

Synthesis and Crosslinking of a New Series of Acrylate Polymers Containing a *m*-Dioxane Ring

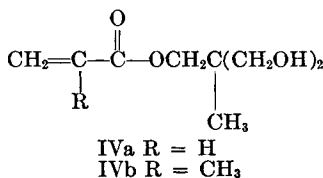
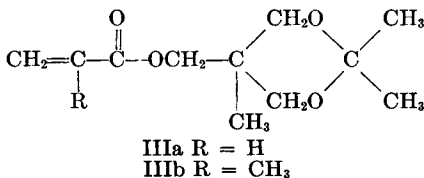
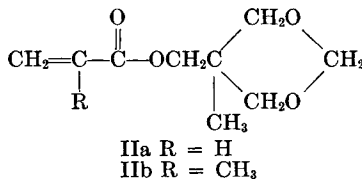
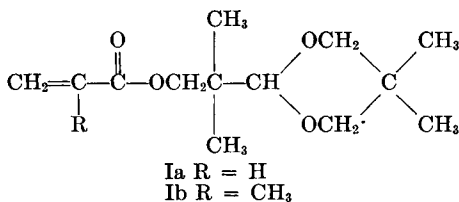
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Synopsis

Several new acrylate and methacrylate ester monomers and polymers which contain three different *m*-dioxane rings are described. All homopolymers have high second-order transition temperatures and softening points and one methacrylate polymer has the highest value reported for an acrylic ester polymer. The *m*-dioxane ring provides a site for crosslinking homopolymers and copolymers by acid and/or peroxide. The order of reactivity of the polymers in crosslinking by peroxide and acid is different, suggesting that ionic and free-radical mechanisms are involved. The order of reactivity is discussed in terms of the structure of the side chain dioxane rings. Oxygen plays a role in the peroxide crosslinking reaction. One of the *m*-dioxane rings in monomer or polymer form is readily opened by water to form hydroxyl-containing materials.

INTRODUCTION

This paper describes some new acrylate and methacrylate monomers, I, II, and III, containing a dioxanyl ring in the alcohol portion of the ester, their homopolymers, and some of their copolymers. Acid- and peroxide-induced crosslinking of polymers are discussed, and certain catalytic responses are related to the structure of the dioxanyl residue. Two new hydroxyl-containing acrylate and methacrylate monomers (IV) derived from acetoneals IIIa and IIIb by hydrolysis were prepared.



A number of polymers containing the *m*-dioxane ring structure have been reported during the past fifty years.¹⁻⁴ Most of them are derived from pentaerythritol and contain a spiro ring structure in the polymer backbone. Poly(vinyl formal) and poly(vinyl butyral) contain a *m*-dioxane ring as part of the polymer backbone without a spiro structure. To our knowledge there are no previously reported linear polymers containing a dioxanyl ring as part of the side chain. One U.S. patent⁵ discloses preparation of spiro bisacrylates and bismethacrylates and their polymers. The polymers were crosslinked as expected from the bifunctionality of the monomers.

Acrylate and methacrylate polymers containing a dioxolane ring structure (a five-membered acetal ring) in the side chain are reported in two patents,^{6,7} and crosslinking of these polymers with acid is described in one. The polymers of Fegley et al.⁶ were not described sufficiently to ascertain whether the acetonal dioxolane structures survived the acid catalyzed cures used in their work.

Crosslinking of certain linear polyester spirodioxanes was reported recently by Pryde and co-workers.³ They found that lead and zinc oxides at 250°C. crosslinked dioxanyl polyesters but did not crosslink polyesters free of the spirodioxane ring system. They speculated that crosslinking occurred via ring opening and acetal exchange reactions. *p*-Toluenesulfonic acid was also reported to be an effective crosslinking catalyst.

EXPERIMENTAL AND RESULTS

Monomer Preparation

Esters I and II were derived from $\beta,\beta,5,5$ -tetramethyl-2-*m*-dioxane β -ethanol and 5-hydroxymethyl-5-methyl-*m*-dioxane, respectively. Synthesis of these *m*-dioxane alcohols has been described in a recent paper.⁸ 5-Hydroxymethyl-2,2,5-trimethyl-*m*-dioxane, used to prepare esters IIIa and IIIb, was prepared as follows. 2-Hydroxymethyl-2-methylpropanediol-1,3 (0.5 mole, 60 g.) was mixed with excess acetone (175 ml.) in a 500-ml. flask equipped with a Dean-Stark trap and reflux condenser. A 2:1 mixture of 2,2-dimethylbutane and *n*-pentane (150 ml.) was added, and the mixture acidified with 1.5 g. of *p*-toluenesulfonic acid hydrate. The mixture was refluxed (40°C.) for 29 hr., during which time 11 ml. of a water-acetone phase was removed. The solution was neutralized with anhydrous sodium acetate and filtered. Solvents were removed by means of a rotating evaporator and the product distilled *in vacuo*. The main fraction (63 g., 79%) boiled at 53-54°C./0.1 mm. The infrared spectrum showed strong bands at 2.8, 9.1, and 12.0 μ which are characteristic of alcohols, ethers, and acetonals respectively.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.97%; H, 10.07%. Found: C, 59.71%; H, 10.04%.

The esters I-III were prepared via ester exchange reactions with methyl acrylate and methyl methacrylate. The preparation of (2,2,5-trimethyl-5-*m*-dioxanyl)methyl methacrylate (IIIb) is typical.

To a mixture of 206 g. (1.29 moles) of 5-hydroxymethyl-2,2,5-trimethyl-*m*-dioxane and 490 g. (4.40 moles) of methyl methacrylate was added 1.2 g. of Ionol and 29 ml. of tetrabutyl titanate. Heat was applied and a methyl methacrylate-methyl alcohol azeotrope (67 ml. 85% methanol) boiling at 64.5–65°C. was removed. The temperature rose to 98–100°C., where 70 ml. of methyl methacrylate was removed. The reaction mixture was cooled and stripped of most of the excess methyl methacrylate, diluted with benzene, and shaken vigorously with 40 ml. of water to destroy the catalyst. The material was filtered, dried over sodium sulfate, stripped of solvents and fractionally distilled through a Vigreux column. The yield of ester was 216.5 g. (74%).

Esters IVa and IVb were prepared in the following manner by acid hydrolysis of the acetonal esters IIIa and IIIb, respectively.

Acrylate ester IIIa (5 g.) was added to 100 ml. of water and the solution pH adjusted to 3 with dilute hydrochloric acid. The two-phase system was heated to 40–45°C. for 2 hr., during which time the oil phase disappeared. The aqueous solution was cooled, neutralized with solid potassium carbonate, filtered, and then extracted three times with chloroform. After drying over anhydrous sodium sulfate, the chloroform was removed and the hydrolyzed monomer used as such. The infrared spectrum indicated complete hydrolysis as judged by the complete disappearance of the acetonal band at 12.0 μ .

Monomer Properties

Table I lists the boiling points and analysis of acrylate and methacrylate esters I–III. Acrylate IIIa is a low-melting crystalline solid. All others are oily liquids.

TABLE I
Characterization of *m*-Dioxane Acrylic Esters

Compound	Empirical formula	B.p., °C./mm. Hg.	Anal., calcd.		Anal., found	
			C, %	H, %	C, %	H, %
Ia	C ₁₃ H ₂₂ O ₄	69/0.25	64.42	9.16	64.63	9.36
Ib	C ₁₄ H ₂₄ O ₄	80.5–82/0.5	65.62	9.38	65.67	9.51
IIa	C ₉ H ₁₄ O ₄	57/0.2	58.05	7.57	57.81	7.16
IIb	C ₁₀ H ₁₆ O ₄	72–73/0.5	60.00	8.00	59.76	8.11
IIIa	C ₁₁ H ₁₈ O ₄	81/1.0	61.65	8.49	62.14	8.95
IIIb	C ₁₂ H ₂₀ O ₄	76–83/0.5–1.0	63.16	8.77	63.29	9.04

Polymer Preparation

Polymers and copolymers of these acrylic monomers were prepared by bulk, solution, or emulsion techniques. These three methods are illustrated by the following examples.

Method I. Bulk Polymerization of Methacrylate IIIb. A glass polymerization cell was prepared in the following manner: Two glass plates

having the dimensions $\frac{1}{4} \times 4 \times 6$ in. were beveled on one edge. These were washed, dried, and coated with a 1% solution of dichlorodimethylsilane in petroleum ether. Igepal CO-630, an ethoxylated nonyl phenol, was then spread on the surface and subsequently washed off with distilled water. The plates were placed atop one another, spaced along the three nonbeveled edges with moist strips of cellophane. The cell was then sealed on these three edges with a gelatin-glycerin mixture containing a small amount of water and dried at 100°C. to harden the seal.

Polymerization was carried out as follows. Methacrylate IIIb (2.0 g.) was mixed with 2 mg. (0.1%) of 2,2-azobisisobutyronitrile. The material was introduced into the polymerization cell by means of a syringe. When the cell was completely filled, the top edge was sealed with the gelatin mixture and placed in an oven at 60°C. After 18 hr., the material had "set" and the temperature was raised to 120°C. over a 2-hr. period and kept at that temperature for 6 hr. After cooling, the polymer was removed by scraping off the gelatin seal and separating the plates.

Method II. Solution Copolymerization of Methacrylate IIb and Methyl Methacrylate. Benzene (12 ml.) was refluxed under argon for $\frac{1}{2}$ hr. in a 100 ml., three-necked, round-bottomed flask equipped with a gas inlet, reflux condenser, syringe cap, and magnetic stirring bar. Argon was also bubbled through the monomer mixture (5 g. of methacrylate IIb and 7.5 g. of methyl methacrylate) for $\frac{1}{2}$ hr. at room temperature. 2,2-Azobisisobutyronitrile (0.020 g.) was dissolved in the monomer mixture which was then added dropwise through the syringe cap to the boiling benzene over a period of one-half hour. After $3\frac{1}{2}$ hr. at reflux, the viscosity of the reaction mixture had increased greatly and additional benzene (2 ml.) was added to make stirring possible. After 7 hr., 2 ml. more benzene was added and the temperature was reduced to 50°C. overnight. After cooling, 50 ml. of benzene was added and the solution was poured into a liter of rapidly stirred methanol. The methanol was removed by suction filtration and the white polymer was washed with additional methanol, filtered, and dried under vacuum.

Method III. Emulsion Copolymerization of Methacrylate Ib and Styrene. Duponol C, a sodium alcohol sulfate, (0.33 g.) in 12 ml. of distilled water was added to a mixture of 5.85 g. of styrene and 4.80 g. of methacrylate Ib. The mixture was shaken vigorously in an addition funnel to emulsify the monomers and a solution of 0.22 g. of potassium persulfate and 0.010 g. of potassium carbonate in 1 ml. of water was added. A portion (7 ml.) of this material was added to a 100-ml. round-bottomed flask equipped with a paddle stirrer, a reflux condenser, and a gas inlet. The reaction mixture was heated to 90°C. under argon and stirred rapidly. After 1 hr., the remaining monomer emulsion was added dropwise (addition time 1 hr.). Temperature was maintained for an additional hour, after which time the emulsion was filtered through a 50- μ screen and coagulated with methanol.

Homopolymer IVb was prepared by mild acid hydrolysis of polymer IIIb

in aqueous acetone or aqueous dioxane. Several attempts to prepare this material from the monomer in an emulsion system gave only insoluble polymers.

Polymer Properties

Homopolymers and copolymers prepared from acrylic monomers, I, II, and III are summarized in Table II. Note that monomers Ib and IIb gave insoluble polymers when polymerized in bulk, while IIIb gave a soluble material of high molecular weight under the same conditions.

TABLE II
Properties of Acrylate and Methacrylate Homopolymers and Copolymers

Polymer	Polymerization method	Solubility ^a	Softening point, °C. ^b	Second-order transition temp., °C. ^c	Inherent viscosity ^d	Barcol hardness
Ib	I	Insoluble	—	—	—	—
Ib	II	Soluble	118-125	104-118	0.23	84
IIb	I	Insoluble	—	—	—	—
IIb	II	Soluble	160-175	142	0.99	84
IIIb	I	Soluble	115-125	—	4.10	—
IIIb	II	Soluble	117-124	100-108	0.35	—
IVb	°	Soluble	—	—	—	—
IVb	III	Insoluble	—	—	—	—
25Ib/75 MMA ^f	II	Soluble	120-130	105-120	0.57	88
25Ib/75St ^f	III	Soluble	100-125	98-111	1.52	76
25Ib/75 <i>n</i> -BA ^f	II	Soluble	Rubbery	—	—	—
25IIb/75 MMA	II	Soluble	138-165	91-138	0.48	90
Ia	II	Soluble	45-55	—	0.25	65
IIa	II	Soluble	60-70	—	0.51	65
IIIa	II	Soluble	41-45	—	0.62	65

^a In benzene and tetrahydrofuran.

^b Softening points determined on a Fisher-Johns melting point apparatus.

^c Determined by differential thermal analysis.

^d Inherent viscosity was measured in tetrahydrofuran at 25°C. with 0.5 g./100 cc. solvent.

^e Prepared by acid hydrolysis of homopolymer, IIIb.

^f MMA = methyl methacrylate; St = styrene; *n*-BA = *n*-butyl acrylate. Numbers refer to the mole weight ratios used in feed.

The *m*-dioxane acrylate polymers are softer, lower-melting materials than the methacrylates, as one would expect. Their softening points are all above room temperature.

Crosslinking of Polymers

Films of methacrylate polymers Ib, IIb, and IIIb were cast from benzene solutions with and without additives on glass plates, and after drying, were cured in a pistol-type drying apparatus provided with a gas inlet and outlet, refluxing 1,1,2,2-tetrachloroethane being used as a constant tempera-

ture source (146°C.). The atmosphere above the film was controlled by maintaining a stream of air, nitrogen, or argon. Dry solvents to test film solubility were used in all cases.

Crosslinking of methacrylate Ib occurred more readily with the use of dicumyl peroxide in air than in argon. An increase in peroxide concentration from 1 to 2%* in air accelerated the onset of insolubility from about three hours down to less than one. Trichloroacetic acid (2%) in an argon atmosphere was not effective in crosslinking polymer Ib. Long heating (15 hr.) in dry air with the same concentration, however, rendered the film completely insoluble, while a film sample heated in moist argon for 15 hr. in the presence or absence of trichloroacetic acid remained soluble.

Polymer IIb cured more readily than polymer from Ib with peroxide or with acid. Polymer IIb film was mostly insoluble in less than 1/2 hr. when 1% dicumyl peroxide in either air or argon was used. Trichloroacetic acid was also an effective catalyst in argon, giving rise to benzene insolubility in less than 1 hr. at 146°C. No insolubility was noted if either catalyst was omitted after 6 hr. in argon.

Attempts at crosslinking polymethacrylate IIIb with peroxide in argon were unsuccessful. Methacrylate polymer IIIb, however, cured very rapidly in an air oven in the presence of *p*-toluenesulfonic acid. After 1/2 hr. the film was very hard (pencil hardness 9H) and completely insoluble in benzene. However, extensive pitting of the film was noted. The infrared spectrum of the cured material was identical to that of polymer IVb, indicating that acetal groups were completely hydrolyzed or nearly so. The onset of insolubility was slower in the absence of catalyst (air oven) but after 17 hr. the film was completely insoluble. Curing under dry argon in the presence of 26% hexamethylene glycol and 2% trichloroacetic acid gave a crosslinked film still containing acetal groups whereas no crosslinking occurred in the absence of the glycol under the same conditions.

Crosslinking of the acrylate dioxane polymers was examined superficially. Curing was carried out in an air oven at 150°C. with the use of 1% dicumyl peroxide or 2% *p*-toluenesulfonic acid. Indications are that the polyacrylates crosslinked more readily than the methacrylates. Cured films were generally hard (6H to above 9H pencil hardness), though heat resistance was not good as evidenced by some browning of the films after 1 1/2 hr. at 150°C. Adhesion to glass in nearly all cases was excellent.

DISCUSSION

Crosslinking of Polymers

Data on crosslinking dioxanyl methacrylate polymers strongly suggests the existence of two distinct mechanisms: one ionic and one free radical. A simplified summary of the crosslinking data appears in Table III.

The order of crosslinking reactivity of the methacrylate homopolymers in

* Percentages are weight per cents based on solid polymer.

TABLE III
Summary of Catalytic Effects in
Crosslinking of Methacrylate Polymers at 140–150°C.

Meth- acrylate polymer	Structure <i>m</i> -dioxane	Peroxide crosslinking		Acid crosslinking	
		Air	Argon	Argon	Air
Ib		Yes	No	No	Yes
IIb		Yes	Yes	Yes	Yes
IIIb		No	No	No	Yes

a peroxide cure, IIb > Ib >>> IIIb, suggests that the hydrogen atoms on C₂ (carbon between the two oxygen atoms) of the ring are involved. When this position is completely blocked (IIIb), no response is observed and when completely unsubstituted (IIb) reactivity is greatest. Supporting evidence that the C₂ position of *m*-dioxanes is reactive in free radical attack is shown by the work of Patrick,^{9,10} where *m*-dioxane was made to add via this position to a maleate ester at 80–100°C. with benzoyl peroxide as catalyst. Hochberg,¹¹ in a discussion of vinyl-substituted cyclic acetals, points out that these compounds absorb oxygen readily forming hydroperoxides at C₂.

The order of crosslinking reactivity of methacrylate polymers with acid is not as clear-cut. It takes the form IIIb > IIb >>> Ib in air under conditions where no attempt is made to exclude moisture. This order is more apparent than real because polymer IIIb loses acetone in air to form polymer IVb which is insoluble in benzene, the solvent used as a diagnostic test for crosslinked polymer. The order of crosslinking reactivity with acid under anhydrous conditions is polymer IIb >>> IIIb. A film of polymethacrylate IIIb remained soluble and its infrared spectrum unchanged when heated with trichloroacetic acid in dry nitrogen, showing that acid-catalyzed crosslinking does not occur with this polymer in the absence of moisture. We expected the acetonal polymer IIIb to ring open and crosslink much more readily than the formal polymer IIb on the basis of reported hydrolysis rate studies of *m*-dioxanes^{12,13} This apparently does not hold true under anhydrous conditions.

Adventitious water in the acid catalyst or in air must be held responsible for loss of acetone in curing films of polymers IIIb. Hydrolysis and loss of

acetone also could be made to occur slowly by heating in air at 150°C. in the absence of added acid. This observation is in accord with the work of Conrad and co-workers,¹⁴ who demonstrated that acetonals can be made to hydrolyze in the absence of catalyst. Crosslinking and insolubilization of polymer IIIb with retention of acetal structure could be made to occur in the absence of water by heating in the presence of acid and less than equivalent amount of dry hexamethylene glycol. More work is required to elucidate the mechanism and structural influences on the acid catalyzed crosslinking reactions of *m*-dioxane polymers.

Second-Order Transition Temperature

The second-order transition temperature of methacrylate IIIb by DTA measurement, 142°C., is unusually high and to our knowledge the highest T_g reported for a methacrylate homopolymer. The following methacrylate polymers containing a cyclic ring on the side chain have second-order transition temperatures equal to or below 111°C.: poly(phenyl methacrylate), 40°C.;¹⁵ poly(cyclohexyl methacrylate), 57°C.;¹⁶ poly(isobornyl methacrylate), 111°C.¹⁶

A high T_g is characteristic of the dioxanyl methacrylates. They all have higher T_g values than that of poly(methyl methacrylate) which we determined by DTA to be 104°C. The latter temperature is in good agreement with reported values for poly(methyl methacrylate).¹⁷ Copolymers of IIB with methyl methacrylate have transitions which lie between the values for the two homopolymers, as expected.¹⁷

The second-order transition temperatures of the dioxanyl acrylate polymers were not determined. Comparison of data in Table II shows that polyacrylate IIa has the highest softening point among the acrylate polymers, as does polymer IIB for the methacrylate polymer series. Furthermore, the high softening range values obtained suggest that the dioxanyl acrylate polymers, like their methacrylate counterparts, have abnormally high second-order transition temperatures.

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Résumé

On décrit plusieurs nouveaux monomères et polymères d'acrylates et méthacrylates, qui contiennent trois cycles *m*-dioxane différents. Tous les homopolymères ont des températures de transition de second ordre et des points de ramollissement élevés et un polymère méthacrylique présente la plus haute valeur approtée pour un ester polyacrylique. Le cycle *m*-dioxane fournit un site de pontage des homo- et copolymères par un acide et/ou un peroxyde. L'ordre de réactivité des polymères lors du pontage par peroxyde et acide est différent, ce qui suggère que des mécanismes ioniques et radicalaires sont impliqués. L'oxygène joue un rôle dans la réaction de pontage par peroxyde. Un seul des cycles *m*-dioxanes présent dans le monomère danste polymère, est rapidement ouvert par l'eau pour former des produits contenant des groupes hydroxyles.

Zusammenfassung

Einige neue Acrylate- und Methylacrylatestermonomere und -polymere, welche drei verschiedene meta-Dioxanringe enthalten, werden beschrieben. Alle Homopolymeren besitzen hohe Umwandlungstemperaturen zweiter Art und hohe Erweichungspunkte; ein methacrylatpolymeres weist den höchsten für ein Acrylesterpolymeres mitgeteilten Wert auf. Der meta-Dioxanring liefert eine Vernetzungsstelle für Homo- und Copolymere durch Säure oder Peroxyd. Die Reihenfolge der Reaktivität der Polymeren ist bei der Vernetzung durch Peroxyd und Säure verschieden, was dafür spricht, dass ionische oder radikalische Mechanismen beteiligt sind. Die Reihenfolge der Reaktivität wird an Hand der Struktur der Seitenkettendioxanringe diskutiert. Sauerstoff spielt bei der Peroxydvernetzungsreaktion eine Rolle. Einer der meta-Dioxanringe in der monomeren oder polymeren Form wird leicht durch Wasser unter Bildung hydroxylhaltiger Stoffe geöffnet.

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