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Dimethacrylate monomers with varied fluorine contents and distributions

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Abstract

Objectives: There are many unique properties associated with fluorinated polymers that make these materials attractive for use in the challenging oral environment. This study was devised to better define the influence of fluorine content and its structural distribution on properties of fluorinated resins and composites, especially with regard to their water-related and mechanical properties.

Methods: A series of fluorinated dimethacrylate monomers was prepared by reaction of aromatic diepoxides with fluoroalcohols and subsequent conversion of the resulting diols to the methacrylates. Composites based on monomer systems comprised of the fluorinated monomers with 1,10-decamethylene dimethacrylate and reinforced with silanized quartz filler were evaluated for conversion, water contact angle, water sorption and diametral tensile strength.

Results: By selection of reactants, fluorine was introduced as trifluoromethyl groups, extended fluoroalkyl pendant chains, or combinations of the two. Photopolymerization conversion among the experimental composites was generally equal to or greater than that of a conventional Bis-GMA/TEGDMA composite. While the water contact angles generally increased with fluorine content, no correlation was obtained between fluorine content and water sorption of the composites. The mechanical strength of the fluorinated composites showed a general decline with increasing fluorine content and consistent variations due to specific structural features.

Significance: A versatile route to fluorinated dimethacrylates with diverse structural and fluorine distribution patterns is presented. Composites from these monomers are very hydrophobic but have relatively low mechanical strength. The monomers described can be considered as useful additives to moderate the water sorption of conventional resins. However, the results of this study point to specific fluorinated resin structures that are expected to provide a more optimal balance between hydrophobicity and mechanical strength that will improve the long-term performance of dental composites. Published by Elsevier Science Ltd. on behalf of the Academy of Dental Materials.

Keywords: Fluorinated polymers; Dimethacrylate monomers; Resins

1. Introduction

With their extremely low surface energies, fluorinated polymers appear to be an ideal choice for use as matrix materials in dental composite restoratives. Organofluorine-rich resins can provide inert polymers that display excellent hydrophobicity and resistance to softening by a wide range of chemicals. Potential resistance to staining and microbial attachment are further reasons to consider these materials for dental applications. Indeed, several previous investigations have examined a variety of fluorinated monomers for use in dental resins [1–11]. While the introduction of fluorine into dental polymers has lead to the development of some extremely hydrophobic materials, the low mechanical strength properties due to the low cohesive energies of amorphous fluoropolymers have limited their practical utility.

In an effort to compare and evaluate the influence of monomer structure and fluorine content on resin and composite properties, a versatile method was needed for fluoromonomer synthesis. The relatively small selection of fluorinated diols available for direct conversion to dimethacrylates prompted the use of a two-step synthetic approach based on diepoxide compounds. With access to large numbers of commercially available fluorinated monoalcohols, even the limited choices of fluorinated diepoxy starting materials can be extended to an immense range of difunctional monomers with great diversity in their molecular architecture. This method also provides access to monomers of substantially higher molecular weight than those available by conversion of existing fluorinated diols to the corresponding dimethacrylates. Without significantly altering the intramolecular distance between reactive vinyl groups, the wide choice of the pendant fluorinated substituent incorporated by epoxide ring opening allows overall monomer size and properties, such as viscosity, to be modified

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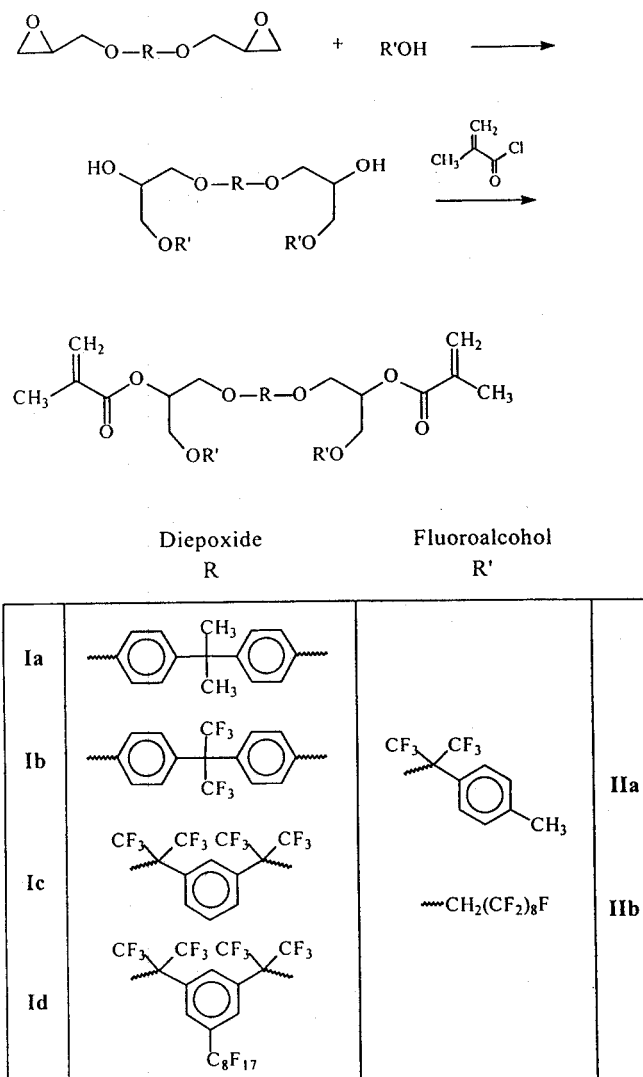*E-mail address:* jeffrey.stansbury@nist.gov (J.W. Stansbury)

Fig. 1. Fluorinated monomer synthesis by ring opening of diepoxides (**I**) with fluoroalcohols (**II**) and conversion of the diol intermediates to the dimethacrylates.

over a wide range. The ability to formulate resins with workable viscosities from monomers of relatively large molecular bulk that require minimal diluent comonomer addition is expected to provide a means to hydrophobic resin-based materials with low polymerization shrinkage. The aim of this study is to evaluate an alternate synthetic route to fluorinated dimethacrylate monomers and elucidate structure/property relationships that will indicate the potential utility of these monomers in photopolymerizable dental resin and composite applications.

2. Materials and methods

2.1. Monomer synthesis and characterization

The general procedure used for the synthesis of fluorinated monomers involved ring opening of a diepoxide with a fluoroalcohol followed by conversion of the resulting diol intermediate to the dimethacrylate (Fig. 1). The following aromatic diepoxides were used to provide the core groups for the series of fluorinated monomers: (1) bisphenol A diglycidyl ether **Ia**; (2) 2,2-bis(4-glycidylphenyl ether)hexafluoropropane **Ib**; (3) 1,3-bis[(2-glycidyl ether)hexafluoro-2-propyl]benzene **Ic**; and (4) 5-perfluorooctyl-1,3-bis[(2-glycidyl ether)hexafluoro-2-propyl]benzene **Id**. Diepoxide **Ib** was synthesized according to the method of Dammont [12]. The fluoroalcohols, either hexafluoro-2(p-tolyl)isopropanol (**IIa**) or 1H,1H-perfluorononanol (**IIb**), were reacted neat with the diepoxides at 100°C in mole ratios of 2.5 and 4.0, respectively. N,N-Dimethylbenzylamine was used as catalyst (mole fraction of 5% based on the diepoxide) [13] and ^{1}H NMR was utilized to monitor reaction progress. When the reaction was complete, excess fluoroalcohol was removed under reduced pressure (13 Pa over a temperature range of 23–150°C). The residue was dissolved in
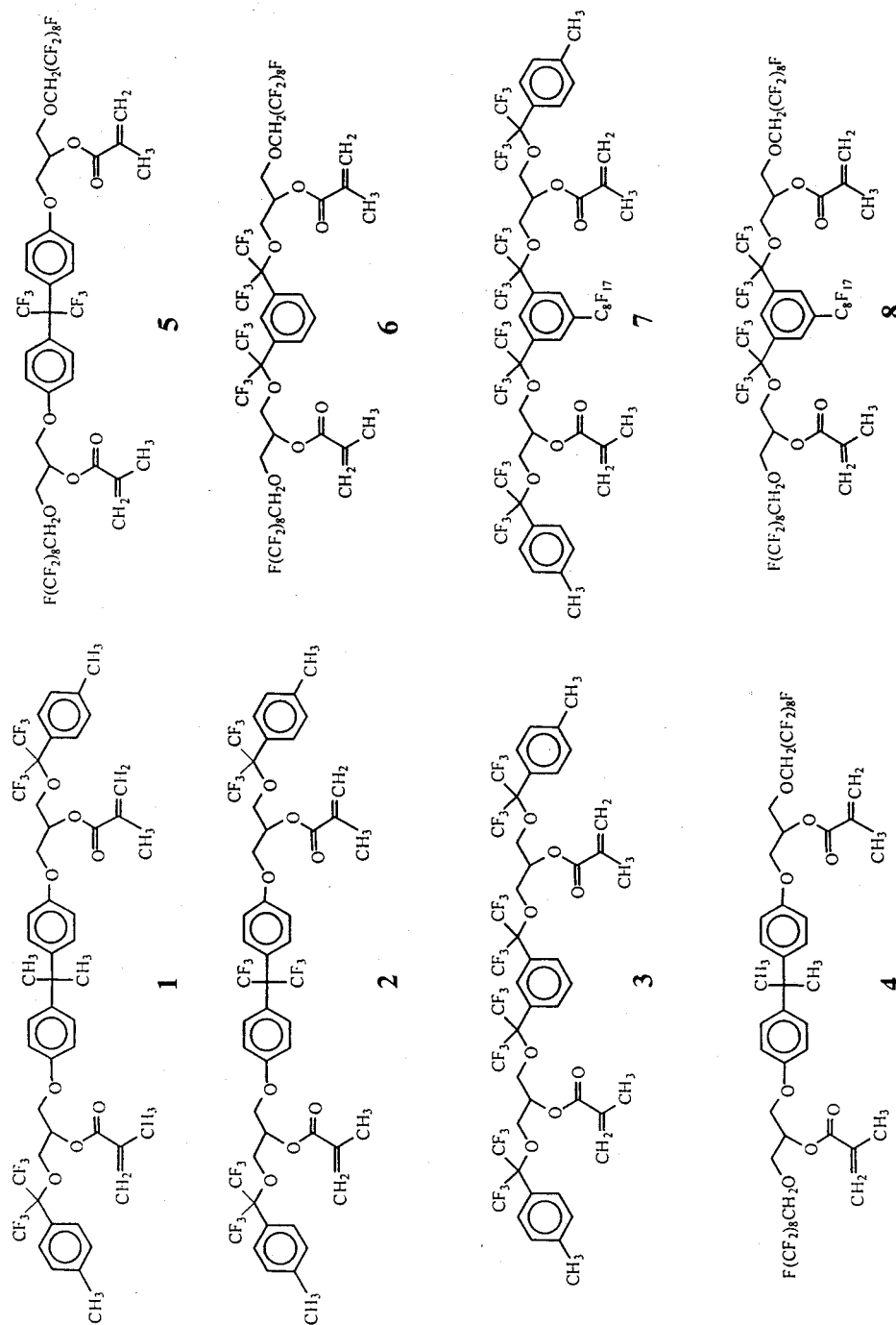
Fig. 2. Structures of fluorinated monomers 1–8.

Table 1
Characterization of fluorinated dimethacrylate monomers

Fluoromonomer	MW[a]	%F as CF_3[b]	%F as $(CF_2)_n$[b]	Total %F[b]	RI[c]
1	993	23.0	0	23.0	1.5003
2	1101	31.1	0	31.1	1.4877
3	1175	38.8	0	38.8	1.4433
4	1377	0	46.9	46.9	1.4206
5	1485	7.9	43.3	51.2	1.4152
6	1559	15.0	41.1	56.1	1.3789
7	1593	28.6	20.3	48.9	1.4110
8	1977	11.7	48.9	60.6	1.3630

[a] Relative molecular mass.
[b] Mass fraction of fluorine in monomer as CF_3, CF_2 or both.
[c] Refractive index measured at 22.5°C (standard uncertainty of ± 0.0003).

dichloromethane (the diol intermediates for monomers **6** and **8** were only sparing soluble in dichloromethane; therefore, acetone was used as the solvent in these reactions) and triethylamine (2.5 mol per mole of diol) was added. The solution was cooled to 5°C and methacryloyl chloride (2.2 mol per mole of diol) in dichloromethane was added dropwise. After 18 h at room temperature, the reaction mixture was sequentially extracted with dilute aqueous HCl and NaOH solutions. The organic layer was decolorized with activated carbon and dried over anhydrous sodium sulfate. Following filtration through a small pad of silica gel, the solvent was removed under reduced pressure (13 Pa over a temperature range of 23–60°C) to yield the fluorinated dimethacrylate monomers **1–8** as nearly colorless oils (Fig. 2). FT-IR and ^{1}H NMR characterization of the various monomers provided spectra that were consistent with the expected products.

2.2. Resin formulation

Resin formulations based on fluoromonomers **1–8** were prepared with equimolar proportions of 1,10-decamethylene dimethacrylate (DMDMA, Esschem Co.). The resins were activated for visible light photopolymerization (440–500 nm) by the addition of camphorquinone (CQ, mass fraction of 0.2%) and ethyl 4-*N*,*N*-dimethylaminobenzoate (EDMAB, mass fraction of 0.8%). A photocurable resin composed of 2,2′-bis[4(2-hydroxy-3-methacryloyloxypropyloxy)phenyl]propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (mass ratio of 7:3) with CQ/EDMAB was also prepared as a control. Fused quartz (25 μm average particle size) silanized with 3-methacryloxypropyltrimethoxylsilane (mass fraction of 0.5%) was mixed with the resins to provide photopolymerizable composite pastes with a filler mass fraction of 60%. For dual cure polymerizations, the quartz filler used had received an additional treatment of benzoyl peroxide (mass fraction of 1%) applied as a coating by the evaporation of a dichloromethane solution.

2.3. Evaluation of resins and composite properties

The degree of conversion of unfilled resin films cured for 60 s (340 mW/cm^2, Max Light, L.D. Caulk Co.) between Mylar sheets was determined by comparison of the FT-IR (Nicolet Magna 550) spectra of pre- and post-cured samples in triplicate. Due to variations in the structures of the fluoromonomers in this series of resins, different aromatic internal reference peaks specific to each resin were identified and used for the normalization of the cured and uncured spectra [14]. Duplicate composite specimen disks (0.5 mm thick by 15 mm diameter) of each material were photocured for 3 min per side (Triad 2000, Dentsply). A goniometer (NRL C.A., Ramé-Hart Inc.) was used for the measurement of the static contact angles (20 s after drop placement) of deionized water on the composite disks. The disks were then placed in distilled water until constant weight was attained. Water uptake was calculated from the difference between the final water-equilibrated weight and the pre-immersion sample weight. The diametral tensile strength (DTS) of the various composite formulations was determined on disk specimens (2 mm thick by 4 mm diameter) photocured for 60 s per side and stored in distilled water for 24 h at 37°C prior to testing to failure on a universal testing machine (Instron 1122) at a crosshead speed of 1 cm/min.

3. Results and discussion

The tertiary amine-catalyzed reaction between aromatic diepoxides (**I**) and fluorinated alcohols (**II**) (Fig. 1) was used to prepare a series of diol intermediates that were then converted to dimethacrylates **1–8**. The disappearance of the characteristic epoxy signals between 2.6 and 3.4 ppm in the ^{1}H NMR spectra was used to monitor diol formation. Of the two fluoroalcohols examined here for addition to the epoxy rings, **IIa** was found to produce more facile reactions, probably because of its greater acidity. The greater difficulty encountered in achieving complete reaction with **IIb** prompted its use in larger excess. The excess

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Table 2
Evaluation of fluorinated resins and composites

Resin composition[a]		RI (resin)[b]	Degree of conversion (%) (resin)[c]	Water contact angle (degrees) (composite)[d]	Mass fraction water uptake (%) (composite)[e]	DTS (sd) (MPa) (composite)[f]	
Monomer	Mass fraction DMDMA (%)					Photocure	Dual cure
1	23.8	1.4905	60.0	74.8	0.05	4.8 (2.7) A	37.2 (1.3) A
2	22.0	1.4808	49.2	76.8	0.10	37.3 (1.7) A	38.0 (0.8) A
3	20.9	1.4483	65.0	84.4	0.05	29.6 (1.4) B	33.1 (1.4) B
4	18.8	1.4303	70.9	85.4	0.05	28.2 (2.6) B	23.3 (1.1) C
5	17.6	1.4304	76.0	88.7	0.13	28.1 (2.4) B	26.0 (0.5) D
6	16.9	1.3978	80.0	77.2	0.09	24.8 (0.9) C	25.4 (0.7) DE
6	16.9	1.3978	–	–	–	26.8 (2.1)[g]	–
7	16.3	1.4230	65.0	91.7	0.04	19.7 (1.4) D	24.8 (0.8) E
8	13.8	1.3825	35.8/77.4[h]	108.8	0.06	–	–
8	31.0% EBPAD[i]	–	–	–	–	13.7 (0.9)	–
Bis-GMA	30% TEGDMA	1.5218	62.3	68.6	1.22	51.0 (3.4) E	–

[a] Except as noted otherwise, resins composed of an equimolar mixture of fluorinated dimethacrylate and 1,10-decamethylene dimethacrylate.
[b] Refractive index at 22.5°C; standard uncertainty of ± 0.0003.
[c] Methacrylate conversion in polymer; standard uncertainty of ± 0.020.
[d] Standard uncertainty ± 1.27deg;.
[e] Mass fraction equilibrium water uptake; relative standard uncertainty of 7plusmn;2.5 %.
[f] Standard uncertainty (sd); letters indicate nonequivalent Duncan's multiple range groupings ($\alpha = 0.05$).
[g] Samples given additional cure cycle.
[h] Resin film irradiated for 3 min.
[i] Ethoxylated bisphenol A dimethacrylate (resin was phase separated prior to polymerization).

1H,1H-perfluorononanol could be recovered during concentration of the reaction mixture under vacuum. The recovered fluoroalcohol was suitable for recycling into subsequent reactions. In the second synthetic step, conversion of the diol intermediates to the corresponding dimethacrylates was followed by the downfield shift of the methine proton from approximately 4.2 to about 5.3 ppm for the products. Monomers were obtained in high overall yields (mass fractions of $\geq$ 78%) from the two-step reactions.

As shown in Table 1, the overall fluorine content within the series of monomers can be differentiated into trifluoromethyl (CF_3) and mainly pendant perfluoroalkyl chain $(CF_2)_n$ components. The combination of diepoxides and fluoroalcohols used here allows the synthesis of a monomer series that includes representatives with exclusive CF_3 or predominantly $(CF_2)_n$ substitution patterns, as well as varied mixtures of the two. Fluorine content is generally proportional to the molecular mass of the monomer; however, the monomers are numbered in ascending order in accordance with increasing molecular mass rather than by fluorine content. The refractive indices of the fluorinated monomers show a strong inverse correlation (Pearson correlation coefficient: $r^2 = 0.98$) with the overall fluorine content. This correlation does not seem to be influenced significantly by structural features such as aromatic rings that range from one to four in number in the various monomers.

Each of the fluorinated dimethacrylate monomers was combined with an equimolar proportion of DMDMA (Table 2) as a reactive diluent to yield a series of photopolymerizable resins. This level of diluent comonomer was necessary to attain workable resin viscosities with the most viscous monomers (1 and 2). DMDMA was selected as comonomer since it allowed the formulation of homogeneous resins over a wide range of monomer ratios. Ethoxylated bisphenol A dimethacrylate and TEGDMA were also examined as potential diluent comonomers; however, phase separation of the resulting resins occurred at relatively low levels of incorporation of these comonomers. Monomer 3, which has a relatively rigid, regular structure, was the only fluorinated dimethacrylate that crystallized upon extended storage in the freezer. Those monomers with high fluorine contents, especially those with a significant proportion of $(CF_2)_n$ substituents, had much lower viscosities and can be used without a diluent comonomer; their low viscosities also suggest their use as potential low-shrinking, hydrophobic diluent comonomers. The dramatic viscosity-lowering effect of the long fluoroalkyl substituents was one of the clear differences noted between the CF_3 and $(CF_2)_n$ modes of fluorine incorporation.

The series of fluorinated monomers prepared here have the methacrylate groups appended almost exclusively as secondary esters (a small percentage of the product arises

from the epoxide ring opening at the more hindered position) rather than as the primary esters that are typical of conventional dimethacrylates. Since with few exceptions the degree of cure values of the fluorinated resins (Table 2) are equal to or exceed that of the Bis-GMA/TEGDMA resin, this structural difference does not appear to hinder the polymerization efficiency of the new monomers. The extent of polymerization resulting from visible light irradiation of unfilled resins showed a general increase that corresponded to the overall fluorine content of the monomer ($r^2 = 0.72$ with the resin containing **8** irradiated for 3 min). This trend (with the exception of the resin formulated with **2**) reaches a maximum with the resin based on monomer **6**, and then the conversion declines precipitously for the resin based on **8**. This reversal can be attributed to the phase separation that accompanies the polymerization of the resins containing monomers **6** and **8**, which have the highest fluorine contents. The phase separation occurs immediately on exposure to the visible light source and was especially evident for the resin based on monomer **8**. The resulting increase in opacity limits transmission of light and, thereby, hinders more complete conversion of the methacrylate groups. Since an extension of the exposure time for the resin with monomer **8** produced a highly cured polymer film in spite of the phase separation behavior, it appears that an attenuated photoinitiation process, resulting from rapid development of opacity, was the only factor limiting conversion. It is noteworthy that all of the most completely cured resins were derived from the 1H,1H-perfluorononanol ring-opened epoxides. This may be related to the decreased steric hindrance and/or a lower glass transition temperature due to the perfluoroalkyl chain compared with its bulkier tolyl branched counterpart.

To prepare photocurable composite pastes from the series of activated resins, particulate amorphous fused quartz silanized with a methacrylate-functionalized coupling agent was incorporated as a reinforcing filler. A relatively low filler loading level was selected to emphasize differences in the resin phase of these materials, while still benefiting from the reinforcing effect of the filler. Amorphous quartz was selected as filler due to its relatively low refractive index ($n_D^{20} = 1.4585$) [15], which provided a reasonably good match over a significant portion of the range of resin formulations (Table 2). Quartz filler was used for this preliminary investigation despite some of its associated drawbacks that include a lack of radiopacity. Compatibility in the refractive index of resin and filler is considered to be an important factor in achieving efficient throughput of light necessary for optimum conversion as well as acceptable esthetics. The resin based on monomer **8** has a refractive index that is significantly lower than that of the filler. Further complicating this refractive index mismatch and the strong phase separation that occurred during polymerization, this formulation displayed an additional problem in that the composite paste prepared was relatively dry compared with those derived from the other monomers.

This indicates that resins with high fluorine contents may be inefficient at wetting this type of filler. This would seriously compromise the potential reinforcing effect of the filler and may require consideration of alternative silane coupling agents that are more compatible. Preliminary studies have demonstrated that significantly higher filler loading levels can be achieved in composites based on fluorinated resins when 10-methacryloxydecyltrimethoxysilane [16] is used in place of 3-methacryloxypropyltrimethoxysilane as the coupling agent.

Contact angle values measured for deionized water on the composite disks photocured against Mylar film showed a weak positive correlation ($r^2 = 0.45$, but this increased to $r^2 = 0.84$ if the resin containing monomer **6** is omitted) with the overall fluorine content of the monomers. For the most part, the composites appeared to be well cured with hard, glossy surfaces and varying degrees of translucency. The composite based on monomer **3**, which had the closest resin–filler refractive index match, was the most translucent. The composite containing monomer **8**, was somewhat of an exception in that it was almost completely opaque and had a slightly softer, non-glossy surface. Even with the additional irradiation time allotted for these composite samples compared with the unfilled resin films, difficulties due to the resin–filler refractive index mismatch and phase separation during polymerization appear to combine to prevent bulk samples of the composite containing monomer **8** from reaching an adequate degree of conversion to polymer. The water contact angle obtained for the composite with the lowest fluorine content was not dramatically greater than that found for the Bis-GMA/TEGDMA composite (Table 2). At the other extreme, the composite containing monomer **8**, with three pendant perfluoroalkyl chains, produced a contact angle close to that of poly(tetrafluoroethylene) (116°) [17]. In the direct comparisons that can be made between the hexafluoroisopropyl aromatic and the fluorinated aliphatic end groups, three out of the four possible pairings show significantly higher contact angles for the materials derived from the monomers with the fluorinated nonyl terminal groups. In general, it appears that a high percentage of fluorine in the resin is necessary to induce a high contact angle value for the composite. It has been suggested [1,18] that oral fluid uptake into marginal gaps occurring at the tooth-restorative interface may be inhibited through use of hydrophobic composite materials with extremely high contact angles.

While water sorption among the series of photocured fluorine-containing composites was quite substantially less than the level taken up by the Bis-GMA/TEGDMA composite specimens (Table 2), there was no correlation between water uptake and the overall fluorine content ($r^2 = 0.02$) of the composites derived from the various fluorinated resins. Therefore, it seems that high water contact angles are not required for composites to demonstrate excellent hydrophobicity in bulk. Structural comparisons of the fluorinated monomers in similar resin systems indicate that there are

no notable differences in water sorption due to the fluorinated aliphatic or arylaliphatic end groups even though the former introduces greater fluorine content and higher water contact angles. However, differences are apparent with respect to the various core group structures. Surprisingly, the nonfluorinated bisphenol A core provided materials (monomers 1 and 4) that were as hydrophobic as those obtained with the highly fluorinated 1,3,5-substituted phenyl group (monomers 7 and 8). The other unexpected observation was that the hexafluoro-bisphenol A core group produced materials (monomers 2 and 5) with the highest water sorption results. Prior studies [9] have shown significant reductions in water sorption for hexafluoro-Bis-GMA compared with Bis-GMA where the fluorinated bisphenol A substructure is the only source of fluorine in the resin. It should be noted that differences in water uptake for the composites reported here are small and that all the materials are very hydrophobic. It was evident that the rates of hydration and dehydration were very rapid for the fluorinated composites compared with the Bis-GMA/TEGDMA resin composites, which required 3 to 4 times longer to equilibrate.

The diametral tensile strength of the various photopolymerized composite materials (Table 2) was measured in an effort to relate mechanical strength with fluorine content and the manner of its distribution. A general decrease is encountered in the composite DTS as the overall fluorine content increased ($r^2 = 0.65$). This is likely a consequence of decreased cohesive energy that reduces the reinforcing effect of polymer chain entanglements. The DTS specimens prepared with the composite containing monomer 8 did not fracture in a brittle manner and, therefore, are not included in the results. Again, an inadequate degree of cure is probably the main cause of the mechanical strength deficiency in this composite. An examination of the structure–property relationships shows that for the various core groups, the fluorinated and nonfluorinated bisphenol A connecting groups gave materials with the highest mechanical strength. Monomers prepared with the fluorinated aromatic end groups also yielded consistently stronger composites than those containing monomers with the fluoroalkyl end groups.

In all cases, the photocured fluorinated composites were substantially weaker than the typical Bis-GMA/TEGDMA composite. This was true even though the refractive index match between the control resin and the quartz filler was poor and resulted in cured samples that were relatively opaque. The DTS value obtained for Bis-GMA/TEGDMA and quartz is quite similar to DTS values obtained with this resin and a barium oxide glass filler, which does provide a good refractive index match. To determine if the mismatch between the resin–filler refractive index contributed significantly to the lower strength values seen for the fluorinated composites, additional DTS specimens were prepared by a dual cure technique in which a slow redox polymerization (not light dependant) is coupled with a rapid photopolymerization [19]. As shown in Table 2, the improvements in

strength were modest at best; however the negative correlation between DTS and monomer fluorine content was improved ($r^2 = 0.82$, with the composite based on 8 omitted). Therefore, resin refractive index should not be considered a dominant factor limiting potential properties of photocured fluorinated composites, at least for specimens of moderate thickness. However, the likely mismatch in the solubility parameters between the fluorinated resins and the interfacial silane phase also may have a detrimental effect on mechanical properties. In addition, while the use of DMDMA with Bis-GMA would undoubtedly result in materials with reduced water sorption compared with the Bis-GMA/TEGDMA control, it also results in decreased mechanical strength properties [20]. Thus, the use of DMDMA as the hydrophobic diluent comonomer in the fluorinated resins probably accounts for some portion of the discrepancy in mechanical strength between the experimental composites and the control. The structure–property results obtained here will aid in the design of new monomers. Further investigations into related di- and multi-functional fluorinated monomers as well as more compatible silane coupling agents are underway to identify materials that retain beneficial low surface energy properties, such as minimal water sorption and solvent resistance, while providing mechanical strength results comparable to those of traditional dental composites.

4. Conclusion

The use of epoxy ring-opening routes to fluorinated methacrylate monomers is an efficient, versatile process. The overall fluorine content of the monomers provides some general prediction of potential composite properties, although no correlation between fluorine content and water sorption was observed. The systematic structural variations present within the series of monomers developed in this study allow direct comparisons of the effects of the individual structural components on specific properties of the resulting composite materials. The use of bisphenol A or its fluorinated analog as a core structure in the monomers provided composites with the highest mechanical strength properties, although still somewhat below those of conventional dental composites. The placement of fluorine in extended perfluoroalkyl chains tended to raise water contact angles but did not decrease water sorption and led to lower mechanical strength compared with use of the alternate fluorinated aromatic terminal group. Monomers of the type described in this study can be considered for use in conventional resins as additive comonomers that would favorably reduce water uptake and possibly polymerization shrinkage. With some modifications, related fluorinated monomers are expected to provide the basis of dental resins with enhanced durability.

Acknowledgements

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