JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 8 (1997) 465–468

Characterization of some aromatic dimethacrylates for dental composite applications

M. SANKARAPANDIAN, H. K. SHOBHA, S. KALACHANDRA*, J. E. MCGRATH
NSF Center, Virginia Tech, Blacksburg, VA-25061, USA

D. F. TAYLOR
School of Dentistry, University of North Carolina, Chapel Hill, NC 27599-7450, USA

Several novel dimethacrylates have been developed as alternative matrix materials for dental composite applications. For the cured bulk polymers the equilibrium water uptake, reduction of glass transition temperatures (T_gs) by water sorption, refractive indices and the surface hardness have been determined. The properties were then compared with those of the control Bis-GMA. These properties correlated well with the structures of the polymers. Polar groups were found to increase the water sorption and thus reduce surface hardness.

1. Introduction

Many commercial dental composite materials utilize 2,2-bis-[4-2-hydroxy-3-methacryloxypropoxy phenyl] propane (Bis-GMA) as the matrix resin [1–5]. Due to the intermolecular hydrogen bonding in Bis-GMA, it possesses very high viscosity and is customarily diluted with low viscosity monomers (such as triethylene glycol dimethacrylate (TEGDMA)) to achieve workable viscosity limits. However, TEGDMA has been shown to adversely affect the properties of the matrix resins by increasing the water sorption and curing shrinkage [2, 6]. Investigations are being carried out in identifying new dimethacrylates which will have moderately low bulk viscosities to eliminate or minimize the use of the diluent monomers. Several systems with improved properties have been reported in the literature [5–12].

Several novel dimethacrylates have been developed in our laboratory based on structural modifications of Bis-GMA in the core and the side chain units. Twelve monomers have been evaluated including the control Bis-GMA and all possible combinations of four core structures and three side chain structures [5]. The core structures are designated by Bis-A, 6F, 3F and P. The side chain units are designated on the basis of the pendant side chains as –OH, –H and CH_3.

The study of the properties of the cured networks made from the neat monomers is important to understand their behaviour in the composites. This work describes the water sorption, T_g behaviour, refractive index and the surface hardness properties of the cured networks made from the neat monomers.

2. Experimental procedures

2.1. Materials

Bis-GMA was obtained from Polysciences, Inc., Warington, PA and used as-received. It was used as a standard for comparison of the experimental monomers. All the monomers used in this study were synthesized in our laboratory. Their structures are shown in Fig. 1.

2.2. Synthesis

A brief description of the synthesis of the monomers employed in the present study is illustrated below.

The core structures of the aromatic dimethacrylates were varied by using different diphenols and the side chain units were varied by employing different reaction pathways. The monomers with hydroxy propyl side chains were prepared by the reaction of the methacrylic acids with the corresponding diglycidyl ethers of the diphenols. The monomers with ethoxyl side chain groups were prepared by the ethoxylation of the diphenols using ethylene carbonate and then methacrylation of the ethoxylated diphenols. The propoxylated monomers were prepared by propoxylation of the diphenols using propylene oxide and sodium hydroxide followed by the methacrylation of the resulting product using methacryloyl chloride and triethyl amine base in tetrahydrofuran (THF) solvent. All the monomers were characterized by ^1H nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopic techniques. A complete description of the synthesis

---

*To whom all correspondence should be addressed. Also at the School of Dentistry, University of North Carolina, Chapel Hill, NC 27599-7450, USA.

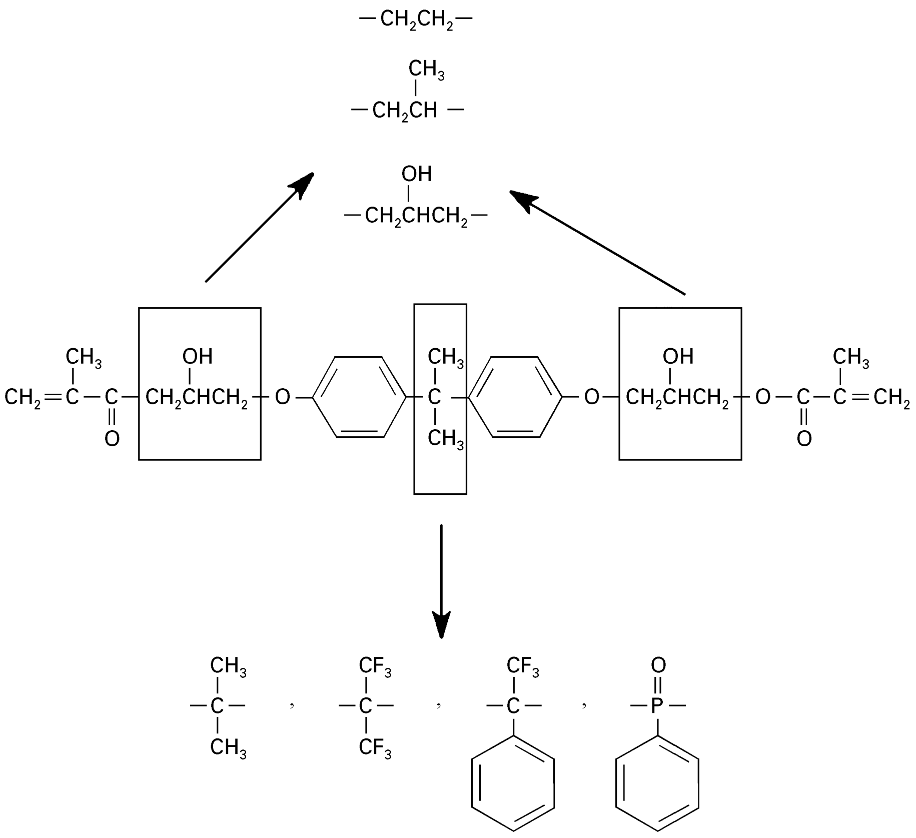

Figure 1 Structures of the dimethacrylates.

and characterization of the monomers is provided elsewhere [13].

2.3. Characterization

FTIR (Nicolet 2000) and ^1H NMR (Varian 400 MHz) spectroscopic techniques were used to characterize the monomers. The glass transition temperatures (T_gs) of the monomers were measured using a Du Pont DSC (Model 1090) instrument, and those of the cured polymers were measured using a Perkin Elmer DMA Instrument (Model DMA-7) in three-point bending mode. The samples were heated at a rate of 2 °C min^{-1} and tested at a frequency of 1 Hz. The refractive indices were measured using a Metricon Refractometer (Model 2000). The Vickers microhardness values were obtained using a Leco Hardness Tester (Model DM-400). The monomers were polymerized in steel moulds, sandwiched between two glass plates. Camphorquinone (0.25 wt %) was used as the photo-initiator and N,N'-dimethyl *p*-toluidine (0.3 wt %) was used as the photosensitizer. The samples were cured at 3 min on each side with a Triad (Dentsply model 2000) photocuring unit. Water uptake by the polymers was determined gravimetrically. The procedures are described in detail in a previous publication [4].

3. Results

The equilibrium water uptakes of the polymers are shown in Table I. The T_g values of some illustrative monomers and their corresponding polymers (ethoxyl

TABLE I Equilibrium water uptake of bulk polymers (in weight percentages)

	Bis-A	6F	3F	P
–OH	3.05	2.53	0.92	–
–H	0.58	0.14	0.37	3.15
$-CH_3$	0.91	0.18	0.16	2.84

TABLE II Glass transition temperatures of the neat monomers and polymers (in dry and wet samples)

System		Monomer T_g(° C)	Polymer T_g(° C)	
Core unit	Side chain		Dry	Wet
Bis-A	–OH	– 6.0	64.5	57.6
Bis-A	–H	– 23.3	66.7	63.6
Bis-A	–CH3	– 26.6	63.0	61.3
6F	–H	– 17.5	67.2	66.1
6F	–CH3	– 15.6	63.8	61.5

TABLE III Refractive indices of the neat films

	Bis-A	6F	3F	P
–OH	1.563	1.520	1.556	–
	(1.549)	(1.509)	(1.550)	
–H	1.562	1.516	1.551	1.569[a]
	(1.556)	(1.512)	(1.556)	
$-CH_3$	1.551	1.514	1.548	1.578[a]
	(1.545)	(1.505)	(1.546)	

The values in the parentheses indicate the calculated values from the group contribution method described in [16].

[a] The group value for the phosphine oxide group is not available.

TABLE IV Vickers hardness numbers for the dry and water saturated samples of the neat polymers

	Dwelling time (s)	Bis-A		6F		3F		P	
		Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
$-OH$	10	24.00	17.66	22.32	19.95	22.17	21.05	–	–
		(0.74)	(0.67)	(0.76)	(0.91)	(0.80)	(1.07)		
	30	22.18	16.25	20.42	18.57	20.87	19.29	–	–
		(0.78)	(0.91)	(0.64)	(0.65)	(0.66)	(0.74)		
$-H$	10	21.56	19.44	21.09	20.37	21.10	20.40	20.93	16.58
		(0.79)	(0.49)	(0.78)	(1.02)	(0.52)	(0.72)	(0.49)	(0.37)
	30	18.80	17.37	18.76	18.50	19.0	18.44	19.79	15.61
		(0.51)	(0.66)	(0.85)	(0.91)	(0.85)	(0.61)	(1.03)	(0.39)
$-CH_3$	10	20.83	18.58	20.23	20.10	20.43	19.95	20.59	17.24
		(1.15)	(0.55)	(1.15)	(1.09)	(0.63)	(0.62)	(0.56)	(0.67)
	30	19.33	17.64	18.26	17.41	18.39	17.72	18.79	16.26
		(0.65)	(0.53)	(0.41)	(0.25)	(0.66)	(0.34)	(0.84)	(0.36)

The values in the parantheses indicate standard deviation for $n = 10$.

and propoxyl side chains and isopropylidene and hexafluoroisopropylidene core units) in the wet and dry condition are given in Table II. Refractive indices of cured thin films were measured for all the cured polymers and the values are provided in Table III. The Vickers hardnesses were measured on rectangular samples (25 mm × 25 mm × 1 mm) with 200 g load at 10 and 30s dwell times. Vickers hardness numbers for the dry and water equilibrated samples are shown in Table IV.

4. Discussion

The equilibrium water uptake of the bulk polymers (Table I) indicates that all but one of the polymers made from the experimental monomers exhibited low water uptake compared to the control Bis-GMA. A general trend that could be noticed in Table I is that the water uptake in the polymers with hydroxy side chain units is relatively high compared to the other polymers. Similarly, the water uptake in systems with phosphine oxide core groups is also high and is close to that of the control Bis-GMA. These factors suggest that in systems which are capable of hydrogen bonding with water, the water uptake is relatively high. Incorporation of fluoro groups in the core units resulted in a more hydrophobic environment and hence it results in reduced water uptake compared to Bis-GMA. The absence of the hydroxyl groups in the ethoxylated and propoxylated monomers also results in lower water uptake. The most favourable monomers, from a water sorption point of view, have been identified to be the systems having fluorine containing core groups and ethoxyl or propoxyl side chain units.

The glass transition temperatures of the polymers were measured for some representative systems containing Bis-A and 6F core units and ethyl and propyl side chain units (Table II). The determination of the T_g of the monomers is very important as it has been demonstrated recently that the aromatic methacrylates with low T_g values, exhibit higher conversions [14]. Among the systems studied, the experimental monomers exhibit low T_gs compared to the control Bis-GMA. In a comparison of the ethoxylated and propoxylated analogues of Bis-A and 6F monomers, the later systems exhibit higher T_gs compared to the Bis-A derivatives due to the rigidity introduced by the relatively bulky fluorine groups in the 6F monomers. In essence, since all the experimental monomers exhibit lower T_gs compared to control Bis-GMA, higher conversions should be achieved using these monomers.

The T_gs of the dry and water saturated samples were measured using DMA (Table II). The glass transition temperatures of the dry polymers were very similar ($65 \pm 2.2\,^\circ C$) indicating that vitrification at ambient temperature during polymerization of the samples limited the complete conversions. However the T_gs of the corresponding water saturated samples were found to be strongly influenced by the hydrophilicity of the monomers. For example Bis-GMA, which takes up 3.05 wt % of water, exhibits a reduction of 7 degrees compared to other systems where the reduction of T_g on saturation with water is only 3 degrees or less. Similarly among the ethoxylated and propoxylated analogues of Bis-A and 6F polymers, the reduction of T_g due to water sorption is lower and similar. The reduction of the T_g by water sorption may be due to the fact that the sorbed water may act as plasticizers in these systems [10].

The refractive indices of the thin films of the polymers made from the experimental monomers are given in Table III. It may be noted that the refractive indices of all the polymers lie in the close range of 1.514 to 1.578. A close match of the refractive indices of the polymer matrix and the filler particles will provide optical clarity to the resulting composite in addition to facilitating in-depth cure of the system during photocuring [15]. Among the polymers studied the phosphine oxide containing polymers exhibited higher refractive indices due to the polar phosphine oxide groups and more aromatic groups in these systems. However, the fluorinated monomers exhibited relatively low refractive indices, especially, the 6F monomers. Fluorinated compounds are known to exhibit low refractive indices [15]. The refractive indices were calculated using the group contribution approach [16] and the calculated values and the experimental values were found to be in close agreement.

The Vickers hardness values of the dry and the water saturated polymers made from the experimental monomers are shown in Table IV. From this table, the following conclusions may be drawn. (i) With increase of dwelling time of the weight, the hardness decreases in all the samples indicating that the materials are viscoelastic. (ii) The polymers with hydroxyl side chain groups exhibit higher hardness values in their dry state, possibly due to intermolecular hydrogen bonding. (iii) The decrease in hardness values in the water saturated samples compared to the dry samples correlates with the extent of water sorption. (iv) In general, the extent of reduction from the dry state to the water saturated samples is small for polymers containing the hydrophobic core groups (6F and 3F). (V) The polymers containing phosphine oxide groups in the core units exhibit large reductions in the microhardness values in the water saturated samples. (vi) Comparison of the experimental monomers (except the polymers with phosphine oxide core groups) with the control Bis-GMA reveals that all the polymers made from the experimental monomers exhibit higher hardness values in the water sorbed samples.

5. Conclusions

Several polymers made from the experimental monomers have been tested for water sorption, T_g (in dry and wet states), refractive index and surface hardness. The conclusions of the present work may be summarized as:

1. The systems having fluorine containing core groups exhibit low water sorption, low reduction in T_g and higher surface hardness values than the control Bis-GMA.
2. The phosphine oxide core group causes more water sorption and hence lower surface hardness in the wet samples.
3. The fluorine containing polymers exhibit lower refractive indices while the phosphine oxide core group containing polymers exhibit relatively high refractive indices.

Acknowledgement

This work was supported by NIH-NIDR grant number DE 10156.

References

1. R. L. BOWEN, US Patent 3066112 (1962).
2. M. BRADEN, *Oper. Dent.* **3** (1978) 97.
3. K. W. M. DEVY, *J. Mater. Sci.: Mater. Med.* **5** (1994) 350.
4. S. KALACHANDRA, D. F. TAYLOR, C. D. DEPORTER, H. J. GRUBBS and J. E. MCGRATH, *Polymer* **34** (1993) 778.
5. D. F. TAYLOR, S. KALACHANDRA, M. SANKARAPANDIAN, Q. XU and J. E. MCGRATH *J. Adv. Mater.* **28** (1996) 59.
6. K. W. M. DAVY and M. BRADEN, *Biomaterials* **12** (1991) 406.
7. M. KAWAGUCHI, T. FUKUSHIMA, K. MIYAZAKI, T. HORIBE, T. HABU and N. SAWAMURA, *Dent. Mater. J.* **3** (1984) 272.
8. T. FUKUSHIMA, M. KAWAGUCHI, Y. INOUE, K. MIYAZAKI and T. HORIBE, *ibid.* **4** (1985) 33.
9. M. W. BEATTY, M. L. SWARTZ, B. K. MOORE, R. W. PHILLIPS and T. A. ROBERTS, *J. Biomed. Mater. Res.* **27** (1993) 403.
10. M. KAWAGUCHI, T. FUKUSHIMA and T. HORIBE, *Dent. Mater. J.* **7** (1988) 174.
11. J. TANAKA, K. INOUE, H. MASAMURA, K. MATSUMURA, H. NAKAI, and K. INOUE, *ibid.* **12** (1993) 11.
12. H. K. SHOBHA, M. SANKARAPANDIAN, S. KALACHANDRA, D. F. TAYLOR and J. E. MCGRATH, *J. Mater. Sci.: Mater. Med.* (in press).
13. M. SANKARAPANDIAN, H. K. SHOBHA, D. F. TAYLOR, S. KALACHANDRA and J. E. MCGRATH, *High Performance Polym.* (in press).
14. H. K. SHOBHA, M. SANKARAPANDIAN, A. R. SHULTZ, J. E. MCGRATH, S. KALACHANDRA and D. F. TAYLOR, Makromol. Chem. Macromol. Symp., “Recent Advances in Free Radical Polymerization” 111 (1996) 73.
15. J. W. STANSBURY, J. M. ANTONUCCI and G. L. SCOTT, *Polym. Prep.* **36** (1995) 831.
16. W. GROH and A. ZIMMERMANN, *Macromolecules* **24** (1991) 6660.

Received 10 October
and accepted 19 November 1996