

**Cationic Copolymerization of 1,3-Dioxolanes
and 1,3-Dioxanes with 3,4-Dihydro-2*H*-pyran-2-
methyl(3,4-dihydro-2*H*-pyran-2-carboxylate).
Nonfriable Pyranyl Foams**

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Synopsis

Various substituted difunctional 1,3-dioxolanes and 1,3-dioxanes were copolymerized with a cyclic vinyl ether, 3,4-dihydro-2*H*-pyran-2-methyl(3,4-dihydro-2*H*-pyran-2-carboxylate), in the presence of boron trifluoride etherate catalyst. The copolymerizations proceeded rapidly and exothermally when initiated at room temperature and produced thermosetting resins. The copolymer products possess improved abrasion resistance and toughness as compared with homopolymer of the di(dihydropyranyl) monomer. As a practical consequence of these copolymerizations it is possible to prepare low-density pyranyl rigid foams with improved friability resistance.

INTRODUCTION

Cationic polymerization of 3,4-dihydro-2*H*-pyran-2-methyl(3,4-dihydro-2*H*-pyran-2-carboxylate), hereinafter referred to as acrolein tetramer, had been reported some time ago.¹ However, since the polymerization processes were extremely rapid and exothermic and the polymers formed were insoluble powders, no commercial use was developed. Recently, procedures were developed, based on this polymerization, to produce pyranyl rigid foams² and coating compositions.³

It is also known that 1,3-dioxolanes and 1,3-dioxanes can undergo ring-opening homopolymerization⁴⁻¹² or copolymerization with trioxane,¹³ epoxides,¹³ and ethylenic compounds,^{9,14} but copolymers with vinyl ethers, such as acrolein tetramer, have not been reported.

This paper describes the synthesis of a variety of multifunctional 1,3-dioxolanes and 1,3-dioxanes, their polymerizability with acrolein tetramer, and, consequently, their use in the preparation of pyranyl-based rigid foams with high friability resistance.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were employed without further purification. The 2-formyl-3,4-dihydro-2*H*-pyran, 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (III), 2-vinyl-5-hydroxymethyl-5-methyl-1,3-dioxane (IX), bisphenol A, and toluene diisocyanate were obtained from Union Carbide Corporation, and 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (V), from Aldrich Chemical Company, Incorporated.

Synthesis of Monomers

3,4-Dihydro-2*H*-pyran-2-methyl(3,4-dihydro-2*H*-pyran-2-carboxylate)

(1). Acrolein tetramer was prepared by the Tischenko reaction of 2-formyl-3,4-dihydro-2*H*-pyran (acrolein dimer) with a catalytic quantity of aluminum isopropoxide as previously described¹⁵; bp 115–119°C (0.50 mm).

1-Hydroxy-1,4-bis(1,3-dioxolan-2-yl)butane (IIa) or 2-(2-Hydroxyethoxy)-6-(1,3-dioxolan-2-yl)pyran (IIb). Freshly distilled acrolein dimer (560.6 g; 5.0 moles) was added dropwise to a solution of 620.1 g (10.0 moles) ethylene glycol and 13 drops concentrated hydrochloric acid in 1500 ml benzene at 80° during 2 hr and 15 min. Water which formed from the reaction was collected by means of a Dean-Stark trap. During the addition of acrolein dimer, the reaction maintained itself at 80°C, and 21.0 g water was collected. When the addition was complete, the mixture was heated for 2.5 hr during which time an additional 65.0 g water was collected; total yield of H₂O, 86.0 g (96%). The reaction mixture was concentrated by distillation of 968 g of the benzene at atmospheric pressure. Calcium oxide (2.0 g) was added and the reaction mixture allowed to stand over the weekend. The remainder of the solvent was stripped at 60° and 0.6 mm pressure. Distillation of the residue afforded 393.4 g (36%) of colorless product (IIa or IIb), bp 125–129°C (0.47–0.48 mm).

ANAL. Calcd. for C₁₆H₁₈O₅: C, 55.03%; H, 8.31%; O, 36.66%. Found: C, 55.14%, 55.17%; H, 8.42%, 8.16%.

The infrared absorption spectrum revealed bands at 2.89 μ (OH) and 3.45, 8.64, 9.15, and 9.40 μ attributable to ether (O—CH₂, C—O, C—O—C) linkages. No peaks due to C=C absorption were revealed.

The NMR spectrum exhibited signals centered at δ 4.78 (two protons, a triplet, attributed to protons at C₂ of the dioxolane rings), 3.77 (ten protons; a multiplet due to ethylene glycol, methine, and hydroxyl protons), and 1.67 ppm (six methylene protons). This spectrum fit either structure IIa or IIb but cannot differentiate between them.

2,4-Bis[4-(2-vinyl-1,3-dioxolan-4-yl)butyl]-*N,N'*-tolyl Carbamate (IV) and 2,4-Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]-*N,N'*-tolyl Carbamate (VI). Compounds IV and VI were prepared by the noncatalyzed addition of 2-vinyl-4-(4-hydroxybutyl)-1,3-dioxolane (III) and 2,2-di-

methyl-4-hydroxymethyl-1,3-dioxolane (V) to toluene diisocyanate, respectively, while maintaining the temperature at 25° to 35°C. The products were obtained as clear colorless nondistillable, noncrystallizable liquids with viscosities of 268,000 cps and 392,000 cps at 25°C for compounds IV and VI, respectively. The residue products were purified by heating at 150°C and 0.20 mm pressure, using a falling film-type still. Infrared analyses were consistent with the assigned structures and revealed the absence of isocyanate.

Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]isophthalate (VII). A 5-liter, four-necked flask equipped with a thermometer, stirrer, nitrogen inlet, and a 10-in. helix packed column was placed 1322 g (10 moles) 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane, 971 g (5 moles) of dimethyl isophthalate, 1700 g dry toluene, and 7 g sodium methoxide, and the mixture was heated to reflux. During 5 hr there was collected 927 g toluene-methanol binary at a head temperature of 95–106°C by maintaining a flask temperature of 137–145°C. After cooling to 25°C, 500 ml dichloromethane was dissolved in the reaction mixture. The resulting mixture was washed with four 1000-ml portions of 5% aqueous sodium chloride solution, and the organic mixture was dried over anhydrous magnesium sulfate, filtered, and evaporated to give a crude amber-colored oil. Distillation afforded 999.5 g (51%) of pure white product, bp 205–212°C (0.50–0.60 mm).

ANAL. Calcd. for $C_{20}H_{26}O_8$: C, 60.91%; H, 6.59%. Found: C, 60.74%; H, 6.83%.

2,4-Bis{1-[1,4-bis(1,3-dioxolan-2-yl)butyl]}-N,N'-tolyl Carbamate (VIIIa) or 2,4-Bis{ β -[2-ethoxy-6-(1,3-dioxolan-2-yl)pyranyl]}-N,N'-tolyl Carbamate (VIIIb) and 2,4-Bis[(2-vinyl-5-methyl-1,3-dioxan-5-yl)-methyl]-N,N'-tolyl Carbamate (X). These compounds were prepared by the noncatalyzed addition of toluene diisocyanate to the corresponding hydroxy acetals, in neat, while maintaining the temperature at 25–30°C. The products were characterized as nondistillable, noncrystallizable, glassy solids and were employed directly in the copolymerizations without attempts at further purification.

1,3-Bis(1,3-dioxolan-2-yl)propane (XI). This bisdioxolanyl derivative was prepared from glutaraldehyde and ethylene glycol by the established route for acetals; bp 103°C (1.6 mm).

ANAL. Calcd. for $C_9H_{16}O_4$: C, 57.43%; H, 8.57%; Found: C, 57.16%; H, 8.72%.

2-(2-Bicyclo[2.2.1]-5-heptene)-5-(2-spirobicyclo[2.2.1]-5-heptene)-1,3-dioxane (XII). This dioxane was obtained by the condensation of bicyclo[2.2.1]-5-heptene-2-carboxaldehyde and bicyclo[2.2.1]-5-heptene-2,2-dimethanol¹⁶ according to the established route for acetal synthesis; yield 51% of pure product after recrystallization from methanol, mp 165–168°C.

ANAL. Calcd. for $C_{17}H_{22}O_2$: C, 79.03%; H, 8.58%. Found: C, 78.82%; H, 8.41%.

Polymerization

The catalyst was rapidly and thoroughly mixed into a solution of 25 g of each of the comonomers in the absence of a solvent at 26°C during a period of 20 sec. The polymerization mixtures were poured into a 3-in.-diameter aluminum mold and the polymerization induction time was taken as the first noticeable deflection of the pyrometer needle, and the peak exotherm (temperature-time profile) was recorded.

Foaming Procedure

The acrolein tetramer, acetal, silicone surfactant, and blowing agent were first preblended at ambient temperature in a 1-quart cardboard container for 30 sec. The acidic catalyst was then added and the mixture vigorously stirred for 20 sec and quickly poured into an 8×8×6-in. metal mold, whereupon the mass foamed and the cream, rise, and tack-free times were recorded. All foams were cured at room temperature for three days before being tested.

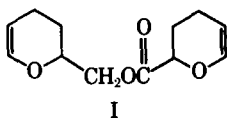
Foam Testing

Foams were tested according to standard ASTM procedures. For measuring friability resistance, a combination of ASTM C367 and C421 tumbling tests were employed. Compressive strengths were determined by ASTM D1621.

RESULTS AND DISCUSSION

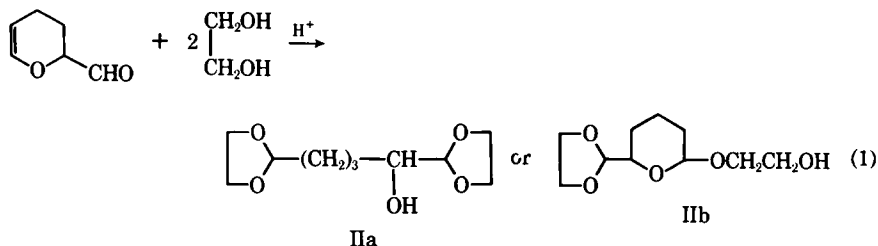
Synthesis of Monomers

Because acrolein tetramer (I) is the key monomer for pyranyl foam manufacture,² copolymerizations were restricted to this bicyclic vinyl ether:

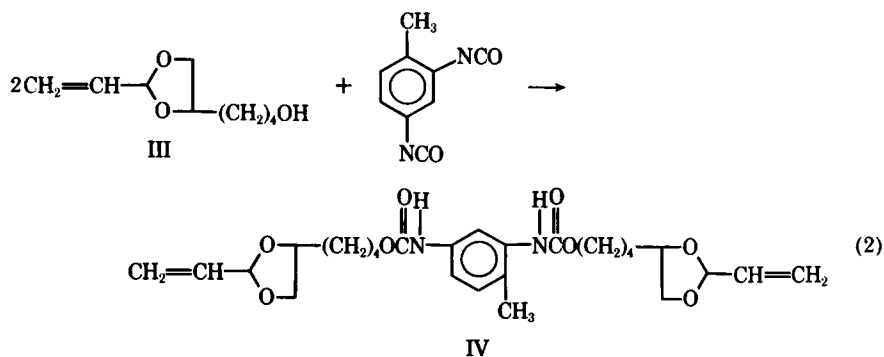


A series of multifunctional 1,3-dioxolanes and 1,3-dioxanes which connect the cyclic acetal groups at either the 2- or 5-position were investigated for copolymerization comparisons which varied in location and type of connecting units and substituents. The cyclic acetals employed were synthesized by the indicated routes in eqs. (1) to (8):

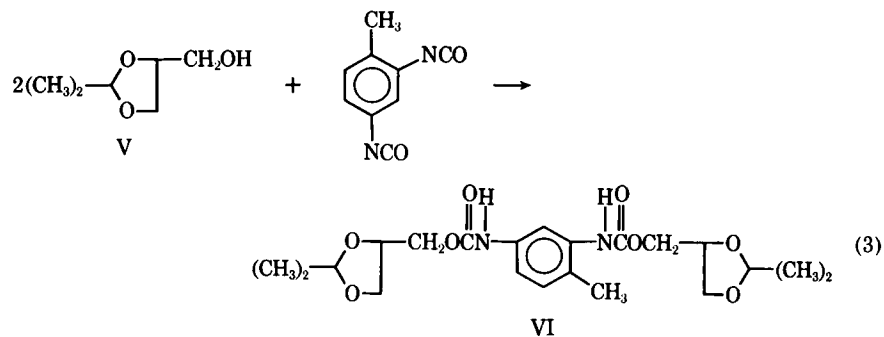
1-Hydroxy-1,4-bis(1,3-dioxolan-2-yl)butane (IIa) or 2-(2-Hydroxyethoxy)-6-(1,3-dioxolan-2-yl)pyran (IIb):



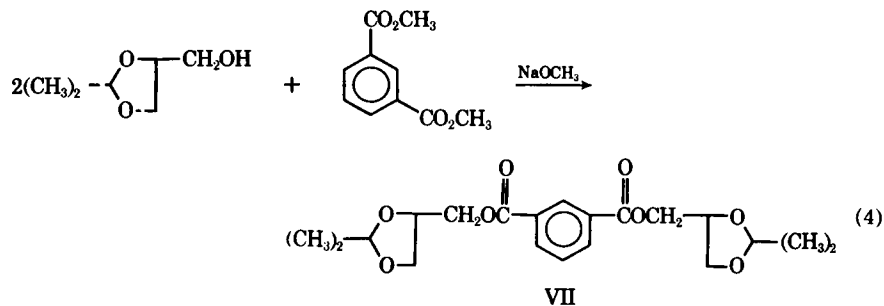
2,4-Bis[4-(2-vinyl-1,3-dioxolan-4-yl)butyl]-N,N'-tolyl Carbamate (IV):



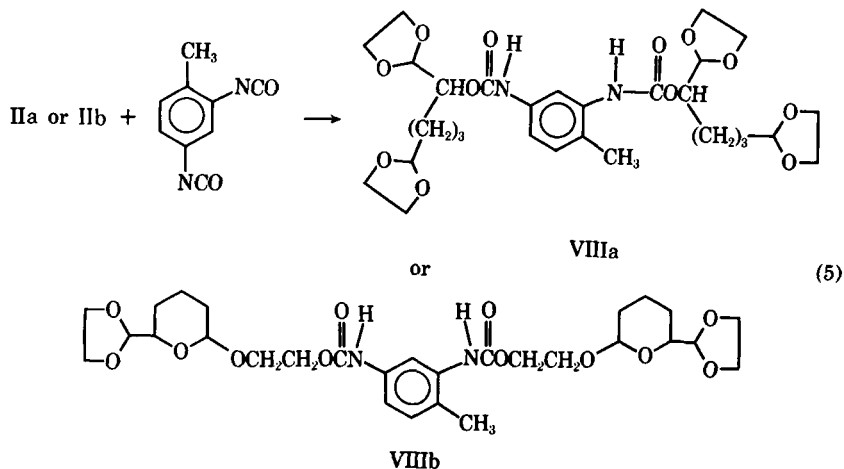
2,4-Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]-N,N'-tolyl Carbamate (VI):



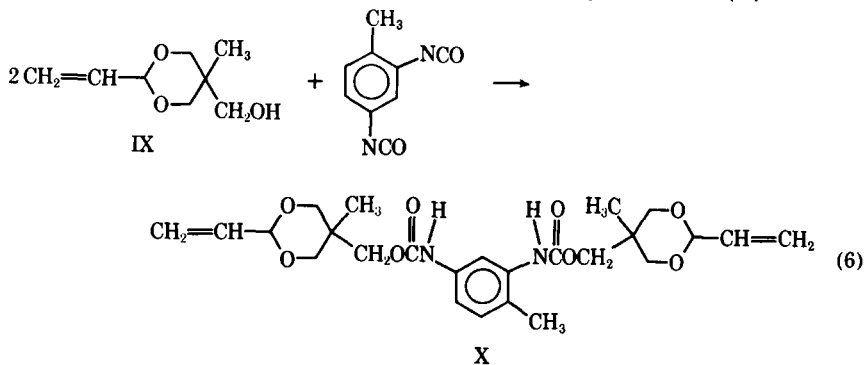
Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] Isophthalate (VII):



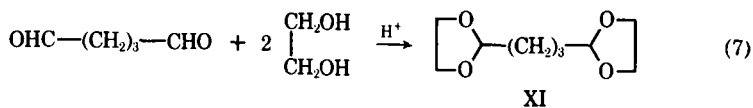
2,4-Bis[1-[1,4-bis(1,3-dioxolan-2-yl)butyl]-N,N'-tolyl Carbamate (VIIIa) or 2,4-Bis[β -[2-ethoxy-6-(1,3-dioxolan-2-yl)pyranyl]-N,N'-tolyl Carbamate (VIIIb):



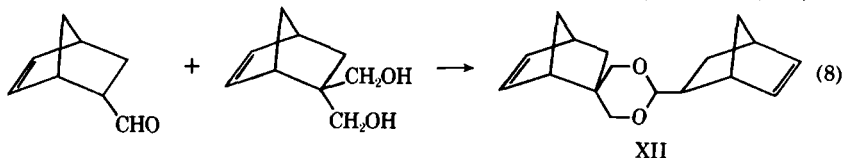
2,4-Bis[(2-vinyl-5-methyl-1,3-dioxan-5-yl)methyl]-N,N'-tolyl Carbamate (X):



1,3-Bis(1,3-dioxolan-2-yl)propane (XI):



2-(2-Bicyclo[2.2.1]-5-heptene)-5-(2-spirobicyclo[2.2.1]-5-heptene)-1,3-dioxane (XII):



Copolymerization

The results of the cationic copolymerization of the 1,3-dioxolanes and 1,3-dioxanes with acrolein tetramer are summarized in Tables I and II, respectively.

TABLE I
Copolymerization of Various 1,3-Dioxolanes with Acrolein Tetramer^a

No.	Acrolein tetramer (M ₁) concn., moles × 10	1,3-Dioxolane (M ₂)		Initiator ^b concn., moles × 10 ⁴	Monomer/initiator (M ₁ + M ₂)/I ^c	Polymer induction, time, sec	Polym. peak exotherm		Product description
		Com- position	Concn., moles × 10				Temp., °C	Time, sec	
1	2.23	none	—	3.53	632	45	176	140	hard, slightly brittle, shrinkage
2	2.23	none	—	7.05	316	40	220	140	hard, slightly brittle, shrinkage
3	1.11	II	1.15	3.53	640	180	88	15.5 min	hard, but tacky surface
4	1.11	II	1.15	7.05	321	90	91	330	hard, but tacky surface
5	1.11	III	1.45	3.53	725	160	147	19.5 min	hard, tough, tacky surface
6	1.11	III	1.45	7.05	363	80	159	400	hard, tough tacky surface
7	1.11	IV	0.481	3.53	451	40	47	28 min	soft, rubbery incomplete polym.
8	1.11	IV	0.481	7.05	226	30	152	160	hard, tough, high gloss
9	1.11	V	1.88	3.53	848	50	100	180	viscous, liquid resin
10	1.11	V	1.88	7.05	425	45	96	155	viscous liquid resin
11	1.11	VI	0.568	3.53	475	50	79	250	hard, brittle, clear plaque
12	1.11	VI	0.568	7.05	238	30	90	150	hard, brittle, amber
13	1.11	VII	0.630	3.53	493	75	92	180	hard, tough, clear
14	1.11	VII	0.630	7.05	247	40	97	180	hard, tough, brown plaque
15	1.11	VIII	0.410	3.53	430	40	103	260	hard, tough, brown
16	1.11	VIII	0.410	7.05	216	45	111	270	hard, tough, brown
17	1.11	XI	1.33	3.53	691	90	110	420	hard, tough, slight shrinkage
18	1.11	XI	1.33	7.05	346	45	140	240	hard, tough, high gloss

^a Polymerization temperature, 25°C.

^b BF₃·O(C₂H₅)₂ (employed as a 10% solution in diethylene glycol).

^c Calculated from molar quantity of monomers and initiator.

TABLE II
Copolymerization of 1,3-Dioxanes with Acrolein Tetramer^a

No.	Acrolein tetramer (M ₁) concn., moles × 10		1,3-Dioxane (M ₂)		Initiator ^b concn., moles × 10 ⁴	Monomer/initiator (M ₁ + M ₂ /I) ^c	Polym. induction time, sec	Polym. peak exotherm		Product description
	(M ₁) concn., moles × 10	Com-position	Concn., moles × 10	Com-position				Temp., °C	Time, sec	
1	1.11	IX	1.58	IX	3.53	762	60	139	225	hard, tough, plaque
2	1.11	IX	1.58	IX	7.05	382	30	153	150	hard, tough
3	1.11	X	0.510	X	3.53	459	30	93	160	hard, tough
4	1.11	X	0.510	X	7.05	230	32	109	100	hard, tough, light brown
5	1.79	XII	1.55	XII	13.40	249	30	145	360	hard, tough, plaque

^a Polymerization temperature, 25°C.

^b BF₃·O(C₂H₅)₂ (employed as a 10% solution in diethylene glycol).

^c Calculated from molar quantity of monomers and initiator employed.

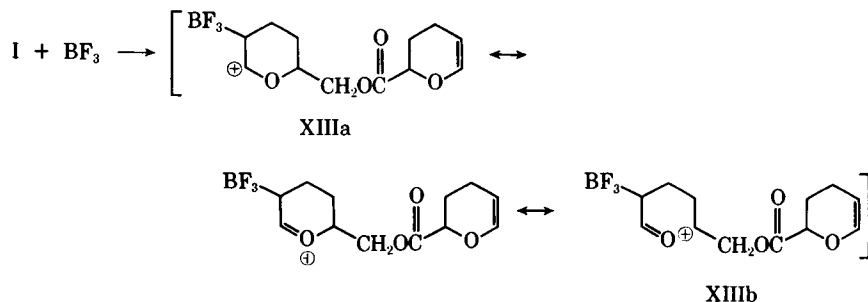
Polymerizations of acrolein tetramer in the presence of boron trifluoride etherate catalyst takes place rapidly and with high exotherm to give a hard but brittle polymer which showed some shrinkage on standing. Generally, copolymerization of acetals with acrolein tetramer exhibited a slight moderating effect by lowering the maximum temperature without significantly affecting polymerization rate. In most cases the copolymers were physically characterized as hard, tough, thermoset materials with very glossy surfaces. Colors ranged from amber to a clear brown.

The copolymerizations with mono-1,3-dioxolanes proceeded rather slowly at high monomer-to-initiator ratios ($M/I = 700-850$). At higher catalyst concentrations ($M/I = 350-400$), the copolymerization rates were vastly increased with essentially no change in maximum exothermic temperature. On the other hand, the vinyl dioxane, 2-vinly-1,3-dioxane (IX), copolymerized readily to high exotherm even at high monomer-to-initiator ratios. The polyfunctional cyclic acetal derivatives led to rapid and complete copolymerization at all concentrations of initiator investigated, and the increased functionality did not raise the peak exotherms.

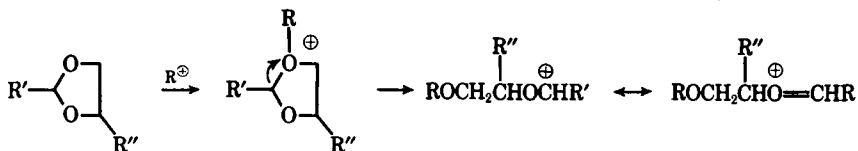
Although copolymerization of the cyclic acetals and cyclic vinyl ether has not been conclusively ascertained, the polymer property improvements seen in rigid foams make it appear unlikely that a mixture of two homopolymers or plasticization of the acrolein tetramer homopolymer by the cyclic acetals could have brought about these improvements.

It is the nature of these rapid, highly exothermic polymerizations to produce thermoset products containing voids as entrained air bubbles which preclude meaningful mechanical property determinations as solid plaques. However, pyranyl rigid foams from acrolein tetramer provided an approach to evaluate some copolymer properties. Rigid foam formation is manifested in attaining the proper balance of polymerization rate, temperature, and gelation; and, therefore, not all cyclic acetals prepared in this study could be evaluated as copolymers in foams.

The individual chemical reactions involved in the copolymerization of acrolein tetramer with the cyclic acetals are extremely numerous and difficult to describe, and the structure of the final resin products are undoubtedly extremely complex. Nevertheless, the growing polymer is a carbonium ion, and a couple of the eight possible propagating species from acrolein tetramer are shown by XIIIa and XIIIb:



Likewise, carbonium ion species can arise from the reaction of catalyst with an acetal ring oxygen of the 1,3-dioxolane or 1,3-dioxane. Copolymerization, by electrophilic attack of a cationic species, can occur easily with 1,3-dioxolanes or 1,3-dioxanes since resonance stabilization of the oxymethylene cation makes possible ring opening of acetal rings free of strain:



In the case of the 2-vinyl-substituted acetals, electrophilic attack on the vinyl group as well as the acetal oxygens is also possible and additional resonance stabilization is thereby gained.¹²

Preparation of Pyranyl Rigid Foams from Copolymerization of 1,3-Dioxolanes and 1,3-Dioxanes and Acrolein Tetramer

Pyranyl rigid foams based on the acid catalyzed polymerization of acrolein tetramer was recently reported.² Because homopolymerization of acrolein tetramer is too rapid and exothermic for proper control of polymer expansion and crosslinking, pyranyl foams are conventionally prepared from mixtures of acrolein tetramer and bisphenol A. The formulation for a typical foam is shown in Table III (foam A).

Combinations of certain 1,3-dioxolanes and 1,3-dioxanes with acrolein tetramer afforded stable rigid foams with acceptable foaming rates and curing times. The cyclic acetals found suitable for copolymerization

TABLE III
Typical Formulations for Preparation of Rigid Pyranyl Foams

	Foam A, parts by wt	Foam B, parts by wt
Component A		
Acrolein tetramer	76	39
Bisphenol A	24	24
Dioxolane IV	—	37
Trichloromonofluoromethane	17	19
Silicone surfactant L-5310*	1.0	0.80
Component B		
Boron trifluoride etherate (10% diethylene glycol)	0.79	0.81
Cream time, sec	50	10
Rise time, sec	80	100
Tack free time, sec	60	100

* Silicone L-5310 (Union Carbide Corporation).

TABLE IV
Physical Properties of a Typical Rigid Pyranyl Foam
and One Containing a 1,3-Dioxolane (IV)*

	Foam A	Foam B
Density, lb/ft ³	2.13	2.14
Closed cells, %	89	91
Compression strength, psi		
parallel to direction of rise	38	35
perpendicular to direction of rise	15	12
Friability, % wt. loss		
2 min	17.6	0.3
10 min	76.9	2.2
20 min	99.2	4.2

* Foam composition is shown in Table III.

in foams were compounds IV, VI, VII, VIII, and X. Table III shows a typical formulation and foaming rates for a foam containing a bis(1,3-dioxolane) (IV).

Properties for rigid pyranyl foams prepared with and without a cyclic acetal are described in Table IV. The friability resistance of foams containing cyclic acetals are illustrated by Figures 1 to 4. Figures 1 and 2 are plots of foam friability resistance versus concentration of a 1,3-dioxolane (IV) and a 1,3-dioxane (X), respectively, in an acrolein tetramer foam where no bisphenol A had been employed in the formulations. Rigid foams from copolymerization of both types of cyclic acetals and acrolein tetramer exhibited marked improvement in friability resistance as com-

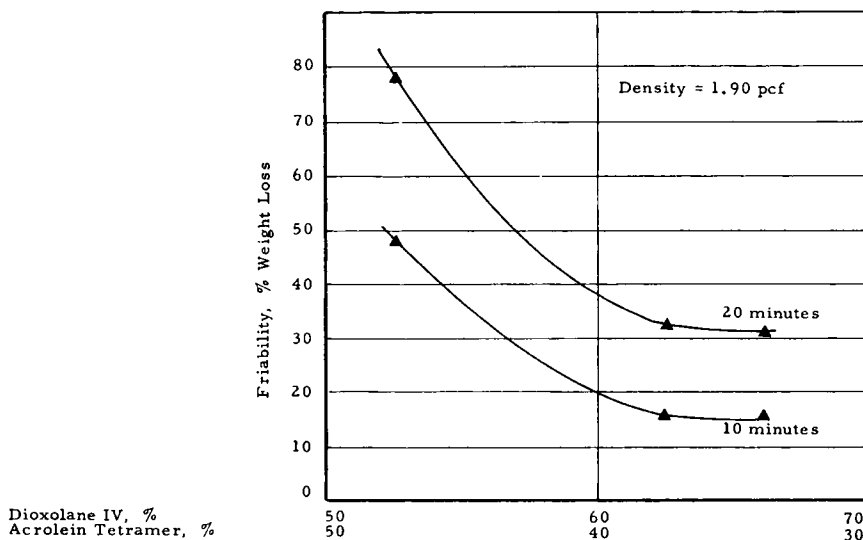


Fig. 1. Friability resistance of rigid pyranyl foams containing a substituted dioxolane (IV).

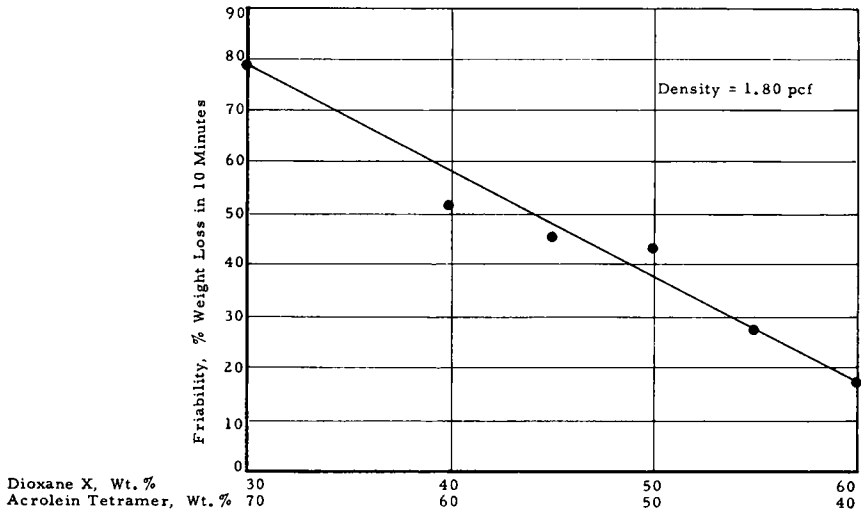


Fig. 2. Friability of rigid foams from copolymerization of a substituted dioxane (X) and acrolein tetramer.

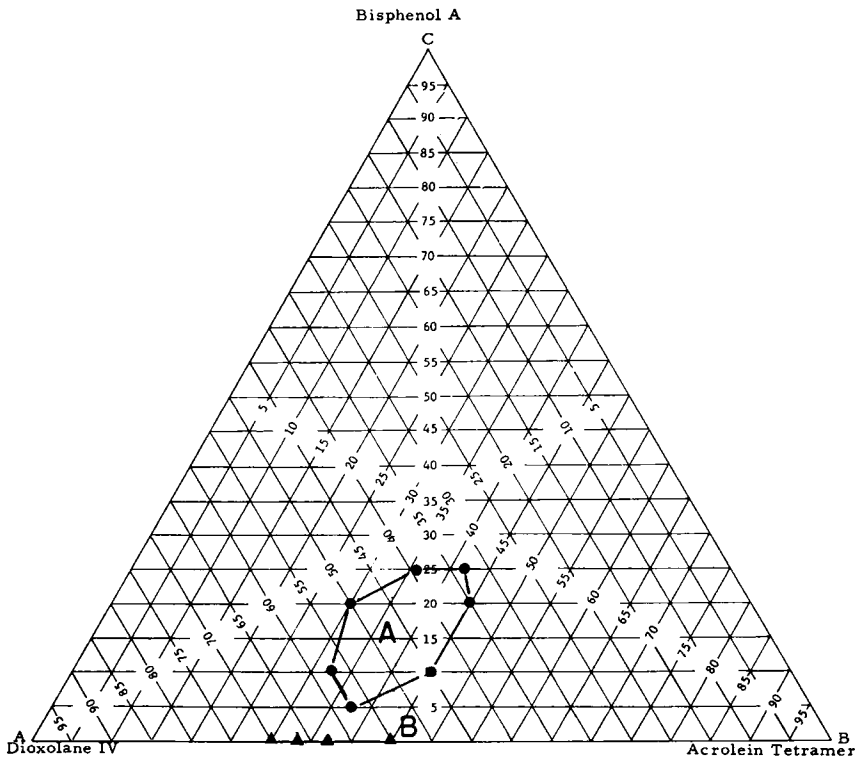


Fig. 3. Definition of low friability regions in which three components vary; area A, less than 15% wt. loss after 20 min; line B, about 30% wt. loss after 20 min.

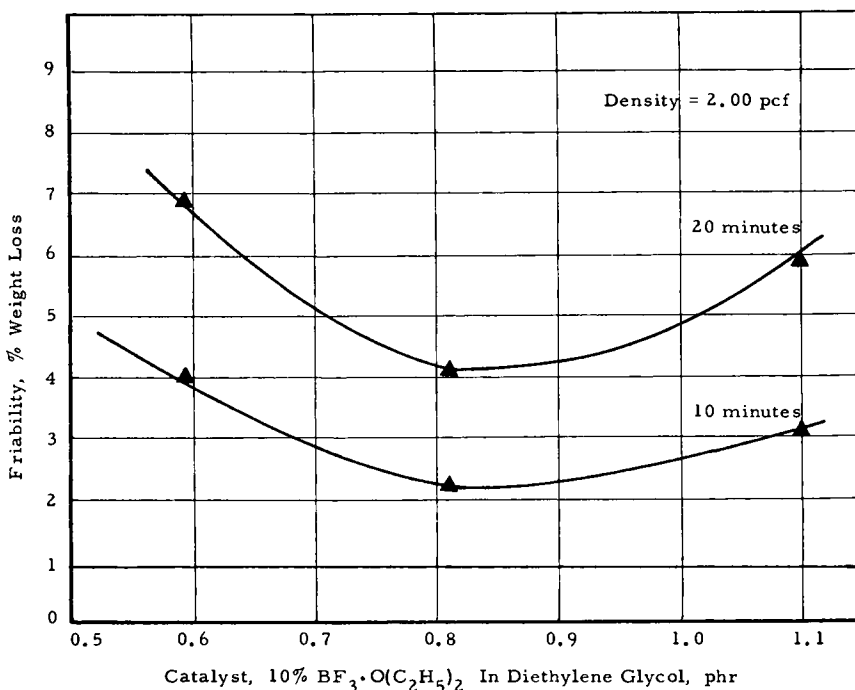


Fig. 4. Effect of catalyst concentration on friability of a substituted dioxolane (IV)-acrolein tetramer-bisphenol A (39/37/24) system.

pared to foams based on the acrolein tetramer-bisphenol A system. At best, conventional pyranyl rigid foams show about 75% weight loss after 10 min by the friability testing procedure, while the copolymer foams lost about 15% under identical test conditions. The improvement was most apparent when the cyclic acetal represented about 55% of the comonomer mixture.

In Figure 3, the variation of friability resistance is shown when bisphenol A was added to a 1,3-dioxolane (IV)-acrolein tetramer copolymer system. Area A represents a region of very high friability resistance (weight losses 5-15% after 20 min). The limits of this region show that systems containing 30-45% acrolein tetramer and 5-25% bisphenol A, with the remainder being a substituted 1,3-dioxolane (IV), provide foams with the highest friability resistance. On the other hand, line B describes the ratios of the 1,3-dioxolane and acrolein tetramer which afforded foam which exhibited about twice the weight loss as compared to foams incorporating bisphenol A.

Figure 4 illustrates the effect of foaming catalyst concentration on friability resistance of a 1,3-dioxolane-acrolein tetramer copolymer system containing bisphenol A. In all cases studied, the friability resistance appeared to be relatively insensitive to catalyst concentration of 0.6 to 1.1 phr. Although Figure 4 shows a minimum weight loss at 0.8

phr, the difference between it and 0.6 and 1.11 phr is small and probably within experimental error of the friability test procedure. With copolymer compositions not containing bisphenol A, the catalyst concentration requirements usually ranged from 1.50 to 3.00 phr for suitable foaming rates and optimum friability resistance.

It is doubtful that the improvements in friability in these copolymer foam systems can be attributed entirely to the relatively small percentage of urethane linkages introduced from some of the acetals. It seems likely that increased chain flexibility resulting from lower crosslink density introduced by the acetals, as compared to acrolein tetramer homopolymer, might be the major factor.

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