ELSEVIER

Polymer 42 (2001) 6363–6369

polymer

www.elsevier.nl/locate/polymer

Network formation and compositional drift during photo-initiated copolymerization of dimethacrylate monomers

Jeffrey W. Stansbury[a,*], Sabine H. Dickens[b]

[a]University of Colorado Health Sciences Center, P.O. Box 6508/Campus Box F436, 12635 East Montview Boulevard, Suite 155,
Aurora, CO 80045-0508, USA
[b]Paffenbarger Research Center, American Dental Association Health Foundation, National Institute of Standards and Technology,
Gaithersburg, MD 20899, USA

Received 9 October 2000; received in revised form 30 January 2001; accepted 30 January 2001

Abstract

The copolymerization of viscous monomers with a nonviscous diluent comonomer was investigated. Overall, photopolymerization kinetics was compared for equimolar mixtures of triethylene glycol dimethacrylate (TEGDMA), a low viscosity monomer, with either a rigid aromatic dimethacrylate (Bis-GMA) or a flexible aliphatic urethane dimethacrylate (UDMA), as examples of viscous comonomers. Sol fraction analysis from partial cure polymerizations provided individual monomer reactivities as a function of conversion. The resin containing UDMA reached greater maximum polymerization rate and final conversion compared with the resin based on Bis-GMA. The viscous monomers (Bis-GMA or UDMA) were found to be less reactive than the diluent comonomer (TEGDMA) at nearly all stages of the photopolymerization process. The reactivity differential was especially dramatic at the latter stages of the polymerization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymerization; Dental materials; Networks

1. Introduction

Typical resins used in dental restorative applications are composed of a mixture of at least two dimethacrylate monomers. Generally, one of the monomers is relatively viscous since the particulate glass filled resin must have sufficient body to allow controlled placement and contouring prior to photopolymerization. Monomers of this type, often referred to as a base monomer, include an adduct of bisphenol A and glycidyl methacrylate (Bis-GMA, Fig. 1) and urethane dimethacrylate (UDMA; product of 2,2,4(2,4,4)-trimethylhexyl diisocyanate and 2-hydroxyethyl methacrylate). The base monomer in a resin serves to minimize polymerization shrinkage by virtue of its relatively large molecular volume and enhances the modulus of the cured polymer [1,2]. In addition, dental resins contain a reactive diluent comonomer, such as triethylene glycol dimethacrylate (TEGDMA). The low viscosity diluent monomer is added in mass fraction proportions commonly ranging between 20 and 50% to reduce the overall resin viscosity and provide good handling properties to the material. The diluent monomer also affords improved copolymer conversion due to its greater flexibility and smaller molecular volume compared with the base monomers [3,4]. The use of comonomer composition to control resin properties, such as viscosity and wetting ability (toward glass filler or tooth substrate), prior to polymerization is fairly well defined [5–7]. Likewise, the influence of resin composition on the resulting polymer properties, such as mechanical strength and water sorption, has been documented extensively [8–12].

Various investigators have explored the photopolymerization kinetics of dental resins [4,13–15]. Other studies have been conducted to measure the evolution of certain properties, such as the development of modulus and stress, as the polymer network is formed [16,17]. These studies assume equivalent reactivity of the comonomers involved. In one previous study involving denture base polymers, the extractable free monomers were differentiated as either methyl methacrylate or a dimethacrylate cross-linking comonomer [18]. However, an understanding of the participation of the individual comonomers in dental resins during the course of the polymerization process has been lacking. The development of polymeric properties as a function of conversion is critically linked to the compositions of

---

[*] Corresponding author. Tel.: +1-303-724-1044; fax: +1-720-859-4110.
E-mail address: jeffrey.stansbury@uchsc.edu (J.W. Stansbury).

PII: S0032-3861(01)00106-9

both the polymer network and the remaining unreacted monomer throughout the polymerization process.

Knowledge of the coreactivity of monomers of varied structure could aid in the design of resins for more efficient copolymerization and help in the prediction of potential leachable products from photocured resins [19]. For obvious reasons, the majority of dental resin and composite extraction studies have been conducted in water to mimic oral conditions. Due to the disparity in aqueous solubility between the relatively hydrophobic base monomers and TEGDMA, a bias in the composition of the free monomer extracted from the polymer may occur. Thus, in prior aqueous extraction studies with Bis-GMA/TEGDMA resins, TEGDMA was found to account for the large majority of extractable monomer regardless of the initial resin composition [20,21]. The use of an ethanol/water extraction medium for dental polymers produced greater quantities of extractable material compared with extractions with water alone [22]. In one previous report involving a chloroform extraction of fully cured Bis-GMA/TEGDMA composites, the sol fraction obtained appeared to be depleted of TEGDMA with respect to the initial resin composition [23]. In a different study of Bis-GMA/TEGDMA composite materials, ethyl acetate extractions at either 10 min or 24 h after photopolymerization were analyzed by HPLC [24]. There, it was demonstrated that over this post-cure interval, the level of TEGDMA in the extract residue decreased more rapidly than Bis-GMA.

Therefore, the objectives of this study were to prepare photocured polymers of typical dental resins having a broad range of conversion values and to determine the comonomer ratio of the soluble fraction extracted from the polymers. This allows analysis of the composition of the polymeric network at various stages of its development and the demonstration of how the different comonomer reactivities contribute to the heterogeneous nature of the cross-linking copolymerization process in dental resins.

2. Materials and method

The monomers employed in this study, Bis-GMA, UDMA and TEGDMA (Fig. 1), were supplied by Esstech (Essington, PA) and were used as received. The resin formulations consisted of equimolar mixtures of either Bis-GMA/TEGDMA (mass ratio of 0.642:0.358) or UDMA/TEGDMA (mass ratio of 0.622:0.378). The resins were activated for visible light photopolymerization by the addition of mass fractions of 0.1% camphorquinone (CQ) and 0.3% ethyl 4-*N*,*N*-dimethylaminobenzoate (4-EDMAB). Resin disks (0.5 mm thick by 20 mm diameter) were photopolymerized between mylar films in a dental curing unit (Triad 2000; Dentsply International, York, PA) with a light intensity of approximately 35 mW cm^{-2} measured by a radiometer at the specimen position. The duration of the specimen irradiation was varied at either 5, 10, 20, 40 or 180 s. Triplicate specimens of each resin were prepared and stored in the dark at 23°C under house vacuum for 10 days. The specimens prepared with the 5 s irradiation interval were stored in the molds with the mylar film boundaries in place to avoid loss of unreacted monomer from the disks.

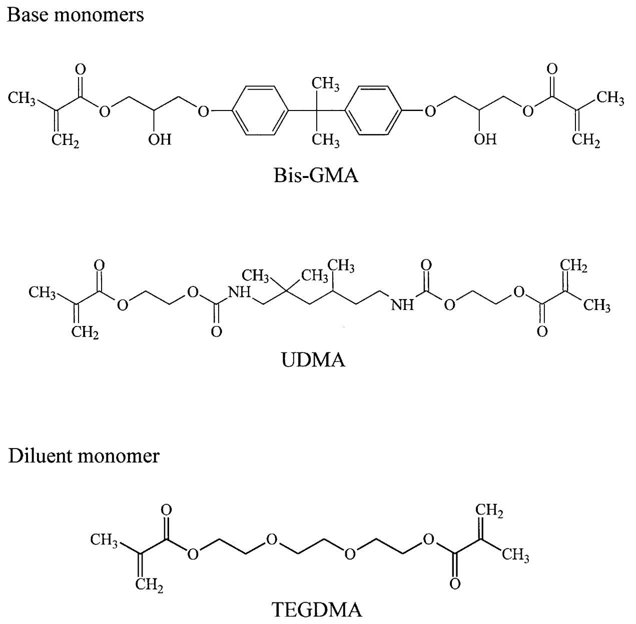

Fig. 1. Structures of monomers used.

2.1. Conversion

Conversion of the photocured resins was determined by a near infrared (NIR) spectroscopic technique (Magna 550 FT-IR; Nicolet, Madison, WI) [25]. Briefly, the area of the methacrylate overtone absorption (=C–H) at 6164 cm^{-1} was normalized against an internal reference: the aromatic absorption at 4623 cm^{-1} was used for the Bis-GMA resins and the urethane absorption (N–H) at 4920 cm^{-1} was used for the UDMA resins. The areas under the =C–H absorptions in the cured specimens were then ratioed against the areas of the =C–H absorptions of the uncured resins. The NIR spectra were obtained after the 10-day storage interval, immediately prior to immersion in the extraction media.

2.2. Extraction studies

After the storage interval, the resin disks were weighed (±0.2 mg) to determine their pre-immersion mass. Individual specimens were placed in 20 ml of dichloromethane (containing 0.1 g l^{-1} 4-methoxyphenol) for 48 h at 23°C. The solvent was collected and the specimens were extracted with a fresh 20 ml portion of dichloromethane (without inhibitor) for an additional 48 h. The combined soluble residue (sol), obtained after rotary evaporation of the extraction solvent, as well as the remaining insoluble polymer (gel) were dried to constant mass under vacuum and the sol and

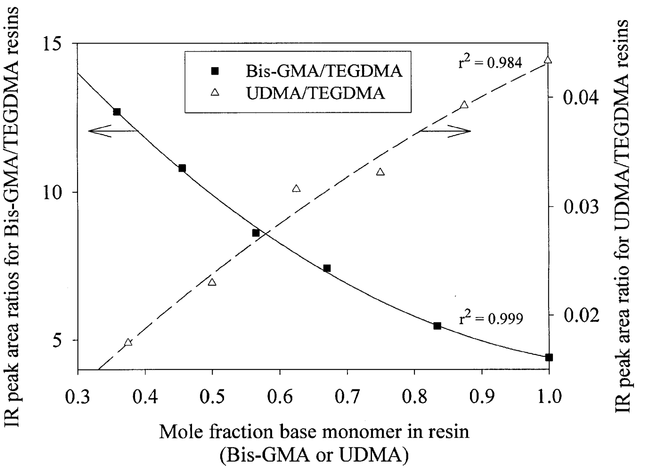

Fig. 2. Standard curves based on the FT-IR analysis of resins of known compositions. The results use absorption ratios that vary continuously as a function of the Bis-GMA/TEGDMA or UDMA/TEGDMA resin composition. The residual standard deviations as a measure of uncertainty are 0.0147 for the Bis-GMA/TEGDMA resin and 0.002 for the UDMA/TEGDMA resin.

gel fractions were determined gravimetrically. For the resin specimens cured for 40 s, complete extraction of unbound monomers was verified by a final extraction of the ground polymer gel in 20 ml chloroform at 50°C for 48 h.

2.3. Sol fractions

Sol fractions were analyzed by FT-IR using specific peak area ratios related to those of a standard curve obtained from varied resin compositions. A range of known ratios of Bis-GMA/TEGDMA and UDMA/TEGDMA were prepared and used to generate the standard curve plots (Fig. 2). The areas of the IR absorptions at 1637 cm^{-1} of the aliphatic C=C stretching (methacrylate) and at 1582 cm^{-1} of the aromatic stretching were used for the Bis-GMA resins while the absorptions at 776 cm^{-1} associated with the aliphatic core of UDMA and at about 2900 cm^{-1} of the broad multiple CH_3 and CH_2 stretching (over the range of 3146 to 2669 cm^{-1}) were used for the UDMA resins.

2.4. Photopolymerization kinetics

The isothermal photopolymerization kinetics of the two resin systems were analyzed by differential photocalorimetry (DPC; 2920 DSC; TA Instruments, Inc., New Castle, DE) with visible light irradiation. Polymerization was conducted under a nitrogen atmosphere with a minimum of a 6 min purge interval prior to irradiation. The specimens, approximately 2 mg contained in open aluminum pans, were irradiated continuously for 12 min at 30°C with a 150 W xenon source filtered to 250 μW cm^{-2} at 470 ± 5 nm with a combination of bandpass and neutral density filters. An indium standard was used for calibration of the DPC. The output of heat flow per time was converted to normalized rate of polymerization as a function of conversion using the methacrylate heat of polymerization (54.8 kJ mol^{-1}) [26] and the resin densities of 1114 and 1107 g l^{-1} for Bis-GMA/TEGDMA and UDMA/TEGDMA, respectively, in the following equation:

$$R_p = \frac{d[M]}{dt} = \frac{\text{heatflow (W g}^{-1}) \times \rho\ (\text{g l}^{-1})}{\Delta H_p\ (\text{J mol}^{-1})}$$

where R_p = rate of polymerization; ρ = density; ΔH_p = heat of polymerization

3. Results and discussion

The overall NIR conversion values associated with the various irradiation intervals are shown in Fig. 3. The standard deviations as a measure of uncertainty are shown as error bars or are less than the size of the symbols. It is evident that the respective resins are essentially equivalent up to approximately 50% conversion. Beyond this level, the UDMA-based resin reaches significantly higher degrees of conversion for a given irradiation interval compared with the Bis-GMA material. As the irradiation time is extended, a progressively greater thermal component accompanies the photopolymerization and contributes to the conversion values observed. The NIR analysis technique applied here provides a convenient method to study conversion in the 0.5 mm thick specimens used in this study. With the relatively low initiator concentrations and the short irradiation times used to limit conversion, it is unlikely that uniform degrees of conversion were achieved throughout the specimens. Thus, the NIR approach, which allows analysis of bulk specimens in transmission mode, provides an overall conversion representing the extent of cure averaged throughout the entire specimen thickness.

In a previous study that validated the newly developed NIR technique for measuring the conversion in cross-linked Bis-GMA/TEGDMA resins, it was determined that use of the aromatic band at 4623 cm^{-1} as an internal reference was not uniformly applicable for all resin compositions containing

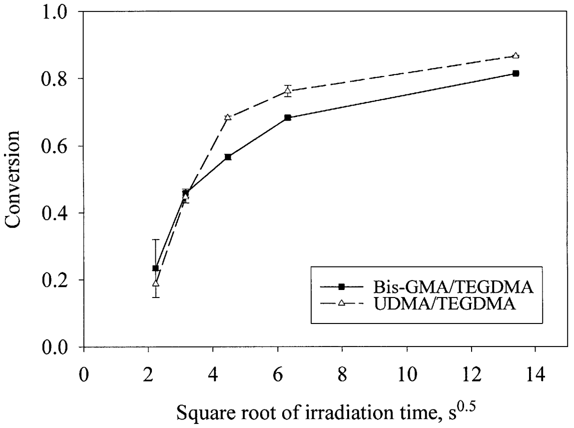

Fig. 3. Resin conversion as a function of irradiation time.

an aromatic moiety due to cure-related changes in adjacent absorptions as conversion progressed [25]. Therefore, use of the aromatic and urethane internal reference peaks were verified for the Bis-GMA and UDMA resins, respectively, by the comparison of a range of conversion measurements obtained with the internal reference approach with those calculated directly from the disappearance of the 6164 cm^{-1} absorption normalized to specimen thickness. Over the range of conversion from approximately 40% to 75%, obtained with five different irradiation intervals, the differences in the conversion values measured by the two techniques were 1.2 ± 0.7% (mean and standard deviation) for the Bis-GMA/TEGDMA resin and 0.7 ± 0.7% for the UDMA/TEGDMA resin. These results demonstrate that conversion in both of these resin systems can be appropriately determined with the internal reference method.

The 10-day incubation interval under vacuum prior to measuring the pre-immersion specimen mass was designed primarily to allow removal of adventitious water present in the polymers that would complicate the determination of the sol/gel fractions. Due to the low volatilities of the monomers involved, it is assumed that the residual free monomer composition is unaffected by exposure to the modest house vacuum (approximately 8 kPa). This storage interval also allows for completion of the post-cure process so that stable levels of conversion are achieved. Yet, it is expected that free radicals remain in some of the polymer specimens, even after this post-cure period. In contrast to the relatively rapid decay of free radicals expected for loosely cross-linked networks formed at low conversion, the highly cross-linked, fully cured polymers yield trapped radicals that can persist on extremely long time scales [27]. Thus, a trace amount of radical inhibitor was included in the initial extraction step to avoid additional conversion that could accompany the increase in mobility associated with the solvent-swollen network.

A more comprehensive view of the photopolymerization kinetics of the two resins is given by the DPC analysis in Fig. 4. While the static IR-based conversion measurements do not indicate differences at the initial stages of polymerization, the dynamic DPC results consistently show the Bis-GMA-based resin to be more reactive up to conversions of approximately 10% [28]. This is probably due to the higher initial viscosity of the Bis-GMA-based resin, which allows autoacceleration from the onset of the polymerization [3,4]. However, the UDMA/TEGDMA resin reaches a higher maximum rate of polymerization and the rate maximum occurs at a later stage of conversion than in the Bis-GMA resin. In addition, the limiting conversion achieved with the UDMA/TEGDMA resin is greater than that for the Bis-GMA/TEGDMA resin. The higher level of conversion at the rate maximum and the higher final conversion for the UDMA-based resin are consistent with the lower overall monomeric glass transition temperature (T_g) and viscosity of the uncured resin compared with that of the Bis-GMA/TEGDMA resin. The calculated monomeric T_gs of the two resins, based on the additive T_gs of the individual comonomers [29], are shown in Table 1. Values for monomeric T_g of Bis-GMA and TEGDMA were taken from a prior study [15], whereas the corresponding value for UDMA (−41.7 ± 0.5°C) was determined in this study from differential scanning calorimeter cooling runs at 5°C min^{-1}. Since the T_gs of the vitrified polymers are limited by the cure temperature, to a first approximation, the resin with the lower initial T_g, which corresponds with enhanced mobility, can be expected to attain higher levels of conversion. Table 1 also provides a comparison of viscosities at near-ambient conditions, which reflects the dramatic differences in mobility that exist between the various individual monomers and the two resin systems.

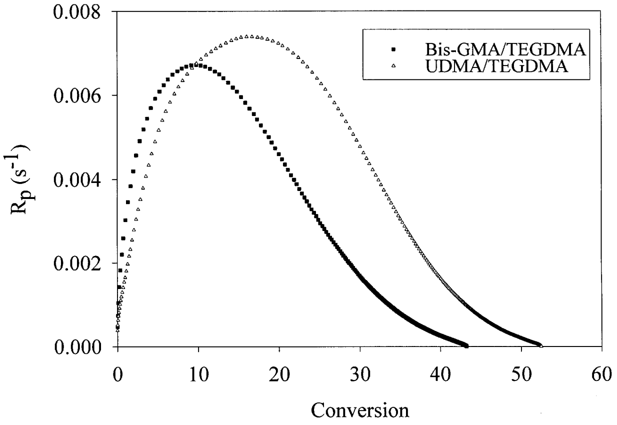

Fig. 4. Photopolymerization kinetics data for equimolar resins analyzed by photo-differential calorimetry where R_p is the rate of polymerization normalized by the initial double bond concentration in the resin.

The ^{1}H NMR spectra of the sol fractions extracted from the Bis-GMA/TEGDMA photocured polymers were analyzed to verify the lack of resonance signals in the saturated aliphatic region (<1.5 ppm). This indicates that no appreciable quantities of soluble oligomeric species were present in the extracts even at relatively low conversion levels. Therefore, over the ranges of conversion reported here, all conversion can be accounted for by changes that occur within the gel. Conversion in cross-linking networks occurs through two mechanisms: free monomer addition to the existing polymer, which increases the gel fraction, and pendant groups engaged in cross-linking, which does not

Table 1
Characterization of uncured monomers and resin compositions

Sample	Monomeric T_g (°C)	Viscosity (Pa s)[a]
TEGDMA	−81.7[b]	0.05
UDMA	−41.7	28.2
Bis-GMA	−6.6[b]	1367.8
UDMA/TEGDMA[c]	−58.6	1.06
Bis-GMA/TEGDMA[c]	−39.4	8.32

[a] Measured at 30°C and 1 Hz with an estimated relative uncertainty of <5%.
[b] Ref. [15].
[c] Equimolar comonomer mixture.

add to the gel fraction. It is evident that as polymerization proceeds and monomer becomes depleted, contributions to conversion from free monomer addition will necessarily decline. Conversely, it can also be expected that as cross-link densities increase in the developing network, the mobility of residual pendant groups available to engage in additional cross-linking will decrease more rapidly than the mobility of remaining free monomer. As Fig. 5 demonstrates, both resins undergo network development with a progressively increasing contribution arising from cross-linking. However, even approaching vitrification, the incorporation of free monomer into the polymer remains the major component driving overall conversion. The solid curve in Fig. 5 represents the predicted gelation model based on the equation:

$$\text{gel fraction} = 1 - (1 - \alpha)^2; \text{ where } \alpha = \text{conversion}$$

There is excellent correlation between the experimental gel fraction results and the prediction by simple gelation theory [30]. Under the curing conditions used here, it is apparent that the UDMA/TEGDMA resin reaches a nearly quantitative and considerably higher gel fraction compared with the Bis-GMA-based material.

With knowledge of both the magnitude and the composition of the sol fraction, the conversion and composition within the gel fraction can be calculated by difference. Thus, as shown in Fig. 6, both resins produce networks in which the gel conversion increase is linear with the overall conversion. Since the gel conversion is directly related to cross-linking within the gel, it is evident that both resins experience similar degrees of cross-linking as a function of conversion, even though the Bis-GMA monomer is considerably more rigid than UDMA.

From the compositional analyses of the extraction residues, the relative reactivities of the comonomers were found to vary significantly with conversion (Fig. 7). Over the range of conversions observed here, the bulkier base monomers are clearly less reactive than TEGDMA throughout the polymerization. At low conversions, the UDMA appears to be nearly comparable in reactivity to the TEGDMA; whereas, the Bis-GMA is significantly enriched in the sol fraction indicating a depressed reactivity compared with TEGDMA. At moderate conversions in both resins, base monomer was found in slight excess over TEGDMA in the sol fractions. As the limiting conversions are approached in the cross-linked networks, the proportion of the base monomer in the sol rises dramatically. In several cases, the composition of the sol was determined separately for each of the two sequential extraction steps. The proportion of the base monomer extracted in the second extraction step was always found to be greater than that obtained in the initial

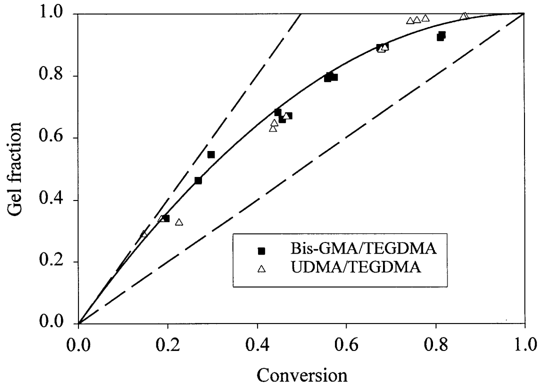

Fig. 5. The development of the gel fraction with overall conversion. The upper dashed line represents the limiting condition where free monomer incorporation is much greater than the cross-linking reaction of pendant groups. The lower dashed line shows equivalent contributions from free monomer addition and pendant group cross-linking in network formation. The solid curve represents the theoretical gelation profile (residual standard deviation = 0.027).

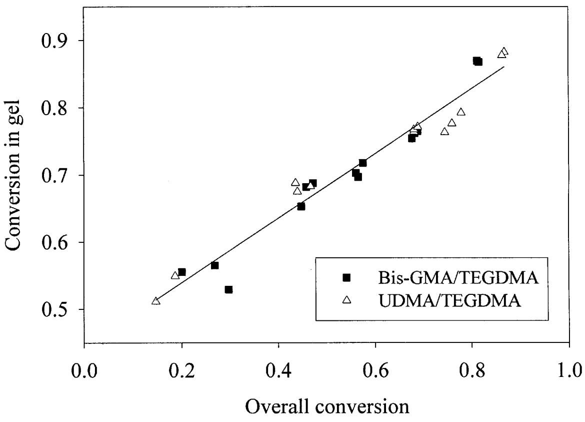

Fig. 6. Conversion in the gel as a function of overall conversion (residual standard deviation = 0.0324).

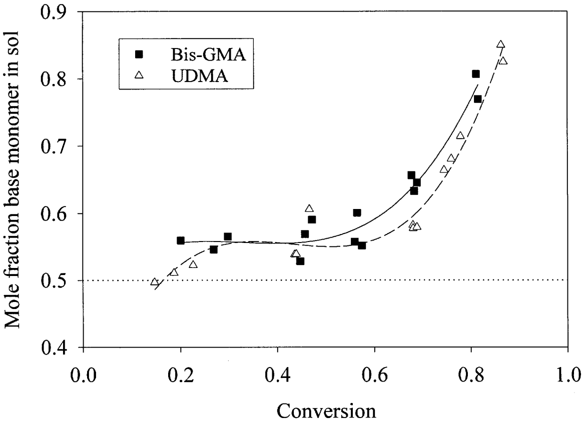

Fig. 7. Composition of the sol fraction as a function of overall conversion. Dotted line represents equivalent reactivities between base monomers and TEGDMA. The residual standard deviations are 0.023 for the Bis-GMA/TEGDMA resin and 0.025 for the UDMA/TEGDMA resin.

Table 2
Analysis of photocured Bis-GMA/TEGDMA resins (0.566:0.434 mole ratio)

Irradiation time (s)	Conversion[a]	Mole fraction Bis-GMA in sol fraction[b]	
		NIR[c]	NMR[d]
5	0.431 ± 0.015	0.614 ± 0.029	0.632 ± 0.017
10	0.541 ± 0.002	0.664 ± 0.050	0.663 ± 0.012
30	0.677 ± 0.004	0.681 ± 0.059	0.692 ± 0.028

[a] Conversion determined by NIR as previously described.

[b] Specimens cured in the Triad 2000 curing unit, stored in the dark at room temperature for 48 h and extracted in dichloromethane.

[c] Monomer composition determined as described previously.

[d] Monomer composition determined from the integrated ratio of the bisphenol A methyl peak to methacrylate methyl peak. Throughout table, ± refers to standard deviation, although sample size was only two.

extraction. This indicates a difference in the solvent-mediated diffusion of the base monomers compared with the smaller TEGDMA diluent comonomer. This disparity in diffusion is likely enhanced further in the unswollen networks. As the polymerization proceeds and the gel fraction rises, there is a progressively diminishing impact of the remaining free monomer composition on the overall gel composition. Therefore, in spite of the large predominance of TEGDMA incorporation in the final stages of network development, this has a relatively small effect on the final gel composition.

While compositional analysis based on the FT-IR spectra of the extraction residues was used in this study, an alternate ^{1}H NMR analytical method was also evaluated. In a pilot study with a resin composed of Bis-GMA/TEGDMA (0.566:0.434 mole ratio) and a photoinitiator system of CQ (mass fraction of 0.2%) and EDMAB (mass fraction of 0.8%), the ratio of the integrated peak areas of the respective methyl resonances arising from the bisphenol A core (at 1.62 ppm) and the methacrylate groups (at 1.94 ppm) was used to determine composition based on an NMR-based standard curve ($r^2 = 0.998$ for Bis-GMA/TEGDMA resin compositions over a similar range as reported in Fig. 2). The comparative analytical results obtained by IR and NMR for this preliminary study are shown in Table 2. The excellent agreement obtained between the two techniques as well as the demonstration of the same trends observed in the subsequent studies with equimolar Bis-GMA/TEGDMA and UDMA/TEGDMA resins further confirms the compositional drift results reported here.

4. Conclusions

It is suggested that the observed similarities between the two structurally different resin systems with respect to gel theory and compositional drift indicate a generalized behavior governed by the higher reactivity of the more mobile diluent monomer when it is combined with a bulkier, more viscous base monomer.

5. Disclaimer

Certain commercial materials and equipment are identified in this paper for adequate definition of the experimental procedure. In no instance does such identification imply recommendation or endorsement by the American Dental Association Health Foundation, or that the material or equipment is necessarily the best available for the purpose.

Acknowledgements

The authors are grateful to Esstech for the generous donation of the monomers employed in this study. This investigation was supported by NIDCR-NIST Interagency agreement no. Y1DE70060 and NIDCR grant no. DE09322.

References

[1] Patel MP, Braden M, Davy KWM. Biomaterials 1987;8:53–6.
[2] Bogdal D, Pielichowski J, Boron A. J Appl Polym Sci 1997;66:2333–7.
[3] Reed BB, Choi KM, Dickens SH, Stansbury JW. Am Chem Soc, Polym Prepr 1997;32(2):108–9.
[4] Lovell LG, Stansbury JW, Syrpes DC, Bowman CN. Macromolecules 1999;32:3913–21.
[5] Taylor DF, Kalachandra S, Sankarapandian M, McGrath JE. Biomaterials 1998;19:197–204.
[6] Sankarapandian V, Xu Q, McGrath JE, Taylor DF, Kalachandra S. J Adv Mater 1996;28:59–63.
[7] Kalachandra S, Taylor DF, DePorter CD, Grubbs HJ, McGrath JE. Polymer 1993;34:778–82.
[8] Ferracane JL, Greener EH. J Biomed Mater Res 1986;20:121–31.
[9] Dermann K, Rupp NW, Brauer GM. J Dent Res 1982;61:1250–4.
[10] Indrani DJ, Cook WD, Televantos F, Tyas MJ, Harcourt JK. Dent Mater 1995;11:201–7.
[11] Venhoven BAM, DeGee AJ, Davidson CL. Biomaterials 1993;14:871–5.
[12] Anseth KS, Goodner MD, Reil MA, Kannurpatti AR, Newman SM, Bowman CN. J Dent Res 1996;75:1607–12.
[13] Cook WD, Simon GP, Burchill PJ, Lau M, Fitch TJ. J Appl Polym Sci 1997;64:769–81.
[14] Lovell LG, Newman SM, Bowman CN. J Dent Res 1999;78:1469–76.
[15] Shobha HK, Sankarapandian M, Sun Y, Kalachandra S, McGrath JE, Taylor DF. J Mater Sci: Mater Med 1997;8:583–6.
[16] Kannurpatti AR, Anseth JW, Bowman CN. Polymer 1998;39:2507–13.
[17] Sakaguchi RL, Peters MCRB, Nelson SR, Douglas WH, Poort HW. J Dent 1992;20:178–82.
[18] Ruyter IE, Øysaed H. J Biomed Mater Res 1982;16:741–54.
[19] Hansel C, Leyhausen G, Mai UEH, Geurtsen W. J Dent Res 1998;77:60–7.
[20] Tanaka K, Taira M, Shintani H, Wakasa K, Yamaki M. J Oral Rehabil 1991;18:353–62.
[21] Ferracane JL, Condon JR. Dent Mater 1992;8:290–5.
[22] Ferracane JL, Mitchem JC. Dent Mater 1994;10:92–9.
[23] Cook WD. J Appl Polym Sci 1991;42:1259–69.

[24] Tarumi H, Imazato S, Ehara A, Kato S, Ebi N, Ebisu S. Dent Mater 1999;15:238–42.

[25] Stansbury JW, Dickens SH. Dent Mater 2001;17:71–7.

[26] Horie K, Mita I, Kambe H. J Polym Sci: Part A-1 1968;6:2663–76.

[27] Burtscher P. Dent Mater 1993;9:218–21.

[28] Dickens SH., Stansbury JW., Choi KM., Floyd CEJ., in preparation.

[29] Fox TG. Bull Am Phys Soc 1956;1:123.

[30] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953.