co. epoxy resin prepolymer—low molecular weight polymer of bisphenol A and epichlorohydrin with epoxide end groups. [b] Rate of polymerization by TSA at 150°. [c] Rate of polymerization of promoters at 100°.

tion temperature being kept below 90° during that period of time after which the nitrogen flow was continued for 15 hr at room temperature and pressure. Unreacted triol was filtered off, and 5.5 g (0.046 mol) was recovered. The filtrate was taken up in methylene chloride and water, and the water layer was washed five times with methylene chloride, while the methylene chloride layer was washed five times with water. The combined methylene chloride extracts were dried over calcium sulfate, the solution was filtered, the solvent evaporated and the residue distilled in a molecular still at 0.0005 mm using butyl acetate vapors (bp 126°) as the heat transfer medium. A total of 12.5 g of HMA (n^{30}D 1.4628) was obtained which both gas chromatography (gc) and thin layer chromatography (tlc) showed to be pure. An additional 2.70 g of pure product was obtained by passing the residue through the molecular still a second time under the same conditions. The total yield of pure material was 15.20 g or 55.8% yield, mp 4–7°.

A homopolymer prepared from this monomer at 190° by the previously described procedure[2] with lead acetate trihydrate as catalyst had the following properties: intrinsic viscosity in benzene at 30° = 0.48, number average molecular weight = 10,200.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.61, 65.67; H, 9.46, 9.50; ash, 0.32, 0.27.

DGA Monomer. Commercially available diglycerol contains large amounts of glycerol and polyglycerols as impurities which are very difficult to remove by distillation. A convenient method of purifying this compound through its diisopropylidene derivative is as follows. Crude diglycerol (30.0 g, City Chemical Co.), 150 ml of 2,2'-dimethoxypropane, 75 ml of acetone, and 0.5 g of *p*-toluenesulfonic acid were refluxed under nitrogen for 3 hr. The volatiles were distilled off until a temperature of 65° was reached, by which time the reaction mixture had turned black. After cooling, the mixture was neutralized to pH 7.5–8.0 with potassium hydroxide in absolute ethanol, and it became yellow. Distillation at 0.7 mm pressure gave a product (bp 91–94°) that was pale yellow in color, n^{30}D 1.4355. This product, redistilled at 0.05 mm pressure and 73–77°, gave 18.61 g (41.3%) of pure bis(isopropylidine)diglycerol. The structure of the product was verified by infrared spectroscopy, and diglycerol could be recovered by hydrolysis with aqueous HCl.

DGA monomer was prepared by combining 6.31 g (0.0256 mol) of bis(isopropylidine)diglycerol, 11.89 g (0.0512 mol) of I and 0.5 g of *p*-toluenesulfonic acid as catalyst. The reactants were heated under water pump vacuum at 90° while nitrogen was bubbled in slowly. The mixture went through various stages of color from purple to green to brown during the reaction. After 25 hr the mixture was cooled and the products were taken up in methylene chloride, washed five times with water, dried over $CaSO_4$, filtered and evaporated. The final crude product was distilled in a molecular still at 184° (0.0005 mm), yielding a colorless liquid, n^{30}D 1.4624, which crystallized in the freezer. Yields of pure product were 30–50%.

Anal. Calcd for $C_{26}H_{46}O_9$: C, 62.12; H, 9.08. Found: C, 61.94; H, 9.08.

BTA Monomer. To a suspension of 7.0 g (0.184 mol) of lithium aluminum hydride in 350 ml of refluxing ethylene glycol dimethyl ether was added dropwise a solution of 13.4 g (0.043 mol) of tetramethyl pyromellitate, mp 139–142°, in 200 ml of ethylene glycol dimethyl ether over a 2-hr period. The mixture was refluxed for 6 hr, kept at room temperature 15 hr, cooled in an ice bath, and the excess hydride decomposed by dropwise addition of 10% H_2SO_4 until the mixture was slightly acidic. The solid was removed by filtration, dried and refluxed with 400 ml of dry pyridine for 1 hr, the pyridine was filtered hot and evaporated to a small volume. Addition of heptane precipitated 5.53 g of the product, and reextraction of the solid with pyridine gave an additional 1.12 g of product for a total yield of 1,2,4,5-tetrakis(hydroxymethyl)benzene of 6.65 g (73.0%). Recrystallization from butanol yielded a white solid, mp 189–191° (lit.[11] mp 191–192°).

A mixture of 6.88 g (0.0347 mol) of 1,2,4,5-tetrakis(hydroxymethyl)benzene, 16.12 g (0.0694 mol) of I and 0.1 g of *p*-toluenesulfonic acid was heated under nitrogen for 2 hr. Methanol was removed continuously by distillation with a total of 3.5 ml collected. The reaction mixture solidified on cooling, and the solid product was dissolved in methylens chloride, the methylene chloride solution washed four time-with water, dried over $CaSO_4$, filtered and evaporated, leave

(11) A. Benning and O. Gosskinsky, *Chem. Ber.*, 87, 54 (1954).

ing a pale yellow solid. Recrystallization from ethanol gave 11.5 g (62.0%) of a white solid, mp 116–120°. Further recrystallization from ethanol broadened the melting point range to 116–125°, but tlc of this product revealed the presence of only a single spot, so this broad melting range may be caused by the presence of a mixture of isomers.

Anal. Calcd for $C_{30}H_{46}O_8$: C, 67.39; H, 8.67. Found: C, 67.25; H, 8.61.

Ester Interchange Polymerization. Polyesterification reactions were run using an approximately twofold molar excess of ethylene glycol, and either calcium oxide (prepared by pyrolysis of calcium carbonate) or lead tetraacetate trihydrate were generally used as the ester interchange catalyst. Approximately 5% catalyst based on the weight of the diester acetal monomer was used, but no stabilizers were used in any of these reactions. Heating schedules were established to allow formation of the bis(hydroxyethyl) esters by elimination of methanol, after which higher temperatures were used to promote polycondensation and elimination of ethylene glycol. Molecular weights in the range of 5,000–10,000 were achieved without difficulty.

Poly(ethylene adipate) Copolymers. Copolymers containing 25 and 50 mol % PEA, DGA and BTA in poly(ethylene adipate) were prepared using a 3:1 molar excess of ethylene glycol based on the total molar amount of both diester monomers. Approximately 0.5 wt % lead acetate trihydrate catalyst was used. The reactants were combined in a small, round-bottom flask which was attached to a 5-in. air condenser to prevent the loss of ethylene glycol. The tube outlet was connected to a Dry Ice trap to collect the methanol formed, and a steady stream of nitrogen was maintained to ensure mixing under a dry atmosphere. After heating at 190° at atmospheric pressure for 20–30 hr, the reaction flask was cooled, the vertical tube was replaced by a short-pass distillation head and collector, and the excess unreacted ethylene glycol was distilled off under reduced pressure at 190°.

Poly(ethylene terephthalate) Copolymers. Copolymers with 5 mol % PEA, DGA and BTA were prepared, again using a threefold excess of ethylene glycol to the combined amount of diester monomers, but for this polymerization reaction, 0.5 wt % CaO catalyst was used. The heating schedules for these reactions started at 190° for 4.5 hr. The temperature was slowly increased to 250° over a period of approximately 1 hr, and the temperature maintained at 250° for 1 hr. The reaction mixture was cooled to room temperature at this point, and the 5-in. vertical air condenser, which was connected to the reaction flask during this initial heating period, was replaced by a short-pass distillation head and a collecting flask. The reaction flask was heated to 250–270° again and vacuum applied until a pressure of 30 mm was reached and maintained for 0.5 hr; then the pressure was reduced to 0.5 mm for 2.5 hr. Excess ethylene glycol was collected and identified by gc. All of the poly(ethylene terephthalate) interpolymers were tough solids. The products were dissolved in 50:50 phenol–tetrachloroethylene solutions and reprecipitated in methanol for purification. Intrinsic viscosities of the precipitated polymers were taken in this solvent.

Quantitative Infrared Analysis. In general, all cyclic acetal polymers and copolymers have characteristic acetal peaks in the region of 1000–1150 cm^{-1}, and for poly(ethylene adipate) copolymers in particular, significant variations are observed in the methylene absorption region between 2508 and 2950 cm^{-1}. In both regions at copolymer contents of 25 and 50%, characteristic peaks can be selected for the quantitative analysis of the copolymers. For the PEA copolymers, for example, an appropriate pair of peaks are those at 1045 and 1165 cm^{-1}. The former is present in the PEA homopolymer but not in poly(ethylene adipate). Significant changes are also observed in the methylene peaks at either 2940 or 2860 cm^{-1}, either of which can be compared to the carbonyl peak at 1720 cm^{-1}. Ratios of the absorbance ratio for pairs, 2940/1720 and 1045/1165, correlated very well with mole fraction comonomer content in the reactants.

Cross-linking Investigations. The procedure used for cross-linking prepolymer samples was the following: a 0.5-g sample of polymer was weighed into a vial and dissolved in approximately 1 ml of tetrahydrofuran. The catalyst, whenever possible, was also dissolved in tetrahydrofuran and an aliquot of the solution was added to the polymer solution. Insoluble catalysts were ground to a fine powder and dispersed in the polymer solution. The polymer–catalyst solution was poured into a tared porcelain boat, and the solvent was evaporated under vacuum until the sample achieved a constant weight. In some cases, a small amount of the solution was also cast on a microscope slide for adhesion studies. The polymer film so formed was cured by placing the boat inside a large flask immersed in a fluidized sand bath, and the temperature of the sample was determined by placing a thermocouple in direct contact with the boat. The flask was purged with nitrogen for 10 min before curing, and a positive pressure of nitrogen was maintained throughout the curing reaction. The time of the cure was measured from the moment the flask was lowered into the heating bath. After the cure, the flask was removed from the sand bath and allowed to cool to room temperature under nitrogen before the boat was removed. The boats were again weighed to determine the weight loss of cured polymer.

The degree of swelling and film solubility were measured as follows: a sample of film of weight W_0 was immersed in 5 ml of chloroform in a covered vial at room temperature for 6 days. This length of time is generally considered necessary for extracting soluble polymers from a network and for measurement of equilibrium swelling values.[12] The swollen film was drained free of excess chloroform and reweighed. If the weight of the swollen film is W_s, the degree of swelling is simply $(W_s/W_0) \times 100$. The portion of film soluble in chloroform and extracted during the 6-day immersion was determined both by reweighing after drying the fully swollen gel under vacuum and by removing the solvent from the extract and weighing the residue. If the weight of the extracted polymer is W_e, the film solubility is simply $(W_e/W_0) \times 100$.

Solubility measurements on cured epoxy and unsaturated polyester resins have been found by others to correlate well with performance properties such as impact strength and hot cut-through temperatures,[13] and determinations of sol content have been used in a large number of investigations for absolute determinations of cross-link densities in vulcanized or network polymers.[14,15]

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(15) K. W. Scott, *ibid.*, **58**, 517 (1962).