precursor to photochemistry is the triplet.[1a,b,2] Thus, it is probable that the size effects on the photochemistry result from distortions in the triplet rather than the singlet state.

The trimethylsilyl-containing copolymers show no regularity in the variation of fluorescence quantum yield with comonomer size. The smallest comonomer, dimethylsilylene, has a quantum yield intermediate between the largest and next largest comonomers. The absorption and fluorescence band maxima, however, are related to size in much the same fashion as in the alkyl series.

The similarity in behavior of the (trimethylsilyl)-methyl-substituted copolymers with cyclohexylmethylsilylene and phenylmethylsilylene comonomers is striking. The absorption maxima, the fluorescence maxima, the fluorescence quantum yields, and the fluorescence bandwidths are the same within experimental error. Only the absorption bandwidths differ and this is most probably a consequence of a second, $\pi-\pi^*$, band at about 280 nm in the phenyl moieties. The phenylmethylsilylene and cyclohexylmethylsilylene homopolymers show entirely different behavior. The poly(phenylmethylsilylene) absorption maximum is shifted 20–22 nm to the red from that of poly(cyclohexylmethylsilylene), a phenomenon that has been attributed to mixing of the ring π states with the chain σ's.[3,8] Apparently the introduction of the trimethylsilyl substituents effectively quenches this $\pi-\sigma$ interaction. The large size of the trimethylsilyl may substantially alter the rotational configuration of the rings with respect to the silicon chain, making this $\pi-\sigma$ mixing less favorable.

Conclusions. The introduction of trimethylsilyl substituents onto polysilylene chains substantially reduces the fluorescence quantum yields over those of the alkyl-substituted polysilylenes. This decrease in fluorescence yield is accompanied by an apparent increase in photosensitivity. Since previous work suggests that triplets are the precursors to photochemistry in alkyl polysilylenes, we suggest that the heightened photosensitivity of these materials is due to an augmentation of the intersystem crossing rate, although the operation of singlet photochemistry, perhaps involving side-chain cleavage, cannot be rigorously ruled out at this time. The increased photosensitivity of the (trimethylsilyl)-substituted polysilylenes cannot be attributed to a substituent size effect since incorporation of a *tert*-butyl moiety in place of the trimethylsilyl group reduces the fluorescence yield without causing increased photochemical sensitivity.

In phenyl-substituted copolymers, the trimethylsilyl unit quenches the $\pi-\sigma$ mixing of the chain and ring states, since little difference exists in the spectroscopic properties between phenyl and cyclohexyl substitution in these copolymers. Work is continuing to ascertain the role of singlet states in the photochemistry of silyl-substituted polysilylenes and to characterize the applicability of these new polymers as resists.

Registry No. *c*-Hex(Me)$SiCl_2$ (homopolymer), 88002-85-1; (*c*-Hex(Me)$SiCl_2$)(*t*-Bu(Me)$SiCl_2$) (copolymer), 109281-90-5; Pr(Me)$SiCl_2$ (homopolymer), 88002-81-7; Me_3(Me)$SiCl_2$ (homopolymer), 109088-90-6; (Me_3Si(Me)$SiCl_2$)((Me)$_2SiCl_2$) (copolymer), 109281-91-6; (Me_3Si(Me)$SiCl_2$)(Pr(Me)$SiCl_2$) (copolymer), 109088-91-7; (Me_3Si(Me)$SiCl_2$)(*c*-Hex(Me)$SiCl_2$) (copolymer), 109088-92-8; (Me_3Si(Me)$SiCl_2$)(Ph(Me)$SiCl_2$) (copolymer), 109088-93-9.

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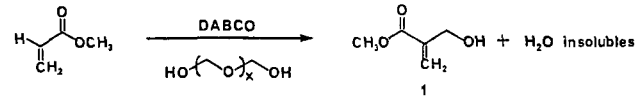
Received February 12, 1987

New Difunctional Methacrylate Ethers and Acetals: Readily Available Derivatives of α-Hydroxymethyl Acrylates

It has been reported that a number of aldehydes can be coupled with acrylate esters under mild conditions in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane).[2-5] Using this approach, we have synthesized and polymerized the simplest derivative of methyl acrylate **1** obtained from formaldehyde (as formalin).[6]



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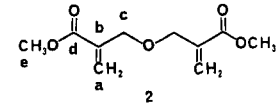
Compound **1** can also be made in ca. 30% yield from paraformaldehyde, the low molecular weight polymer of formaldehyde.[7] Workup of the reaction mixture by water extraction resulted in a water-insoluble fraction which did not display hydroxyl peaks in the IR. GC analysis indicated a complex mixture of products. Column chromatography[7] resulted in separation of the three main components **2–4**.



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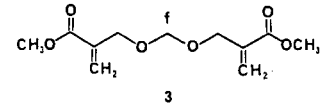

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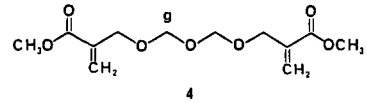

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Identification of these compounds involved purification and spectral characterization.[8] While none of the three displayed alcohol peaks in the IR, they all showed bands corresponding to ester and conjugated olefin groups. Peaks later identified as either and acetal bands were also observed. Most informative were the ^{13}C NMR spectra shown in Figure 1. Peaks were evident for all carbons found in the alcohol **1** but with significant differences in

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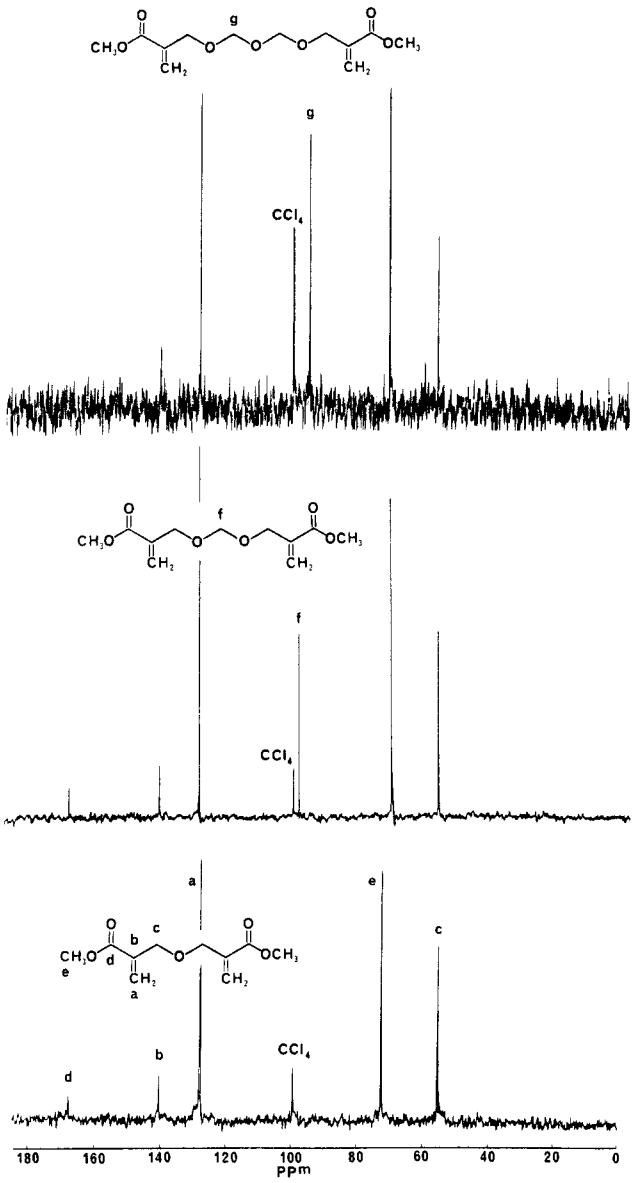


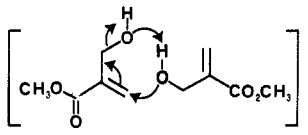
Figure 1. ^{13}C NMR spectra of ethers **2**, **3**, and **4** obtained in CCl_4 with a Bruker MSL-200 spectrometer.

the chemical shifts. More important was the new peak observed for **3** and not found in **2** corresponding to the middle acetal carbon (peak f in the spectrum). This new peak was shifted in going to **4** and became more intense relative to the peak for the adjacent methylene carbons. ^1H NMR confirmed the presence of methyl esters, alkene and ether CH_2's, and especially the acetal methylenes for **3** and **4**.

These new difunctional monomers are potentially valuable cross-linking agents and may also be capable of cyclopolymerization. Ether **2**, for example, readily underwent polymerization in dimethyl sulfoxide initiated with 2,2′-azobisisobutyronitrile to give a clear, tough swollen gel that was insoluble and highly cross-linked. This material was surprisingly tenacious in retaining solvent even upon extended extraction with water. Photopolymerization of a thin film of **2** in the presence of a catalytic amount of benzoin isopropyl ether gave a clear film with good physical properties. The IR spectrum of this film confirmed disappearance of monomer and formation of polymer.

The mechanism of formation of the ether and acetals appears to involve MHMA as an intermediate. GC analysis of the reacting mixture showed rapid buildup of MHMA followed by gradual formation of **2**–**4** and higher homologues. The acetals should be available from the reaction of two molecules of MHMA with monomeric and oligomeric formaldehyde.

Ether formation under basic conditions is surprising, especially under the mild conditions used here. This suggests a low-energy pathway different from that normally seen in ether synthesis. In fact, we have shown that purified MHMA can be converted to the ether in 60–70% yield by heating in the presence of DABCO. A possible ene-type mechanism would involve a six-membered transition state (**5**) through which simultaneous or sequential



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transfer of a hydrogen atom, loss of water, and formation of an ether bond occur. We are currently synthesizing MHMA with deuterium-labeling at the hydroxyl CH_2 to further evaluate the mechanism of this reaction.

Analogous ethers and acetals to these derivatives have also been made starting with the apropropriate alkyl acrylate. For example, we have also made the ethyl and *n*-butyl ester analogues of compounds **2**–**4**. Thus, a whole new family of difunctional acrylates are now synthetically available.

The difunctional acrylate ethers and acetals have the potential to replace existing diacrylate esters as cross-linking agents in a variety of applications such as photocurable coatings and photolithography. The ethers should lead to cured products which are more hydrolytically stable then presently used diacrylates since hydrolysis of the ester groups will not lead to a decrease in the polymer cross-link density. On the other hand, compounds **3** and **4** will give materials more easily hydrolyzed at the acetal linkage than presently used diacrylate esters and may find application where eventual degradation and dissolution of cross-linked materials is desirable.

Acknowledgment. We gratefully ackowledge a grant from S. C. Johnson and Son, Inc., for partial support of this research, the Fullbright Visiting Scholars Program for arranging travel and partial subsistance support for S.H.K., and the Department of Defense through the Office of Naval Research for the instrumentation grant used to purchase our Bruker MSL-200 NMR spectrometer.

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(7) Typical reaction conditions involved stirring a mixture of methyl acrylate (129 g, 1.5 mol), paraformaldehyde (30 g, 1 mol), and DABCO (5.6 g, 0.05 mol) for 8 days at room temperature. The reaction was stopped when all of the paraformaldehyde had reacted. Excess methyl acrylate was removed by evaporation and the remaining liquid extracted 3 times with water. The aqueous solution was made acidic with HCl and extracted with ether to give 90% pure compound **1**; 30.2 g, 33% yield. The water-insoluble fraction was separated by column chromatography on silica gel with elution by 10:1 pentane/diethyl ether. The order of elution from the column and in the GC was **2** first, followed by **3** and then **4**.
(8) Compound **2** as obtained as white needles from pentane, mp 48 °C. ^1H NMR δ 6.2 and 5.8 (H_a, 4 H), 4.2 (H_c, 4 H), 3.7 (H_e, 6 H). Major IR peaks (cm^{-1}) 1730 (carbonyl), 1620 (alkene),

1270 and 1100 (C–O–C). Compound **3** was obtained as white needles from pentane, mp 27 °C. ^{1}H NMR δ 6.2 and 5.8 (H_a, 4 H), 4.8 (H_f, 2 H), 4.3 (H_c, 4 H), 3.8 (H_e, 6 H). IR (cm^{-1}) 1730 (carbonyl), 1620 (alkene), 1125 and 975 (C–O–C). Compound **4** was obtained as a clear oil. ^{1}H NMR δ 6.2 and 5.8 (H_a, 4 H), 4.8 (H_g, 4 H), 4.2 (H_c, 4 H), 3.7 (H_e, 6 H). IR (cm^{-1}) 1750 (carbonyl), 1610 (alkene), 1125 and 975 (C–O–C). All compounds gave satisfactory elemental analyses.

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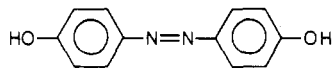
New Polyesters and Polyformals Containing Multiple *p*-Aryleneazo Groups: Liquid-Crystal Polyazoaryl Sebacates

Introduction. Liquid-crystal (lc) polymers have been of great interest in recent years (for recent reviews, see ref 1–4). Lc polymers come in several types: (1) the entire chain is mesogenic; (2) mesogenic groups are in the side chain; (3) mesogenic groups are in main chain. Our study will be confined to polymers in class 3. Polymers based on stilbene derivatives, tolanes, and aromatic polyimines have been reported to display lc properties. However, although the *p*-phenyleneazo link is known to favor lc behavior in small molecules, it has only recently been briefly reported to cause lc polymer formation.[5]

Polyesters have been the most popular type of thermotropic lc polymer. Accordingly, in this work we have synthesized a number of aromatic and aliphatic polyesters from bisphenols containing one to three *p*-phenyleneazo groups. The polymers have been examined for their lc properties. Aromatic formals have come into attention recently,[6,7] and we also synthesized them from a number of azobis(phenols).

Results. Monomers: Bis(phenols). The bis(phenol) monomers in this study are described in Table I. In general, they were obtained as indicated by the literature or were synthesized by standard procedures involving aryldiazonium ion couplings.[8,9] Although most of these compounds were reported in the literature (see references included in Table I), none (except 1) offered detailed procedures, elemental analyses, or melting points. Representative synthesis procedures are given in the Experimental Section.



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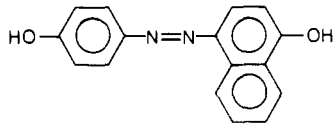

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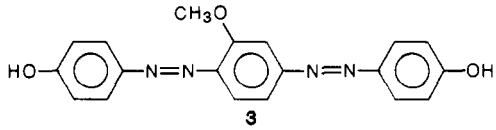

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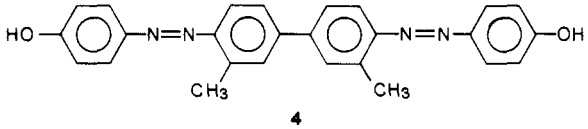

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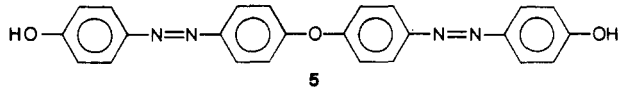

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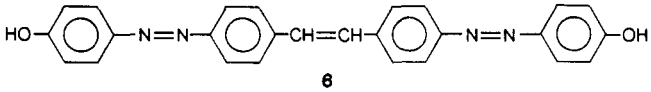

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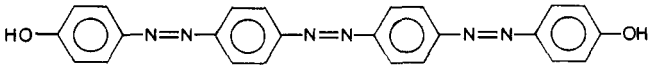

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Diacids. An important factor in these studies was the tractibility of the polymers. We wanted to avoid intractable, infusible "brick dust". Inasmuch as the *p*-phenyleneazo group tends to form intractable polymers, we used relatively "soft" diacyl halides to offset the "hard" bis(phenol). Because the "soft" diacid components possessed meta aromatic or aliphatic structures, the resulting combinations represent a trade-off between lc character and tractability. Isophthaloyl chloride and 5-*tert*-butylisophthaloyl chloride were the aromatic acid chlorides employed. As an aliphatic diacid, sebacic acid was used.

Polymerizations. All of the polyesters were synthesized by interfacial polycondensation. The results are given in Table II.

Polyformals were synthesized by use of excess dichloromethane in *N*-methylpyrrolidone solution as described in the literature.[7]

Properties of Polymers. The properties of the polymers we synthesized are collected in Table II. These include data on polymer melting behavior, inherent viscosities, film-forming ability, color, and lc behavior.

Polymer solubility was increased by the 5-*tert*-butyl group in isophthalic acid and the methoxy group in **3**. Derivatives of the bis(phenols) **2** and **5** had the greatest solubility. This factor helped us to achieve a higher molecular weight by keeping the polymer in solution longer. Films were cast from the polymer solution by evaporating the solvent. For those chloroform-soluble polymers, GPC chromatograms were obtained. They showed broad molecular weight distribution with the highest concentration at MW 14 000 for **2**-5-*t*-BuI, 10 000 for **3**-Seb, and 35 000 for **5**-5-*t*-BuI.

LC Behavior. The occurrence of lc behavior depended strongly on the bis(phenol) monomer and on the diacid. Both small molecules (Tables I and III) and polysebacates (Table II) based on **4** and **7** uniformly showed lc characteristic melting point behavior. Polysebacates based on **2**, **3**, and **5** also showed lc properties. On the other hand, monomer or derivatives of **5** showed no lc behavior. All the liquid-crystalline compounds and polymers, as listed in Table I–III, showed nematic textures. Some of the optical textures of these small molecules and polymers in the liquid-crystal state, as observed with a hot-stage polarizing microscope, are shown in Figures 1 and 2.

Discussion. We have synthesized new thermotropic liquid-crystal polyesters based on various azobis(phenols). Polyformals were also synthesized from these monomers. The polymers were fusible and soluble in organic solvents and hence were processable. They represent a novel class of polymers.

Thermotropic lc behavior was found for the polysebacates of **2**, **3**, **4**, **5**, and **7**. On the other hand, no lc properties were displayed by any of the polyisophthalates or poly(5-*tert*-butylisophthalates). Weak lc behavior was seen for the polyformal of **4**.

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