

## New Families of Photocurable Oligomeric Fluoromonomers for Use in Dental Composites

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Since their discovery in the 1930s, fluoropolymers have evolved from curiosities to essential specialty materials. The initial utility of fluoropolymers relied on their excellent resistance to aggressive chemical environments. However, the combination of low surface energy with other unique properties, such as thermal and oxidative stability, low coefficients of thermal expansion and friction, and low dielectric constants, has led to a great diversity of applications for fluorine-rich polymers.<sup>1</sup>

Due to the advantageous blend of chemical inertness, including extreme hydrophobicity, with generally good biocompatibility, fluoropolymers have become widely utilized as components of medical devices. As the demand for advanced fluoropolymers with specific physical properties has grown, the molecular design of new types of fluorinated monomers has become an important area in synthetic polymer chemistry.<sup>2–7</sup> In biomaterials, the requirements for durable fluoropolymers include high hydrophobicity, chemical and physical resistance, mechanical strength, and resilience along with low surface energy, polymerization shrinkage, toxicity, and abrasion. In this study, we have focused on the development of new families of oligomeric fluoromonomers designed to improve the performance of aesthetic polymeric dental restorative materials.

A photocurable dimethacrylate monomer, 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenylene]-propane (Bis-GMA) synthesized from the diglycidyl ether of bisphenol A and methacrylic acid has been used extensively as the basis of dental composite filling materials.<sup>8–14</sup> Dental resins based on Bis-GMA and related methacrylate monomers, while generally good,

lack long-term durability and are prone to brittle fracture and wear.<sup>10–13</sup> Fluoropolymers can potentially provide improvements in these areas.

In the current investigation, we have examined several types of moderately to highly fluorinated methacrylate-based monomers with the initial intent of identifying new fluoropolymers that exhibit low polymerization shrinkage along with excellent hydrophobicity and physical strength. In general, the physical strength of polymers rich in fluorine is reduced with increasing fluorine content due to the low cohesive energy associated with amorphous fluoropolymers.

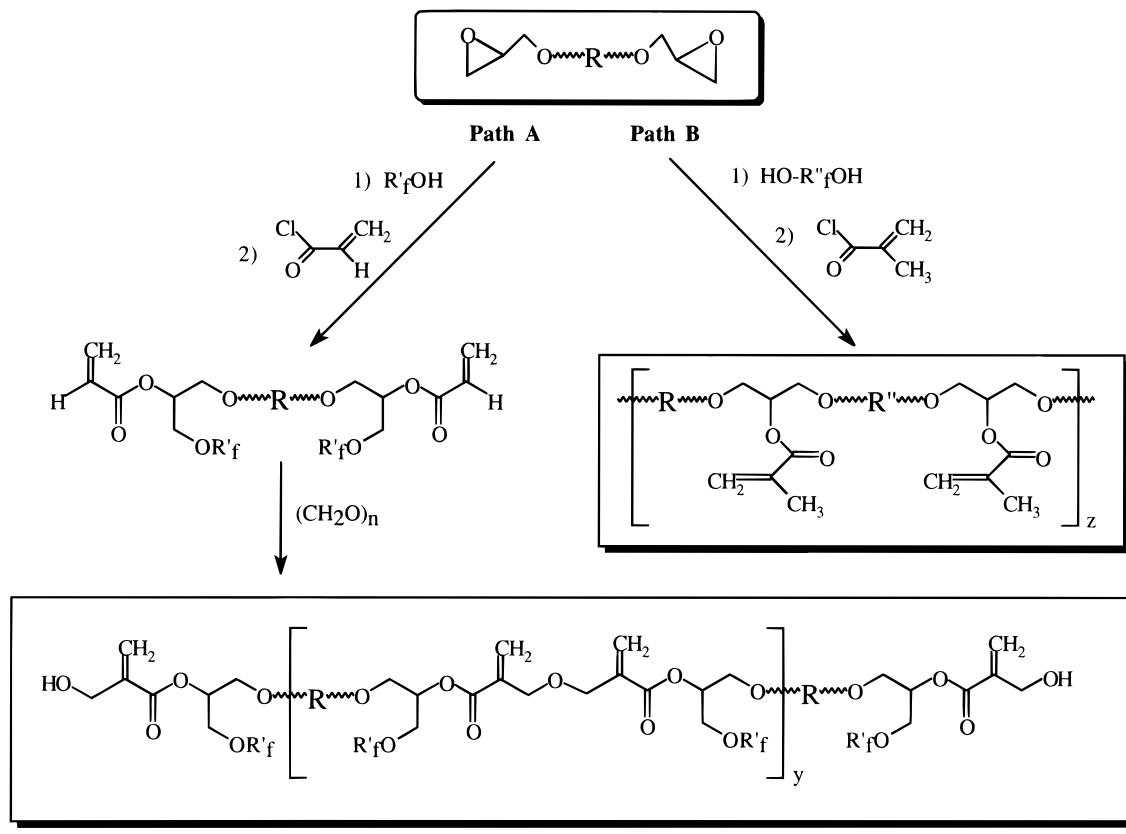
As shown in Figure 1, the general theme pursued involved the relatively facile addition of fluoro alcohols to epoxy starting materials followed by the introduction of polymerizable methacrylate groups to yield oligomeric multifunctional monomers. Both routes to the fluorinated oligomers are designed to provide low levels of polymerization shrinkage. Monomer synthesis according to path A utilizes acrylate functional groups to generate 1,6-diene linkages situated along the backbone of the oligomer. The ability of nonconjugated diolefins compounds to undergo cyclopolymerization has been introduced previously in the polymerization of ether-fused dimethacrylates and multifunctional oligomers.<sup>15–22</sup> The cyclopolymerization process involving multifunctional oligomers of this type has been found to result in approximately 30% reductions in the extent of polymerization shrinkage compared with dimethacrylate monomers at similar degrees of conversion. Alternatively, path B leads to oligomers in which the pendant methacrylate functionality is separated by spacer groups that serve to decrease the density of reactive sites and thereby reduce polymerization shrinkage.

The oligomeric nature of the fluorinated monomers was devised as a means to enhance the cross-link density in the fluoropolymers to compensate for otherwise low cohesive energies. It was anticipated that this approach would aid in the goal to produce moderately to highly fluorinated polymers with good mechanical strength. The introduction of fluorinated substituents facilitates this reactive prepolymer approach since lower viscosities are obtained than would be available with similar hydrocarbon oligomers. The use of reactive polymers also minimizes biocompatibility concerns related to leachable components.

Figure 2 shows the synthetic procedure used to prepare fluoromonomers **M-1** and **M-2**. A difunctional epoxide (diglycidyl ether of bisphenol A, DER 332, or diglycidyl ether of 3,3',5,5'-tetrabromo bisphenol A, DER 542) was heated neat with heptafluoro-1-butanol in the presence of *N,N*-dimethylbenzylamine as catalyst. The resulting diols were converted to diacrylates by reaction with triethylamine and acryloyl chloride. Finally, the difunctional acrylate intermediates were reacted with paraformaldehyde and a catalytic amount of 1,4-

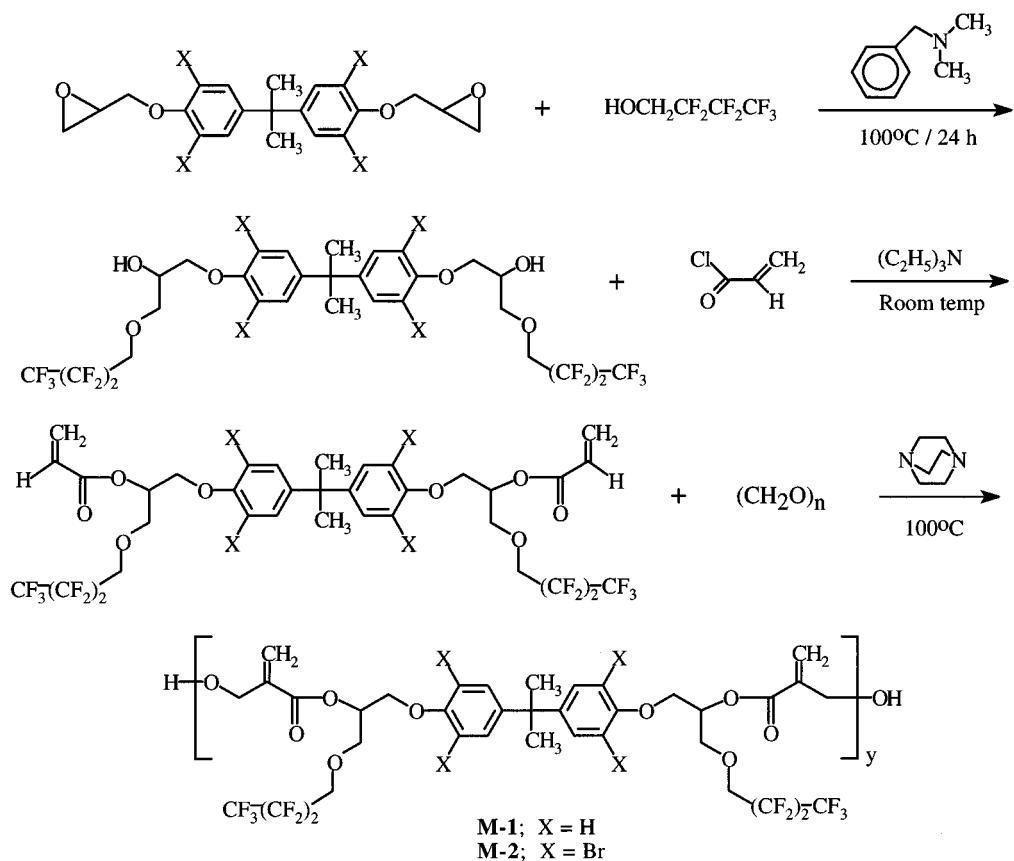
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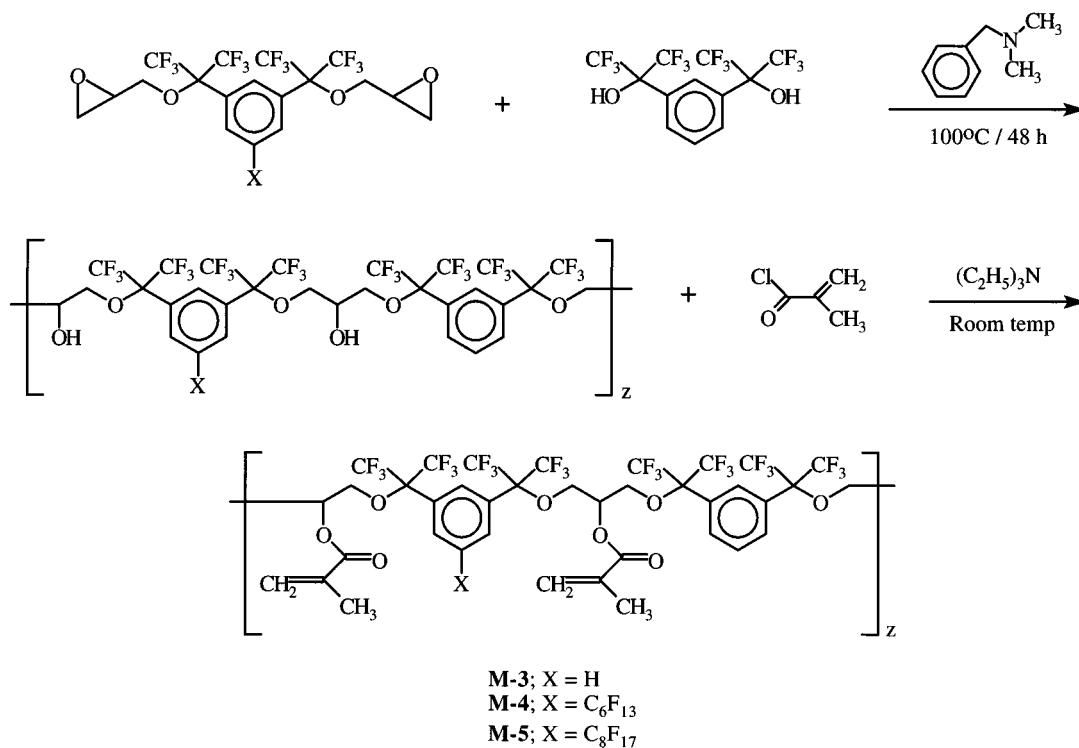


$R$  = alkyl group,  $R'fOH$  and  $R''fOH$ : fluoroalcohols

**Figure 1.** General synthesis of fluorinated oligomers from epoxy starting materials. Path A utilizes the formation of cyclopolymerizable 1,6-diene linkages to develop the oligomeric structure. Path B relies on a simple diol–diepoxide chain-extension reaction.



**Figure 2.** Preparation of the fluorocarbon and brominated fluorocarbon oligomers (**M-1** and **M-2**, respectively) capable of cyclopolymerization via the ether-fused 1,6-dienes located along the backbone.



**Figure 3.** Synthesis of highly fluorinated multifunctional oligomers (**M-3** - **M-5**) based on the facile ring-opening condensation reaction between diepoxides and fluorinated diols.

diazabicyclo[2.2.2]octane (DABCO) to generate  $\alpha$ -(hydroxymethyl)acrylate groups which couple via condensation to yield the cyclopolymerizable 1,6-diene linkages in multifunctional oligomers **M-1** and **M-2**.

An alternative approach was taken in the design of a separate family of fluorinated monomers as shown in Figure 3. A series of related fluorinated diepoxides were oligomerized by reaction with an aromatic fluorinated diol. For the synthesis of oligomer **M-3**, 1,3-bis(hexafluoro-2-hydroxypropyl)benzene diglycidyl ether and  $\alpha,\alpha,\alpha',\alpha'$ -tetrakis(trifluoromethyl)-1,3-benzenedimethanol were combined to produce the epoxy chain-extension reaction. The resulting oligomeric polyol intermediate was converted to the multimethacrylate oligomer by reaction with triethylamine and methacryloyl chloride. The same procedures were followed in the syntheses of oligomers **M-4** and **M-5**. This new type of fluoromonomer has the capability to contain high percentages of fluorine by substitution at the pendent group  $X$  (Figure 3);<sup>23</sup> the mass percentage of fluorine in oligomers **M-3**, **M-4**, and **M-5** is 42.7, 50.7, and 52.4%, respectively.

To evaluate their potential as components of dental resins, the various fluoromonomers were formulated with a diluent comonomer, 1,10-decamethylene glycol dimethacrylate (DMDM). The proportion of diluent used with each fluorinated monomer was selected such that resins with consistent viscosity were obtained. A visible-light photoinitiator system comprised of camphorquinone (CQ) and ethyl 4-(*N,N*-dimethylamino)-benzoate (EDMAB) was added to the resins. The polymerization shrinkages of these unfilled resins were measured with a mercury dilatometer.<sup>24,25</sup> Composite pastes were formulated by the addition of either si-

**Table 1. Composition of Dental Composites Based on New Fluorooligomers<sup>a</sup>**

oligomer	DMDM (mass %)	fillers (filler: resin, mass ratio)		fluorine (mass %) oligomer/resin
		glass	quartz	
<b>M-1Q</b>	21.0		2.0	29.9/23.6
<b>M-1G</b>	21.0	3.9		29.9/23.6
<b>M-2Q</b>	18.9		2.0	22.0/17.8
<b>M-2G</b>	18.9	3.1		22.0/17.8
<b>M-3Q</b>	19.6		2.0	42.7/34.3
<b>M-3G</b>	19.6	2.0		42.7/34.3
<b>M-4Q</b>	14.4		2.2	50.7/43.4
<b>M-4G</b>	14.4	3.0		50.7/43.4
<b>M-5Q</b>	13.0		2.5	52.4/45.6
<b>M-5G</b>	13.0	3.6		52.4/45.6

<sup>a</sup> DMDM = 1,10-decamethylene glycol dimethacrylate; Q = quartz filler; G = glass filler.

lanized aluminum borosilicate glass or silanized amorphous fused quartz particulate filler to the activated resins; the compositions are listed in Table 1.

The composite pastes were photopolymerized with a visible light source (470 nm maximum). Physical properties of the photocured composites, including water contact angles, transverse strengths (TS), water uptake,<sup>26</sup> densities of unfilled and filled resins, and polymerization shrinkages, were measured and are reported in Table 2. In addition, the properties of a conventional dental composite with a resin based on Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) are included in Table 2. It is apparent that the water contact angles of all the fluorinated resin composites are much greater than that of the conventional hydrocarbon composite control.

In a comparison of photocured composites derived from oligomers **M-1** and **M-2**, the introduction of bro-

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**Table 2. Physical Properties of Resins and Composites Based on New Fluoroooligomers**

oligomer	TS (MPa) <sup>a</sup>	CA <sup>b</sup>	RI <sup>c</sup> M* (M + DMDM)	PS (%) <sup>d</sup> unfilled resins	water uptake (mass %)	density (g/cm <sup>3</sup> ) <sup>e</sup> unfilled resins	density (g/cm <sup>3</sup> ) <sup>e</sup> filled resins
<b>M-1Q</b>	64.7 ± 5.1	86.0	1.4680 (1.4655)	4.14	0.725	1.2684	1.8483
<b>M-1G</b>	73.9 ± 8.2	85.5	1.4680 (1.4655)	4.14	0.544	1.2684	2.2950
<b>M-2Q</b>	73.9 ± 8.7	84.5	1.4905 (1.4845)	5.57	0.515	1.3416	1.9809
<b>M-2G</b>	75.3 ± 7.6	85.0	1.4905 (1.4845)	5.57	0.278	1.3416	2.4950
<b>M-3Q</b>	119.6 ± 6.8	88.0	1.4340 (1.4400)	3.56	0.229	1.2855	1.9047
<b>M-3G</b>	108.9 ± 4.4	86.0	1.4340 (1.4400)	3.56	0.133	1.2855	2.3016
<b>M-4Q</b>	82.6 ± 7.7	85.0	1.4150 (1.4235)	3.38	0.134	1.4480	1.9714
<b>M-4G</b>	92.8 ± 3.5	86.0	1.4150 (1.4235)	3.38	0.113	1.4480	2.4411
<b>M-5Q</b>	70.7 ± 8.9	84.0	1.4125 (1.4223)	4.06	0.108	1.5187	2.4727
<b>M-5G</b>	77.6 ± 1.0	89.0	1.4125 (1.4223)	4.06	0.148	1.5187	2.7218
control <sup>f</sup>	91.4 ± 8.5 <sup>g</sup>	68.5 <sup>h</sup>	1.5218	7.20	1.220 <sup>h</sup>	1.1330	

<sup>a</sup> TS = transverse strength (±standard deviation). <sup>b</sup> CA = water contact angle measurements. <sup>c</sup> RI = refractive index measurements of unpolymerized oligomers (M\*) and resins at 23 °C. <sup>d</sup> PS = volumetric polymerization shrinkage measurements. <sup>e</sup> Density measurements at 23.5 °C. <sup>f</sup> Control resin = Bis-GMA/TEGDMA (7:3 mass ratio). <sup>g</sup> Glass-filled composite with filler/resin mass ratio of 4. <sup>h</sup> Quartz-filled composite with filler/resin mass ratio of 2. Q = quartz filler; G = glass filler.

mine appeared to slightly improve mechanical strength, decrease water uptake, and raise the refractive index of the resin. Thus, use of the bromine-containing fluorinated resins provides some latitude to modify the resin refractive index to match that of a particular filler.

Within the series of composites based on oligomers **M-3**, **M-4**, and **M-5**, the mechanical strengths decreased with increasing fluorine content. However, all these materials, and especially composites containing oligomer **M-3**, demonstrated good strength properties. The enhanced mechanical strength observed with oligomer **M-3** was probably due to its very rigid, regular backbone structure. The water uptake among this series of composites was extremely low and was not significantly influenced by the overall percentage of fluorine in the resin.

The low values of polymerization shrinkage associated with all these novel fluorinated composites is another important criteria in judging their potential as prospective dental materials. Minimized polymerization shrinkage improves the clinical performance of composite restorations. Since traditional dental resins produce volumetric shrinkages of 7–9%, some of the novel

fluorinated resins described here offer reductions in polymerization shrinkage of 50% or more. This benefit, coupled with the strong, hydrophobic character of certain of the fluorinated composites examined here, makes these materials excellent candidates for further evaluation as dental restoratives with the potential for improved durability.

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**Supporting Information Available:** Details of the synthesis and characterization of the fluorinated oligomers are provided along with complete procedures used for evaluation of the unfilled resin and composite materials (6 pages). Ordering information is given on any current masthead page.

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