Difunctional and Multifunctional Monomers Capable of Cyclopolymerization

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ABSTRACT: The reaction of an acrylate ester with paraformaldehyde in the presence of diazabicyclo-[2.2.2]octane has been shown to provide access to novel ether-fused dimethacrylate-like monomers that can undergo cyclopolymerization. This study examined the influence of the pendant ester functionality on the synthesis and polymerization of these monomers. While bulky ester groups were generally found to reduce the rate of reaction in monomer synthesis, the more hindered monomers appear to polymerize through the available intramolecular cyclization pathway with greater efficiency than monomers without significant steric constraints. Polymerizations in solution lead to mainly cyclized, soluble polymers up to relatively high monomer concentrations. Bulk polymerizations provided brittle, cross-linked polymers with high degrees of conversion. This work was extended to include the synthesis of a multifunctional oligomer based on the same 1,6-diene substructure. The polymerization of this oligomer produced a tough, highly cross-linked polymer.

Introduction

The ability of certain nonconjugated diolefinic compounds to undergo efficient cyclopolymerization has been a topic of periodic interest in the polymer chemistry literature since the early reports of this phenomenon by Butler and Marvel in the 1950s.[1-4] A recent series of papers by Mathias[5-7] has introduced the synthesis and polymerization of a new class of ether-fused, dimethacrylate-like monomers. The ease of synthesis of these monomers as well as the unique properties associated with their polymers has prompted this further investigation. The unusual 1,6-diene configuration characteristic of these 2,2'-[oxybis(methylene)]bis-2-propenylate monomers, which for simplicity can be referred to as oxybismethacrylates, makes them well suited to polymerize through a process involving an intramolecular cyclization.

The oxybismethacrylates of interest here were obtained from the hydroxymethylation reaction of acrylate esters with paraformaldehyde and a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) as shown in Scheme I. Apparently, the difunctional condensation products generated from this procedure, initially described by Hoffmann and Rabe,[8] were not observed prior to the report of Mathias.[5] This current project represents an attempt to improve the synthetic accessibility of the cyclopolymerizable oxybismethacrylate monomers and to extend the scope of this procedure to achieve multifunctional oligomeric monomers based on the same chemistry. In addition, the polymerization of the new monomers was studied to gain some understanding of the factors influencing the cyclopolymerization process, shown in Scheme II.

Experimental Section

The acrylate starting materials utilized in this study were commercially obtained and were used as received without removal of the included inhibitor. IR spectra were acquired on a Perkin-Elmer 1420 instrument controlled through a data station. The ^1H and proton-decoupled ^{13}C NMR spectra were obtained on a JEOL GSX-270(FT) spectrometer operated at 270 and 68.1 MHz, respectively. All solution NMR analyses were conducted in $CDCl_3$. The chemical shifts are given in ppm downfield relative to tetramethylsilane. The initial synthetic procedure used to prepare the monomers was that of Hoffmann and Rabe.[8] Subsequently, this technique was modified by the use of stoichiometric quantities of the starting acrylate and paraformaldehyde and by the use of shorter reaction times at correspondingly higher temperatures.

Difunctional monomer synthesis: Typical reaction conditions for the modified procedure involve the addition of ethyl acrylate (5.0 g, 50 mmol), paraformaldehyde (1.5 g, 50 mmol), and DABCO (0.56 g, 5 mmol) to a screw-capped vial. The vial was tightly sealed to prevent loss of formaldehyde and then submerged in an oil bath at 80–90 °C. The reaction mixture, which was agitated with a small magnetic stir bar, became homogeneous after several hours. After 25 h, the vial was opened and the slightly cloudy contents were fractionated by chromatography on a silica gel column (5 × 8 cm) with 20% ethyl acetate in hexane as eluant. Evaporation of the solvent provided an 82% yield of the diethyl oxybismethacrylate **2b** as a colorless liquid.

Multifunctional monomer synthesis: Typical reaction conditions involve the combination of ethoxylated bisphenol A diacrylate[9] (0.85 g, 1.8 mmol, Arco Chemical Co.) with paraformaldehyde (0.11 g, 3.6 mmol) and DABCO (40 mg, 0.36 mmol) in a 1-mL screw-capped vial. The vial was tightly sealed and placed in an oil bath at 80–90 °C for 25 h. Upon completion, the resulting viscous material was dissolved in 2 mL of dichloromethane. The dropwise addition of this solution to 50 mL of methanol caused the precipitation of the oligomeric product. The methanol was decanted, and the residual solvent removed under vacuum (to 13 Pa) at 50 °C to furnish the multifunctional oligomer as an extremely viscous, colorless oil in 74% yield.

All polymerizations, unless otherwise noted, were conducted at 65 ± 1 °C with azobis(isobutyronitrile) (AIBN) utilized as free-radical initiator. Solution polymerizations were carried out in argon-saturated benzene, and the bulk polymerizations of the degassed monomers were run in evacuated sealed tubes. The soluble polymers were precipitated twice from methanol and then characterized by their IR and ^1H NMR spectra. The presence of any residual unsaturation in the polymers was determined qualitatively by IR (C=C absorption at 1638 cm^{-1}) and quantitatively by ^1H NMR (=CH_2 signals near δ 5.9 and 6.3). The cross-linked polymers obtained from the bulk polymerizations were analyzed by solid state CP-MAS ^{13}C NMR techniques[10] without extraction of any residual monomer.

Results and Discussion

Monomer synthesis: Initially, the difunctional oxybismethacrylate monomers were prepared by the room-temperature reaction of an acrylate ester and paraformaldehyde with a catalytic amount of DABCO. In addition to the α-(hydroxymethyl)acrylate intermediate 1 and the

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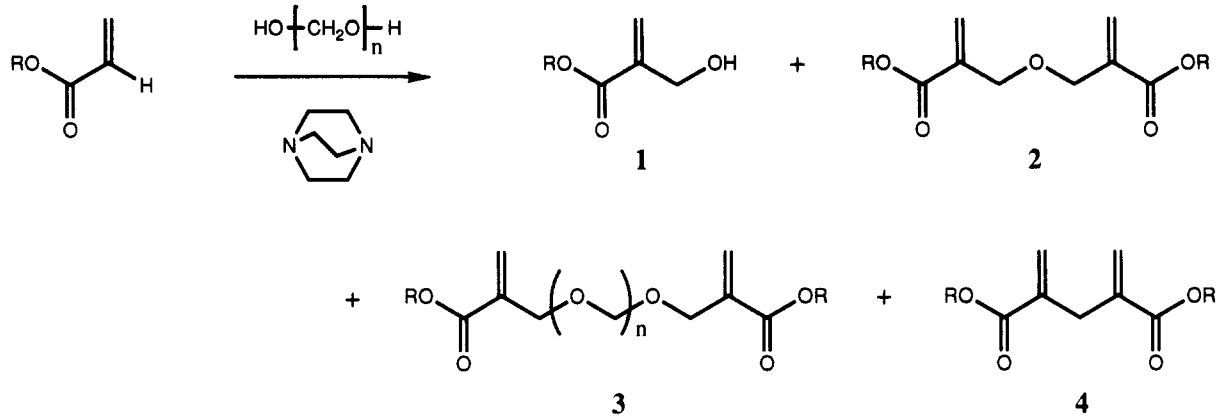
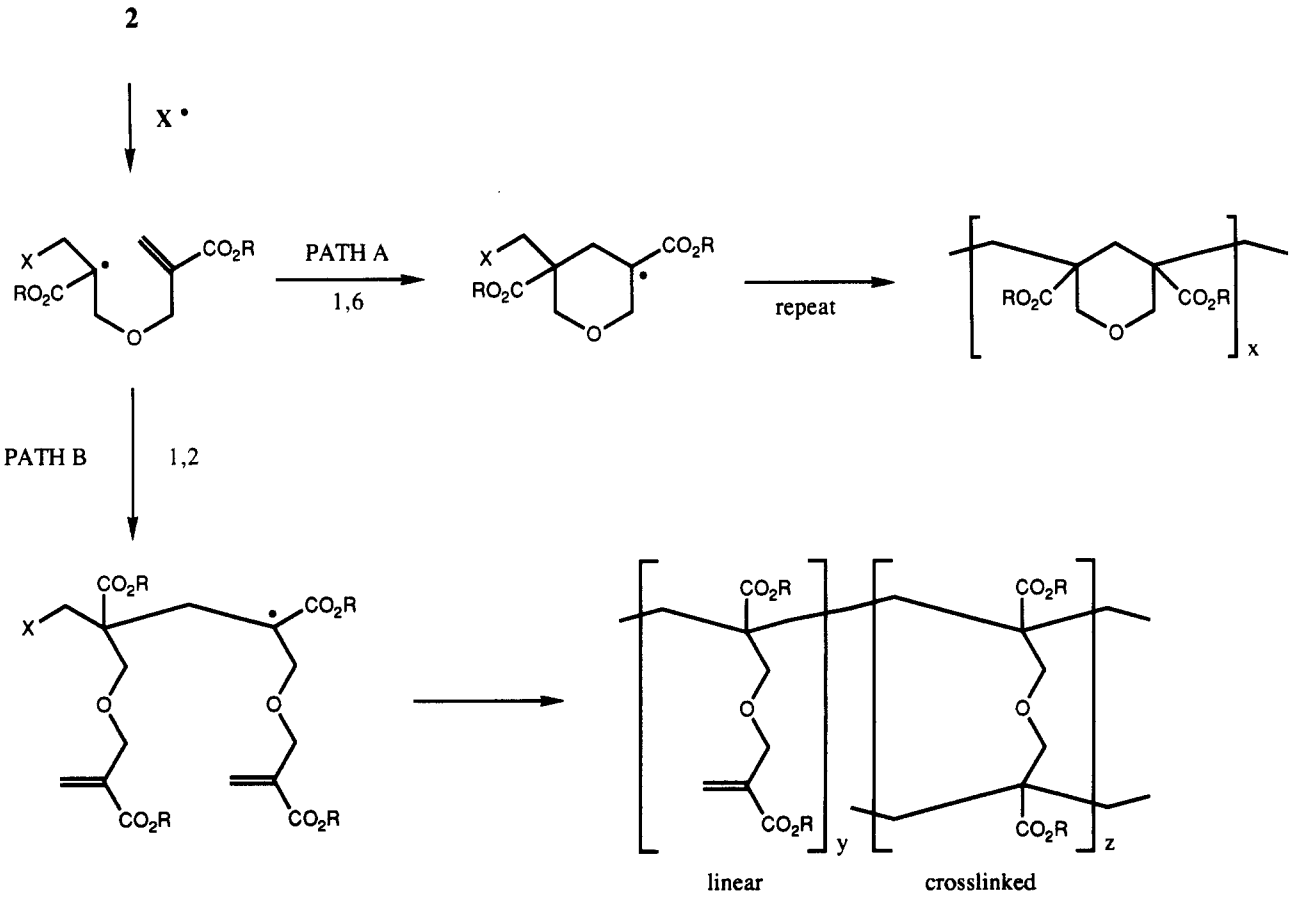
Scheme I



Scheme II



desired monomer **2**, other relatively minor products associated with the reaction included the extended difunctional compounds of type **3** and the 1,4-diene **4**. These latter two products are not expected to effectively cyclize on polymerization due to ring-size considerations. A proposed mechanism detailing the formation of products **2** and **4** from the common α-(hydroxymethyl)acrylate intermediate is shown in Scheme III.

Table I provides a comparison of the product distributions obtained from the treatment of ethyl acrylate with paraformaldehyde and DABCO at room temperature and at 80–90 °C. The results for the required reaction times and the yields of the desired monomer **2b** indicate the advantage of conducting this reaction at elevated temperatures. These benefits are obtained through the efficient utilization of the starting acrylate and the minimization of the type **1** and **3** products. The elimination of nearly all the impurities other than the more polar α-hydroxymethyl-substituted compound greatly facilitated the chromatographic purification.

A series of the oxybismethacrylates were prepared from a variety of acrylate esters to evaluate the effect of the ester group on monomer synthesis. In Table II, the influence of the ester functionality is demonstrated in the crude yields resulting from the room-temperature reactions. It is clear that the efficiency of the reactions involving acrylates with bulky ester groups was severely limited under these conditions. The reason for the higher yield of **2d** compared with **2c** is not readily apparent. The results seem to indicate that the incorporation of an aromatic ring in the ester functionality offers an effective method of increasing bulk without compromising reaction efficiency. The enhanced yield observed for the tetrahydrofurfuryl ester may be the result of increased solubility of the paraformaldehyde with this particular acrylate. Where determined, the isolated yields of the oxybis-

Scheme III

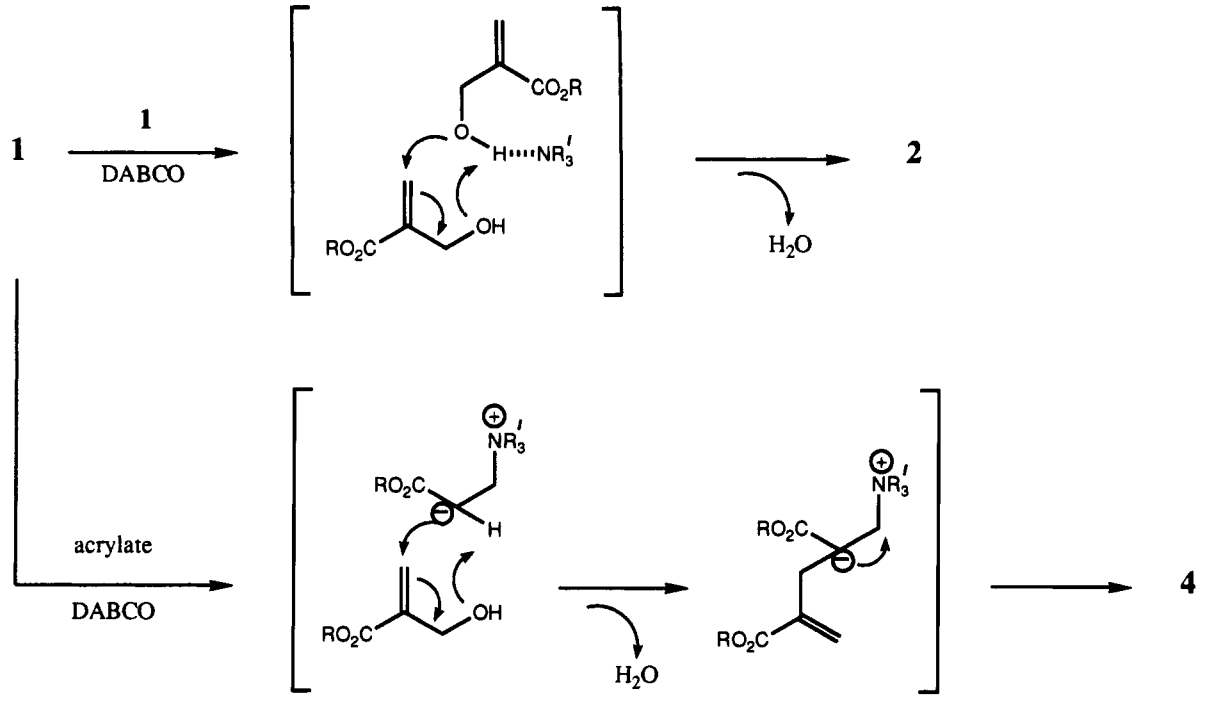


Table I
Effect of Reaction Conditions on Product Distribution[a]

products	reaction conditions: 12 days, 23 °C	reaction conditions: 25 h, 80–90 °C
1b	26	15
2b	41	83
3b(n=1)	20	1
3b(n=2)	2	~0
4b	4	1
unreacted ethyl acrylate	7	~0

[a] Results are from the reaction of ethyl acrylate with paraformaldehyde and DABCO. The reported yields are the percentages based on acrylate equivalents. These values were spectroscopically determined from the crude reaction mixtures.

Table II
Synthesis and Characterization of Difunctional Monomers

acrylate ester, R =	combined yield of products 2 + 3,[a] 10 days at 23 °C, %	isolated yield of 2, 80–90 °C synthesis, % (time, h)	compd, mp, °C
methyl	58	67 (16)	**2a**, 47
ethyl	50	82 (25)	**2b**, liq
n-butyl	31	78 (30)	**2c**, liq
isobutyl	38		**2d**, liq
tert-butyl	4	66 (30)	**2e**, ~22
neopentyl	6		**2f**
benzyl	63	58 (18)	**2g**, 46
tetrahydrofurfuryl	71		**2h**
phenethyl	49	42 (28)	**2i**, 43
trimethylcyclohexyl	4	37 (40)	**2j**, 96

[a] Spectroscopically determined from the crude reaction mixtures.

methacrylate monomers obtained from extended room-temperature preparations were only 10–25%.

When the analogous reactions were conducted in sealed vials at elevated temperatures (80–90 °C), the reaction times could be dramatically reduced while the overall isolated yields were improved significantly (Table II). The synthesis of the methyl-substituted monomer **2a** at room temperature and at elevated temperatures produced considerably more of the type **3** byproducts than that observed for the other esters that exhibit somewhat greater steric demand. Further, there was a relatively large yield of the dimethylmethylenebisacrylate (12% **4a** from the 80 °C/16 h reaction procedure) from the reaction with methyl acrylate. This product, which requires the ester groups to be in closer proximity to each other than in **2**, was seen in only trace amounts or not at all in reactions involving the bulkier acrylate esters. The ^{1}H and ^{13}C NMR characterization of the monomers is given in Table III. The chemical shifts associated with the ether methylene and vinylmethylene groups of the monomers with the bulkiest esters were slightly upfield relative to the analogous signals from the compounds with smaller ester substituents. This effect was more pronounced in the case of monomer **2e** with the *tert*-butyl ester groups. The presence of type **3** products resulting from the insertion of multiple formaldehyde units was indicated by the appearance of signals associated with the O–CH_2–O group in the vicinity of 90–95 ppm in the ^{13}C NMR spectra. The 1,4-diene structure of **4** could be readily distinguished by the relative upfield location of the $=CH_E$ signal (ca. 5.6 ppm) in the ^{1}H NMR spectra.

The synthesis of the oxybismethacrylates was broadened to include the production of multifunctional oligomeric products with the same 1,6-diene substructure.[11] The preparation of the linear, multifunctional compounds (**6**, Scheme IV) was identical with the modified technique utilized to obtain the difunctional monomers except that 2 equiv of the formaldehyde/mol of the diacrylate **5** was required. The purification of the oligomeric products was a simple matter of precipitation from methanol in which the starting diacrylate and lower molecular weight hydroxymethyl-terminated materials were soluble. There was no residual diacrylate starting material present in the oligomers as determined by TLC and GPC analyses.

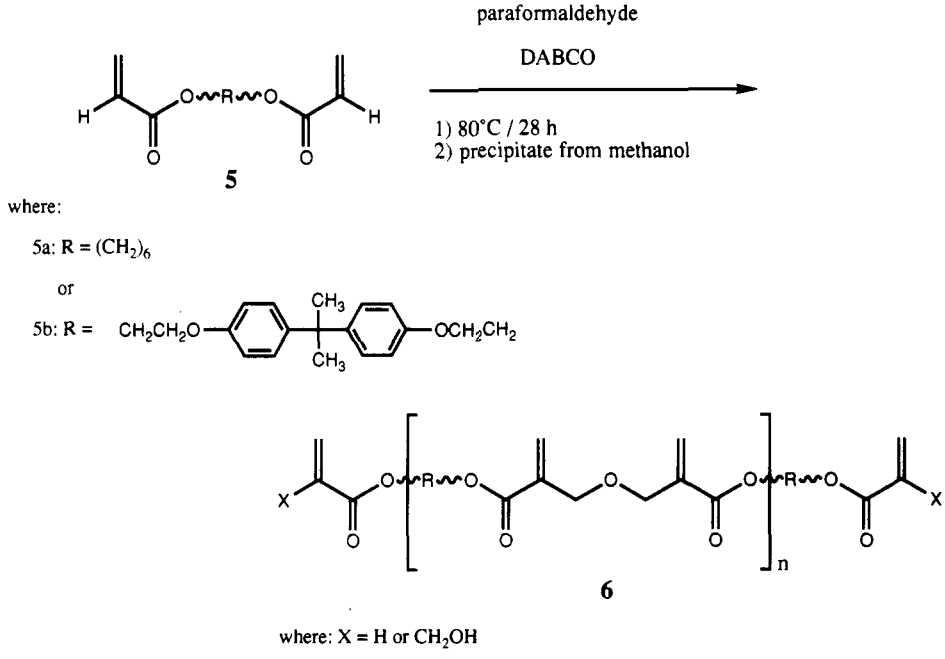
The extent of the oligomerization reaction appears to be limited to the incorporation of approximately three to five repeat units on average. The integrated ^{1}H NMR spectra provided the information on the number of repeat units and the identity of the terminal groups that consist of the unreacted acrylate and the α-hydroxymethyl-substituted acrylate groups. The polystyrene equivalent

Table III
NMR Characterization of Oxybismethacrylates

ester, R =	^{1}H chem shift $-CH_2O-$	$=CH_E$	$=CH_Z$	R
methyl	4.26	5.91	6.32	3.77 (CH_3)
ethyl	4.26	5.90	6.32	1.31 (CH_3), 4.23 (CH_2)
n-butyl	4.26	5.90	6.31	0.95 (CH_3), 1.41 (CH_2CH_3), 1.66 (OCH_2CH_2), 4.17 (OCH_2)
isobutyl	4.27	5.91	6.33	0.96 (CH_3), 1.99 (CH), 3.95 (CH_2)
tert-butyl	4.21	5.81	6.21	1.50 (CH_3)
benzyl	4.28	5.91	6.36	5.21 (CH_2), 7.36 (arom)
phenethyl	4.21	5.88	6.29	2.98 (CH_2Ph), 4.38 (OCH_2), 7.27 (arom)
trimethylcyclohexyl[20]	4.23	5.86	6.27	0.80 (C_2H_{ax}), 0.88 (C_6H_{ax}), 0.91 (C_5CH_3), 0.96 ($C_3CH_{3ax,eq}$), 1.16 (C_4H_{ax}), 1.36 (C_2H_{eq}), 1.72 (C_4H_{eq} + C_5H_{ax}), 2.01 (C_6H_{eq}), 4.98 (C_1H_{ax})

monomer	^{13}C chem shift $-CH_2O-$	$=CH_2$	C=	C=O	R
2a	68.8	126.0	136.9	166.2	51.3 (CH_3)
2b	68.9	125.5	137.2	165.7	14.1 (CH_3), 60.7 (CH_2)
2c	68.9	125.5	137.2	165.8	13.7 (CH_3), 19.2 (CH_2CH_3), 30.6 (OCH_2CH_2), 64.6 (OCH_2)
2d	68.9	125.6	137.2	165.7	19.1 (CH_3), 27.7 (CH), 70.7 (CH_2)
2e	69.0	124.4	138.6	165.1	28.0 (CH_3), 80.9 (C_{quat})
2g	68.9	126.3	136.9	165.5	66.4 (CH_2), 128.0 + 128.2 + 128.5 + 135.8 (arom)
2i	68.8	125.9	137.0	165.6	35.1 (CH_2Ph), 65.2 (OCH_2), 126.6 + 128.5 + 128.9 + 137.7 (arom)
2j	68.9	125.2	137.6	165.3	22.2 (C_5CH_3), 25.5 (C_3CH_{3ax}), 27.0 (C_5), 32.2 (C_3), 33.0 (C_3CH_{3eq}), 40.3 (C_6), 43.9 (C_4), 47.4 (C_2), 71.6 (C_1)

Scheme IV



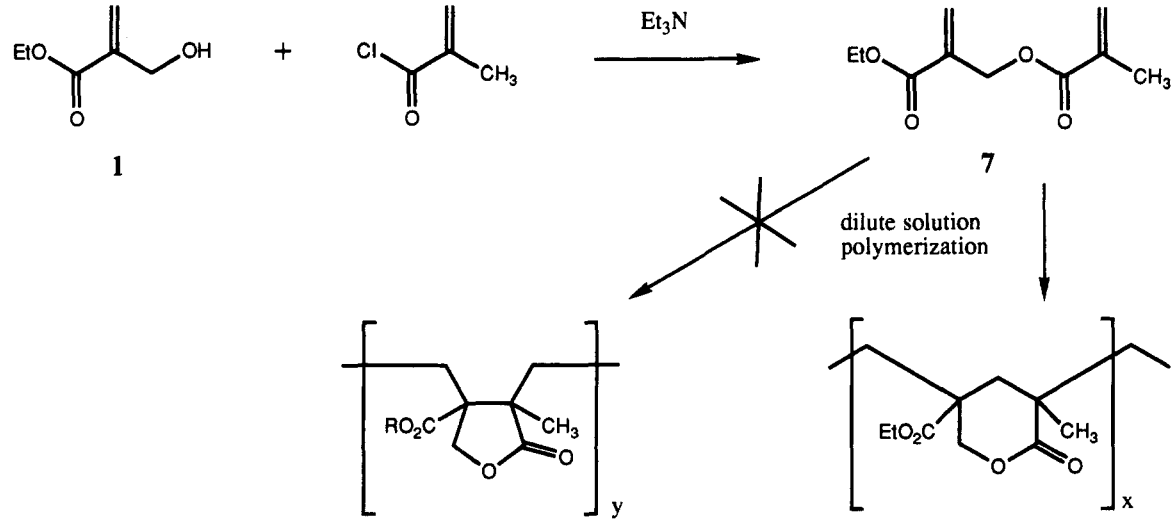
molecular weights calculated by GPC for samples of **6b** were in good agreement with the NMR-derived molecular weight estimates. The polydispersity of the oligomer varied directly with the molecular weight of the samples. For oligomer **6b**, polystyrene equivalent polydispersities of 1.9 and 2.6 were obtained for the samples with n = 3.0 and 4.2, respectively. The NMR spectra also indicated that there were trace amounts of the type **3** and **4** linkages present in the oligomer samples. The use of solvent to offset the increase in viscosity that accompanies the diacrylate extension reaction can simplify production isolation, although other solvent effects are not well defined. As seen in Table IV, the addition of THF does not appear to significantly influence the average molecular weight attained by the oligomers. It does, however, result in greatly decreased yields of oligomer **6a** based on the 1,6-hexamethylenediacrylate. A general decrease in rate was noted for the reaction of monofunctional acrylates in either dimethyl sulfoxide, THF, or dichloromethane solutions. The more polar DMSO and THF solvents exerted less of an adverse effect on the rate than the dichloromethane. The NMR characterization of oligomers **6a** and **6b** is provided in Table V.

Table IV
Synthesis and Characterization of Multifunctional Oligomers[a]

starting acrylate	reaction type	yield of 6, %	n	end groups,[b] X = -H	end groups,[b] X = $-CH_2OH$
5a	neat	57	4.3	5	14
5a	soln, 10% THF	16	5.2	5	11
5a	soln, 50% THF	8	4.6	7	11
5b	neat	74	4.2	2	17
5b	soln, 10% THF	76	3.0	7	18
5b	soln, 50% THF	63	3.8	3	18

[a] The values of n and the end-group analyses were obtained from the integrated ^{1}H NMR spectra. [b] These values represent the percentage of total acrylate equivalents that are either unreacted acrylate end groups (X = H) or reacted α-(hydroxymethyl)acrylate groups (X = CH_2OH).

Scheme V



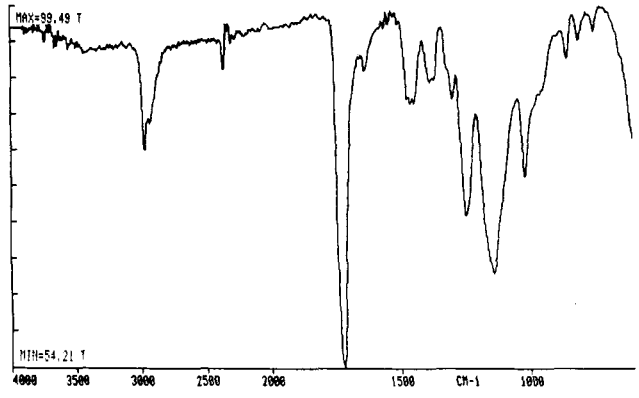


Figure 1. IR spectrum of the polymer of asymmetric diene 7.

Table V
NMR Characterization of Repeat Units in Multifunctional Oligomers

Oligomer **6a** (from 1,6-Hexamethylene Diacrylate)
^{1}H NMR δ 1.42 (m, CH_2 $C_{3,4}$), 1.69 (m, CH_2 $C_{2,5}$), 4.16 (t, OCH_2 $C_{1,6}$), 4.26 (s, $=CCH_2O$), 5.90 (d, $=CH_E$), 6.31 (d, $=CH_Z$)
^{13}C NMR δ 25.6 (CH_2 $C_{3,4}$), 28.4 (CH_2 $C_{2,5}$), 64.6 (OCH_2 $C_{1,6}$), 68.8 ($=CCH_2O$), 125.6 ($=CH_2$), 137.1 ($C=CH_2$), 165.7 (C=O)
Oligomer **6b** (from Ethoxylated Bisphenol A Diacrylate)
^{1}H NMR δ 1.62 (s, CH_3), 3.6–4.5 (series of t, OCH_2CH_2O), 4.24 (s, $=CCH_2O$), 5.92 (br s, $=CH_E$), 6.33 (br s, $=CH_Z$), 6.80 (arom $C_{2,6}$), 7.12 (arom $C_{3,5}$)
^{13}C NMR δ 31.0 (CH_3), 41.7 (Ph_2CMe_2), 63–70 (signals from OCH_2CH_2O), 69.8 ($=CCH_2O$), 113.9 (arom $C_{2,6}$), 126.3 ($=CH_2$), 127.7 (arom $C_{3,5}$), 136.7 ($C=CH_2$), 143.3 (arom C_4), 156.3 (arom C_1), 165.3 (C=O)

Polymerization: The free-radical polymerization of selected oxybismethacrylate monomers was examined in solution and in bulk. When polymerized under dilute solution conditions (1–2% by weight in benzene with 0.2 wt % AIBN), the resulting polymers were high molecular weight (intrinsic viscosities in chloroform at 25 °C ranged from 0.38 to 0.86 dL/g), powdery solids that were readily soluble in common organic solvents including benzene, chloroform, and THF. In all cases, quantitative conversion of the vinyl groups was achieved as determined by IR and ^{1}H NMR spectroscopy. The lack of both residual unsaturation and cross-link formation in these materials indicates the exclusive operation of the intramolecular cyclization mode of polymerization.

While the thermodynamically favored six-membered cyclic structure is proposed for the polymers, there is also the potential for 1,5-cycloaddition. There are numerous examples of 1,6-dienes that favor the formation of a five-membered ring via 1,5 head-to-head addition during cyclopolymerization.[12] The direct analysis of the current cyclopolymers by IR or NMR techniques did not clearly define the structure. To obtain additional information about the ring-closing process, the asymmetric difunctional monomer 7[13] was prepared from the α-(hydroxymethyl)acrylate **1b** and methacryloyl chloride as shown in Scheme V. The dilute solution cyclopolymerization of 7 (2% in benzene) yielded a soluble polymer based on an ester-substituted lactone repeat unit. The IR spectrum of the polymer film (Figure 1) showed a sharp carbonyl absorption at 1735 cm^{-1}, which is consistent with a structure comprised of free ester and δ-lactone. A 1,5-cyclopolymerization would introduce a γ-lactone, which would be expected to provide a C=O band at significantly shorter wavelengths. While the asymmetric monomer 7 appears to be a good model, more work needs to be done to verify the cyclopolymer structure associated with the oxybismethacrylates. Related to this, the early investigations by Marvel and Vest[14,15] into the polymerization of α,α'-dimethylenepimelate esters, which are the hydrocarbon analogues of the oxybismethacrylate monomers described here, reportedly gave cyclopolymers with the six-membered cyclic structure as well.

As the monomer concentration was increased beyond the dilute solution range, the polymerization of the oxybismethacrylates began to yield a mixed-mode process involving both 1,6-intramolecular cyclopolymerization (path A; Scheme II) and simple 1,2-vinyl polymerization (path B). The distribution of these two pathways appears to be dictated not only by monomer concentration but also by steric influences derived from the ester functionality. Polymerization temperature and initiator concentration may also influence the mode of polymerization, but these variables were not addressed in this investigation. The extent of 1,2-addition polymerization occurring can be directly determined from the amount of residual unsaturation in soluble polymers or indirectly estimated by the cross-link density associated with insoluble polymers.

At high conversions, the 0.5 M solution polymerization of the monomers shown in Table VI yielded cross-linked materials with the exception of the *tert*-butyl-substituted homopolymer from monomer **2e**. This polymer was completely soluble and contained no trace of residual unsaturation. Likewise, both the soluble and cross-linked portions of the polymer formed from monomer **2j** provided no evidence of residual unsaturation. The loosely cross-

Table VI
High Conversion Solution Polymerization of Oxybismethacrylates

monomer	0.5 M soln polymerization[a] wt %	yield, %	polym solubility[b]
2a	10.7	88	insol
2b	12.1	46	insol
2c	14.9	74	insol
2e	14.9	79	sol
2j	21.7	35/5	insol/sol

[a] Polymerizations were conducted in benzene solutions with 0.5 mol % AIBN at 65 °C for 16 h. [b] In chloroform.

Table VII
Effect of Monomer Concentration on the Solution Polymerization of Oxybismethacrylates[a]

monomer concn, M	wt %	time, h	yield, %	1,2-addition,[b] %
R = Ethyl, **2b**				
0.5	12.1	4.0	18	6
1.0	24.2	3.0	15	9
1.5	36.3	1.5	5	13
2.0	48.4	0.8	6	18
R = *tert*-Butyl, **2e**				
0.5	14.9	4.0	21	0
1.0	29.8	3.0	32	tr[c]
1.5	44.7	0.5	13	4
2.0	59.7	0.4	3	6

[a] Monomers with 0.5 mol % AIBN were dissolved in benzene and heated in sealed vials for the time indicated. The polymers were then isolated by two precipitations from methanol. [b] Determined from the integrated ^{1}H NMR spectra. [c] Trace.

linked polymer sample of **2j** was readily swollen to a very diffuse network in ethyl acetate. Contrasting this was the solution polymer obtained from monomer **2a**, which had very little residual unsaturation and appears to be a highly cross-linked material that could not be swollen by ethyl acetate. While the cross-linked polymers derived from the 0.5 M solution polymerization of monomers **2b** and **2c** had somewhat more residual unsaturation (by IR) than the solution polymer of **2a**, these polymers were swollen by ethyl acetate, indicating a lower relative cross-link density.

At low levels of conversion, the solution polymerization of **2a** produced soluble polymers with relatively large amounts of residual unsaturation. For example, at 10% conversion the 1.5 M solution polymerization of monomer **2a** yielded a soluble polymer composed of 19% 1,2-addition units arising from path B. The methyl-substituted compound was also prone to cross-linking at low monomer concentrations and conversions compared with the other monomers examined. As detailed in Table VII, a comparison of the low-conversion solution polymerization of monomers **2b** and **2e** was conducted at various concentrations. It is apparent that the unimolecular cyclization is favored over the bimolecular addition as the monomer concentration decreases. The data also provide an additional demonstration of the enhanced cyclopolymerization efficiency associated with the more hindered monomers. If plots of the data were extrapolated out to bulk polymerization conditions, the 1,2-addition component predicted would be approximately 35 and 15%, respectively, for polymers of **2b** and **2e**. Therefore, it can be concluded that with the bulkier monomers, the rate of the intramolecular 1,6-cyclization step is increased relative to the intermolecular 1,2-addition reaction.

A series of the oxybismethacrylate monomers were polymerized in bulk, which resulted in the formation of glassy cross-linked polymers in each case. While the amount of 1,2-addition associated with this process is not known, the extent of conversion in the cross-linked polymers was determined by solid-state ^{13}C NMR analysis of ground samples (Table VIII). Once again an ester substituent effect was evident. The bulk polymer from monomer **2a** contained significantly more residual unsaturation than the polymers obtained from the other oxybismethacrylate monomers. This indicates a greater contribution from the 1,2-addition pathway for the nonhindered methyl ester. The conversion levels associated with the bulkier monomers may be limited by the relatively high glass transition temperatures (T_g), which may be predicted[7] for the more completely cyclopolymerized materials. Therefore, it appears that the choice of the pendant ester group can be used to influence the extent of cyclopolymerization and cross-linking as well as other polymer properties such as T_g.

Table VIII
Bulk Polymerization of Oxybismethacrylates[a]

monomer	degree of conv, %
methyl, **2a**	79
ethyl, **2b**	95
isobutyl, **2d**	93
tert-butyl, **2e**	88
phenethyl, **2i**	100
trimethylcyclohexyl, **2j**	88

[a] Polymerized with 0.5% AIBN at 65 °C for 18 h.

The bulk homopolymerization of the multifunctional oligomer **6b** was conducted at 60 °C with 0.5% AIBN for 24 h. The resulting material was a tough, clear polymer that appears to be highly cross-linked. The extent to which the 1,6-cyclization is involved in the polymerization of the oligomer could not be readily determined. An evaluation of both the difunctional oxybismethacrylate monomers and the multifunctional oligomers as ingredients in dental resin composite formulations has been conducted.[16-18] These monomers are of particular interest due to their ability to attain high degrees of conversion under near-ambient curing conditions. Another significant advantage seen for the cyclopolymers is the potential for reduced polymerization shrinkage when compared with polymers from conventional diacrylate monomers. Highly fluorinated difunctional and multifunctional monomers have also been prepared by methods similar to those described here.[19]

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