Photopolymerization Kinetics of Methacrylate Dental Resins

S. H. Dickens,* J. W. Stansbury,[†] K. M. Choi,[‡] and C. J. E. Floyd

American Dental Association Foundation, Paffenbarger Research Center,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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ABSTRACT: The photopolymerization kinetics of typical dental dimethacrylate monomers were studied by differential photocalorimetry. Increasing proportions of the low-viscosity diluent monomer triethylene glycol dimethacrylate (TEGDMA) were added to either Bis-GMA (2,2-bis[*p*-(2′-hydroxy-3′-methacryloxypropoxy)phenylene]propane), EBADMA (ethoxylated bisphenol A dimethacrylate), or UDMA (1,6-bis-(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane) to provide three base resins that differed in their hydrogen-bonding potential and, therefore, resulted in compositions covering a broad range of viscosities. When compared at similar diluent concentrations, UDMA resins were significantly more reactive than Bis-GMA and EBADMA resins. At higher diluent concentrations, EBADMA resins provided the lowest photopolymerization reactivities. Optimum reactivities in the UDMA and EBADMA resin systems were obtained with the addition of relatively small amounts of TEGDMA, whereas the Bis-GMA/TEGDMA resin system required near equivalent mole ratios for highest reactivity. The hydrogen-bonding interactions, which substantially influence the Bis-GMA and UDMA resin series, were examined by Fourier transform infrared spectroscopy and resin viscosity. Synergistic effects of base and diluent monomer on the polymerization rate and the final conversion were found for the two base resins having hydrogen-bonding interactions. The structures of the individual monomers and, consequently, the resin viscosities of the comonomer mixtures strongly influence both the rate and the extent of conversion of the photopolymerization process.

Introduction

Among a wide variety of applications, mono- and multimethacrylates are employed in preventive and restorative dentistry using thermal and ambient photocuring techniques to control the properties of pit and fissure sealants, adhesives, veneer materials, and esthetic or load-bearing composite restoratives. While some efforts are underway to develop photocurable resins from a single monomer, typically, dental resins are composed of mixtures of two or more monomers that combine a relatively viscous dimethacrylate base monomer such as 2,2-bis[*p*-(2′-hydroxy-3′-methacryloxypropoxy)phenylene]propane (Bis-GMA) with a low-viscosity dimethacrylate comonomer such as triethylene glycol dimethacrylate (TEGDMA).[1] Aside from considerations of the physical and mechanical properties of the final polymers, one of the main factors in the selection of the comonomer proportions is the initial resin viscosity, which dictates the handling properties of the resulting dental materials. While a reasonable understanding exists as to how variations in the monomeric structure and the comonomer ratio affect the initial resin viscosity, few systematic studies have explored how these factors combine to control the photopolymerization kinetics of multifunctional (meth)acrylate resins.[2−5]

A recent article has reviewed the mechanism and kinetics of radical-initiated polymerization with special emphasis on the correlation of kinetics with conformational properties and other parameters, i.e., choice of initiators, inhibitors, initiation source (light or radiation), and intensity, which influence the rate and course of the three-dimensional radical polymerization.[6] Several other studies examined the curing kinetics and the effects of comonomer compositions in UV-light-activated dimethacrylate dental resins.[3,7,8] While these studies were conducted at much lower light intensities (on the order of 0.8−3 mW/cm^2) than commonly employed when dental curing lights are used (450−1600 mW/cm^2), they provide valuable information about the reaction kinetics and interactions of the comonomers. Comparison of the conversion for a series of resin compositions of Bis-GMA and TEGDMA obtained by photo-DSC at 0.1 mW/cm^2 or by near-infrared spectroscopy using a dental curing light (450 mW/cm^2)[9] showed that the relative conversion rankings for the resin compositions analyzed by the different methods were consistent; however, the resins polymerized with the higher intensity dental curing light were offset by approximately 30% higher conversion due to the greater energy input and the larger specimen geometry used for NIR.

Other studies have focused on the influence of the initiator concentration, light intensity, and temperature on the cure properties of dimethacrylate homopolymerizations and copolymerizations of unfilled resins in the visible range of the spectrum.[10−14] When cured at ambient temperature, visible-light-initiated free radicals from the camphorquinone/tertiary amine initiator system rapidly convert the resin to a cross-linked three-dimensional polymer network with methacrylate conversions ranging from about 50% to 75%, depending on the resin composition.[10−16]

The rapid and efficient photopolymerization of dental resins with minimal light exposure is a critical aspect of the clinical use of dental adhesives, composites, and sealants. Moreover, optimized cure is one of the most

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[†] National Institute of Standards and Technology. Now University of Colorado Health Sciences Center, P.O. Box 6508/Campus Box F436, Aurora, CO 80045-0508.

[‡] Current address: Bell Laboratory, Lucent Technologies, Murray Hill, NJ 07974.

* To whom inquiries should be sent. E-mail: sabine.dickens@nist.gov.

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crucial parameters that governs the long-term performance of the polymeric material, affecting mechanical properties, i.e., fracture toughness,[17,18] elastic moduli, flexural strength, and hardness,[18] or the biocompatibility when potentially cytotoxic materials leach from the cured polymers.[19,20] In this study we compared the visible-light-initiated photopolymerization kinetics of three resin series formed by incremental additions of the low-viscosity diluent comonomer TEGDMA to the high-viscosity base monomers Bis-GMA, ethoxylated bisphenol A dimethacrylate (EBADMA), and 1,6-bis-(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA). The base resins used are among those most commonly employed in commercial dental resin-based materials. They are incorporated into dental polymers to enhance the modulus of the cured polymer and to minimize polymerization shrinkage by virtue of their relatively low methacrylate double-bond concentrations.[21,22] The objective of this study was to ascertain how the low-viscosity diluent monomer affects the diffusion-controlled parameters, e.g., the autoacceleration, autodeceleration, and the rate and extent of polymerization of polymers cured at near-oral temperature. The hypothesis is that differences in the structures of the base monomers and TEGDMA and their comonomer compositions will, in complex interactions between intrinsic viscosity and polymerization kinetics, determine the respective cure profiles and network formation in nonlinear dependencies. The results of this study will aid in the identification of factors that govern the structure/property relationship with respect to comonomer composition, polymerization reactivity, and conversion efficiency.

Materials and Methods[44]

Since it was suggested that chromatographic column purification did not affect the curing behavior,[12] the dimethacrylate monomers EBADMA, Bis-GMA, UDMA, and TEGDMA (Figure 1) were used as received (all monomers: Esstech, Essington, PA). In three separate series, resins 1−9 were formulated by adding the diluent monomer TEGDMA to either EBADMA, Bis-GMA, or UDMA in mole fractions of 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, and 0.875 providing resins E1 to E9, B1 to B9, and U1 to U9, respectively. Fixed photoinitiator concentrations of camphorquinone (CQ, mole fraction of 0.6%) and ethyl 4-(dimethylamino)benzoate (EDMAB, mole fraction of 2.0%) were dissolved in each of the individual monomers.

Monomeric glass transition temperatures (T_g) of the resin formulations were determined in duplicate by DSC at a heating rate of 10 °C/min.

Fourier transform infrared spectra (Nicolet Magna 550, Nicolet Inc., Madison, WI) in the fundamental region (mid-IR) of the Bis-GMA/TEGDMA and UDMA/TEGDMA resins were obtained in transmission from thin films of the unpolymerized resins between potassium bromide plates or in the near-infrared (NIR) region from 2 mm thick resin samples between glass slides.

Dynamic viscosities of the monomers EBADMA, Bis-GMA, UDMA, and TEGDMA as well as the entire range of the TEGDMA-diluted comonomer mixtures, without any added photoinitiators, were measured with a rheometer (Rheometric Scientific SR5000, Piscataway, NJ) in parallel plate shear mode. The viscosities reported for the various resins were obtained at a shear rate of 1 Hz at 30 °C.

Nonreactive hydrogenated analogues of Bis-GMA and TEGDMA were prepared by the catalytic reduction of the double-bond unsaturation with palladium on carbon (mass fraction of 2% with respect to carbon support) in ethyl acetate. The catalyst was used at a mass fraction of 5% based on the monomer. The complete hydrogenation of the methacrylate C=C bonds was verified by ^{1}H NMR and FT-IR spectroscopic analyses.

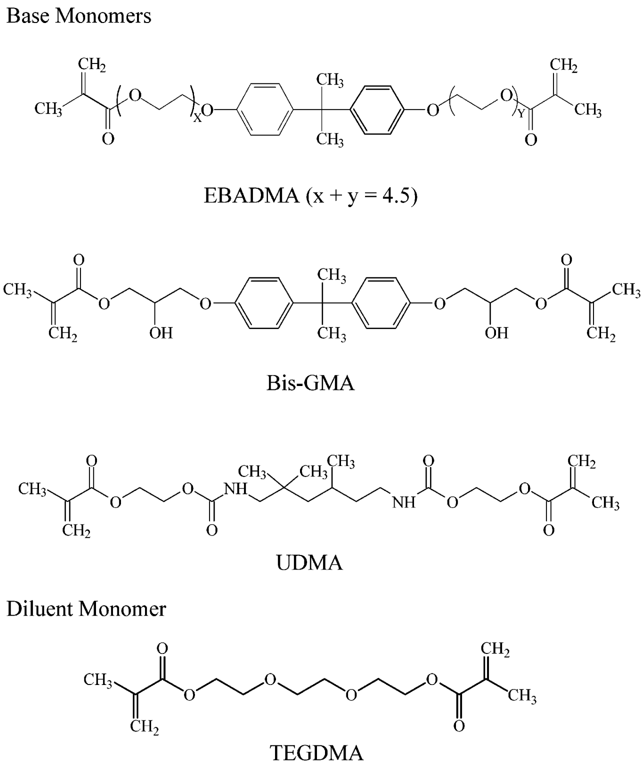

Figure 1. Structures of monomers used.

Table 1. Characterization of Dimethacrylate Monomers

monomer	molecular mass	T_g (K)	viscosity (Pa s)[a]	density (g/mL)[b]	C=C separation (Å)[c]
Bis-GMA	512	263	1369	1.140	15.8
EBADMA[d]	562	231	3	1.121	16.3
UDMA	471	235	28	1.129	25.1
TEGDMA	286	188	0.05	1.073	15.4

[a] Determined at 30 °C and 1 Hz. [b] Taken from manufacturer's literature. [c] Modeled through-space intramolecular distance between methacrylate α-carbons of energy-minimized conformations. [d] Determined from the integrated ^{1}H NMR spectrum.

Photopolymerization studies of the dimethacrylate resins were conducted with a differential scanning photocalorimeter (DSC; TA Instruments 2920 DSC, New Castle, DE) equipped with a 150 W xenon light source. The wavelength and intensity of the irradiation were controlled with band-pass and neutral density filters to 470 ± 5 nm (standard deviation as a measure of standard uncertainty) and 100 ± 5 μW/cm^2, respectively. The power density at the specimen surface was controlled by a carbon disk technique and monitored with a radiometer. All DSC photopolymerization experiments were conducted in duplicate under a nitrogen atmosphere (with a 6 min purge interval prior to irradiation) at 28 °C on sample sizes that ranged between 2 and 4 mg. The DSC was calibrated with an indium melting standard.

Results and Discussion

Discussion of Technique and Methods. The monomers (Figure 1) used to prepare the resin formulations for this study vary in size, shape, and physical properties, as indicated in Table 1. The effect of monomer structure of the base monomers and the influence of TEGDMA dilution on the monomeric T_g and the ultimate viscosities of the resin mixtures are demonstrated in Figures 2 and 3, respectively. The DSC thermograms of the base resins and of TEGDMA are shown in Figure

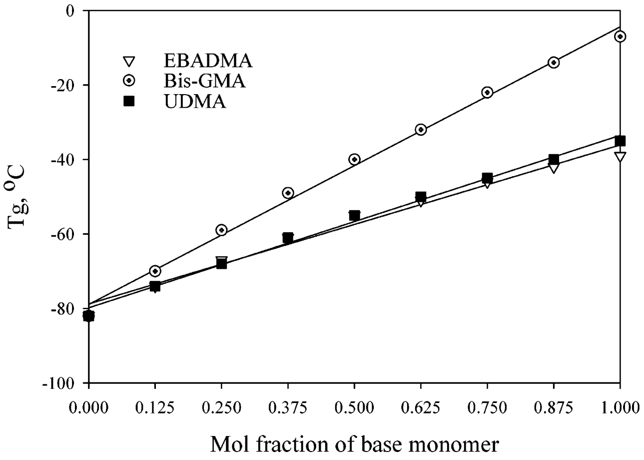

Figure 2. Monomeric glass transition temperatures (T_g) of resin mixtures. The error of the estimate of the linear regression lines for the EBADMA, Bis-GMA, and the UDMA series are 2, 2, and 1 °C, respectively.

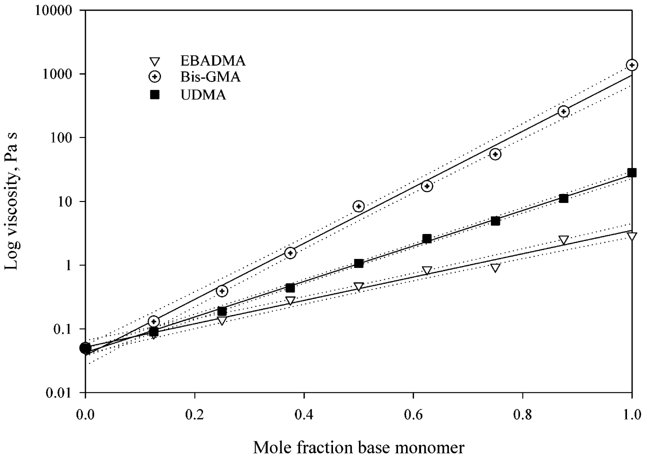

Figure 3. Log viscosity of mixtures of EBADMA, Bis-GMA, and UDMA with TEGDMA with linear regression and 95% confidence intervals ($R^2 = 0.987$, 0.995 and 0.998, respectively).

4a. The normalized measured heat flow (W/g) then allowed calculating the polymerization rate.

$$R_p\ (\text{mol L}^{-1}\ \text{s}^{-1}) = -\text{d}[\text{M}]/\text{d}t = \text{heat flow (W/g)} \times \rho\ (\text{g/L})/\Delta H_p\ (\text{J/mol}) \quad (1)$$

where R_p = rate of polymerization; [M] = methacrylate concentration, mol/L; ΔH_p = heat of polymerization; and ρ = resin density. The polymerization kinetics profiles from homopolymerizations of the four monomers studied show R_p as a function of the conversion of double bonds (Figure 4b).

Several assumptions are made in the application of eq 1 to the comonomer resin systems examined here. First, the theoretical heat of polymerization of the various resin formulations is calculated from the generally accepted heat of polymerization for methacrylates of 54.8 kJ/mol (13.1 kcal/mol).[23] In addition, the densities of the resins in each series were not measured, but rather were estimated on the basis of the additive proportions of the individual monomers. Comparing the estimated densities for Bis-GMA/TEGDMA resins ranging from 1140 to 1073 g/L to measured values[24] demonstrated a good linear fit (correlation coefficient r = 0.988; the residual standard deviation to the fitted line as a measure of uncertainty is 4 g/L), suggesting that this additive principle is valid. With the exception of TEGDMA, which was run in triplicate, the DSC data are based on back-to-back duplicate runs. The resin series involving the hydrogenated resins are based on single runs, which seemed acceptable as it was confirmed that back-to-back runs were very reproducible with a maximum deviation in the normalized polymerization rates from the averaged runs of ±0.0001 s^{-1}.

The series of EBADMA, Bis-GMA, and UDMA resins containing TEGDMA as diluent comonomer were photopolymerized in the DSC at relatively low light intensity not only to ensure linear thermal response but also to highlight the differences between the various materials. At higher irradiation intensities, typical of commercial dental curing units (450−1600 mW/cm^2), it was expected that the lag in instrument response would obscure differences between monomer compositions, and therefore, distinctions due to structural and compositional effects would be more difficult to discern. Under the controlled polymerization conditions applied here, with reactions occurring over minutes rather than seconds, the DSC response is adequate to follow the exothermic polymerizations and allow direct comparison of the various resin systems.

Rate/Conversion Profiles. The DSC cure profiles are characterized by a number of important parameters, e.g., the maximum rate of polymerization ($R_{p,\max}$), the time to and the conversion at $R_{p,\max}$, and the extent of conversion. The rate/conversion curves of TEGDMA (resin 1, Figure 5) showed an initial rapid increase in rate followed by a sharp break at very low conversion that leads to a broad rate maximum at approximately 20% conversion, leading ultimately to a conversion of about 34%. Compared to some other polymerization studies,[7,12,25] which report conversion values of about 65%, the relatively low conversion found in this study is likely due to the use of the very low light intensity, the narrow bandwidth, and use of visible light irradiation. The presence of impurities in TEGDMA and/or somewhat higher concentration of inhibitor are other possible factors, which may have had a greater impact due to the low light intensity. However, as already mentioned, a well-correlated trend between conversion data obtained with a dental light to the results presented here[9] supports the notion that the low level of light intensity, chosen to allow sufficient time for the DSC response, still provides for reasonable, valuable data for comparison with a given set of conditions.

The bimodal profile seen in TEGDMA resin is also evident in resins E2 through E5 (Figure 5a), resins B2 and B3 (Figure 5b), and resins U2 and U3 (Figure 5c) and is characterized by the initial break point occurring at higher rates and higher conversions as the base monomer content in the resins is increased. This pattern is limited to low-viscosity resin formulations with relatively high content of TEGDMA. While all dimethacrylate resins have an initial high rate of polymerization, only resins with a low initial viscosity demonstrate the bimodal profile due to a delayed onset of diffusion limitation and autoacceleration. The appearance of such bimodal profiles in TEGDMA and in resin mixtures with low initial viscosity could suggest that, compared with resins predominantly composed of base monomers, these resins rich in TEGDMA initially react more extensively through primary cyclization reactions rather than effective cross-links. The latter has been demonstrated by modeling Bis-GMA/TEGDMA curing kinetics, where

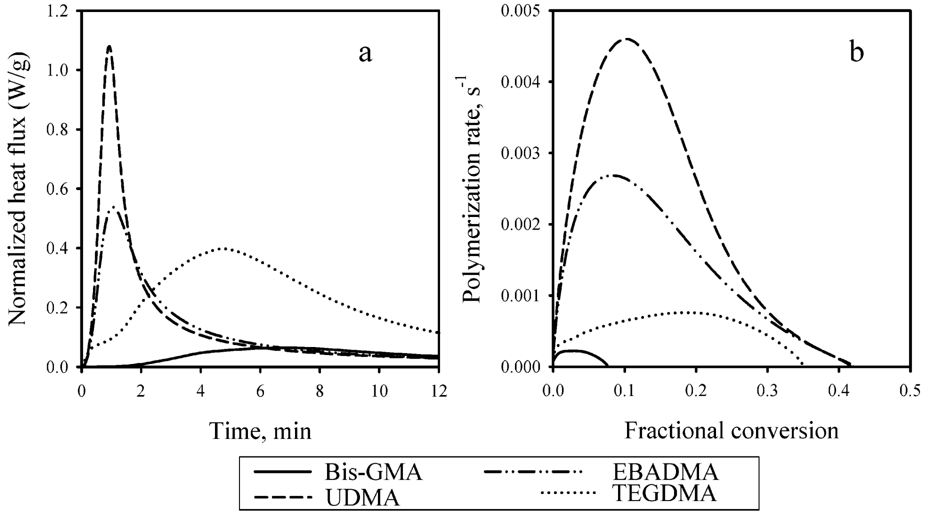

Figure 4. Thermograms (a) and rate/conversion profiles (b) of the DSC homopolymerizations of the three base resins and the diluent monomer TEGDMA (light intensity: 100 μW/cm^2). The early onset of the autoacceleration is particularly noticeable for UDMA and EBADMA, while Bis-GMA and TEGDMA demonstrate a sluggish onset of the polymerization with very low conversion for Bis-GMA and low polymerization rates.

it was confirmed that TEGDMA forms approximately 3 times more primary cycles than Bis-GMA.[26] Similar bimodal rate results have been reported by Horie et al.[27] for methyl methacrylate/ethylene glycol dimethacrylate copolymerizations and were interpreted as being caused by microgel formation, while Bressers et al.[28] believed that the bimodal rate vs time curves reported by Horie et al. were due to monomer evaporation. In contrast, other authors did not observe this effect,[29] whereas Kloosterboer[30] attributed it to a change in reactivity of pendant methacrylate groups throughout the course of polymerization. While there appears to be a significant amount of controversy, which was discussed in greater detail by Cook,[12] he also observed the formation of double maxima during photopolymerization of a number of ethylene oxide dimethacrylates and provided reasonable evidence that these results were not artifacts. From a refined model he predicted the resin photopolymerization kinetics, which agreed reasonably well with the experimental data. The apparent shoulder was also explained using the model, suggesting that at very low conversion the model predicts the reaction to proceed already at a very fast rate and that the rate increases more slowly as the reaction continues due to a number of parameters, e.g., the initiation efficiency, which decreases constantly during the reaction, and the course of the propagation and termination constants.[12]

With more viscous systems, autoacceleration occurs at much lower conversions, resulting in a steady rise to the rate maximum rather than a stepped or bimodal rise. The onset of autoacceleration is influenced by the size and the mobility of the macroradicals. Thus, early on, the termination in resins with a low initial viscosity (TEGDMA and TEGDMA-rich mixtures) occurs through translation, i.e., the chain-length-dependent diffusion of a macroradical, and, as the viscosity increases, through segmental diffusion, which is the chain-length-independent segmental reorientation of macroradicals. At this point, which usually occurs near the maximum reaction rate when autoacceleration stops, the network is generally too stiff and dense to allow termination via diffusion, and thus termination occurs through chemical reaction; i.e., propagation of radicals attached to the polymer chain proceeds through reaction with double bonds.[8,25] As demonstrated for resins E1 to E5 (Figure 5a), these events, i.e., the onset of diffusion-controlled termination and the change to reaction−diffusion-controlled termination, move closer and closer and eventually merge in the more viscous resin systems, where reaction−diffusion-controlled termination dominates essentially from the beginning of polymerization.[2,8,31] As shown in Figure 6, the plot of $R_p^2/[M]$ vs conversion (where [M] is the concentration of remaining double bonds available for reaction) allows differentiation of the various stages in the termination and propagation reactions.[25] While the rates of both propagation and termination decrease dramatically over the course of the polymerization process, changes in the relative ratios of these rates are primarily responsible for the different overall polymerization rate profiles observed here. When the termination reaction becomes reaction−diffusion-controlled, the curve begins to plateau, indicating proportionality between the termination and propagation reactions (Figure 6a, resin 5 at about 3% conversion). If the curve continues to plateau, the propagation remains reaction controlled, whereas when it begins to decline (resins 8 and 9, Figure 6a), the propagation is diffusion-controlled.[25]

When the non-hydrogen-bonding EBADMA resin is used as base monomer (Figure 5a for the rate/conversion profiles and Figure 6a for the $R_p^2/[M]$ profiles), a steady increase in reactivity with increasing amounts of the base resin was observed, resulting for both maximum reaction rates and conversion in an additive type of behavior. In contrast, for the Bis-GMA-based resin series (Figures 5b and 6b), the highest reaction rate and conversion were observed for the equimolar mixture.

As both Bis-GMA and EBADMA resins contain the kinked and rigid bisphenol A core structure, it is suggested that this connecting-group rigidity is primarily responsible for limiting the extent of conversion prior to the rate maxima. Compared with the 2-hydroxypropyl groups connecting the bisphenol A core to the methacrylate groups in Bis-GMA, the longer and more flexible ethoxylated linkages in EBADMA and the lack of the hydrogen bonding allow a greater degree of mobility that extends beyond the point of maximum reaction rate. This would account for the higher overall

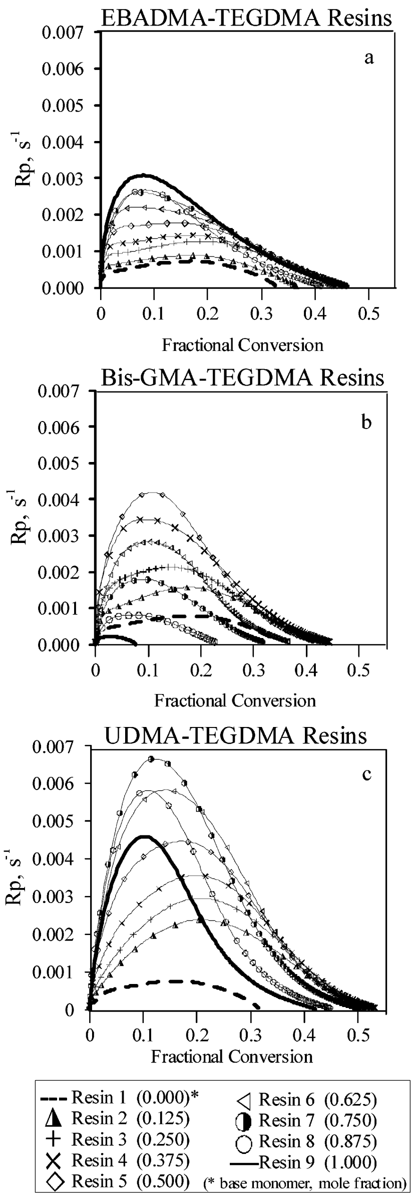

Figure 5. Rate of polymerization (R_p/s) as a function of fractional conversion for all resins in the EBADMA (a), Bis-GMA (b), and UDMA (c) resin series.

conversion observed for the EBADMA resins compared with those based primarily on Bis-GMA.

The R_p^2/[M]–conversion profile for the homopolymerization of Bis-GMA (Figure 6b), which contains both a very stiff center core (bisphenol A) and strong hydrogen bonding through its hydroxyl groups, indicates reaction–diffusion control of the termination at the very low conversion of about 2%–3%. In contrast, the equimolar mixture of Bis-GMA and TEGDMA displays a delay in the onset of the reaction–diffusion control of the termination, but also, owing to the fairly high initial viscosity of the mixture, an almost immediate beginning of diffusion control of the propagation and thus a rapid decline limiting the conversion to about 42%. TEGDMA shows the onset of the reaction–diffusion-controlled termination at the much higher conversion of about 20%, and because of its structural mobility, the R_p^2/[M]–conversion remains at the plateau until a rapid decline begins at about 30% conversion because of diffusion control of the propagation reaction. The TEGDMA-rich resin B2 has a very similar profile, but with improved reactivity reaching a much higher R_p^2/[M] level due to the addition of Bis-GMA and the increase in initial viscosity. The maximum reactivity in resins containing Bis-GMA occurs in the vicinity of the equimolar Bis-GMA/TEGDMA composition as has been reported for the acrylate analogue of Bis-GMA[4] and for Bis-GMA/TEGDMA mixtures.[8,13]

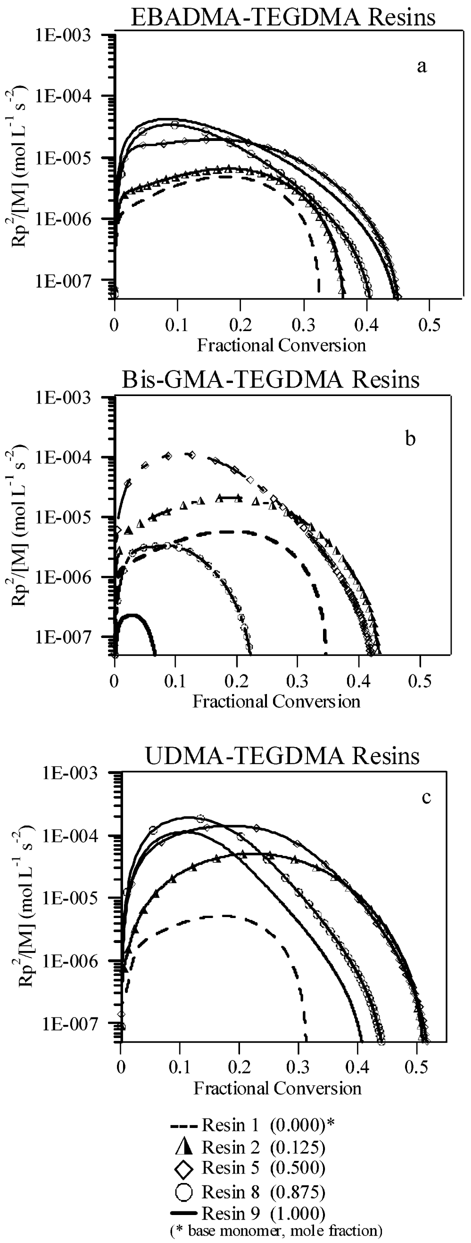

Figure 6. Rate of polymerization squared (R_p^2) divided by the methacrylate concentration [M] as a function of fractional conversion of resins 1, 2, 5, 8, and 9 in the EBADMA (a), Bis-GMA (b), and UDMA (c) resin series.

The UDMA-based resins (Figures 5c and 6c) show, analogous to the Bis-GMA-based resins, that the presence of only a small amount of UDMA (0.125 mole fraction) results in a tremendous increase in rate and, consequently, higher conversion. As seen from the R_p^2/[M] profiles (Figure 6c), the termination reaction becomes reaction–diffusion-controlled at about the same conversion as the Bis-GMA/TEGDMA resin at the same molar composition (resin 2). However, because of much higher flexibility of the UDMA molecule compared to that of the Bis-GMA molecule, the propagation proceeds

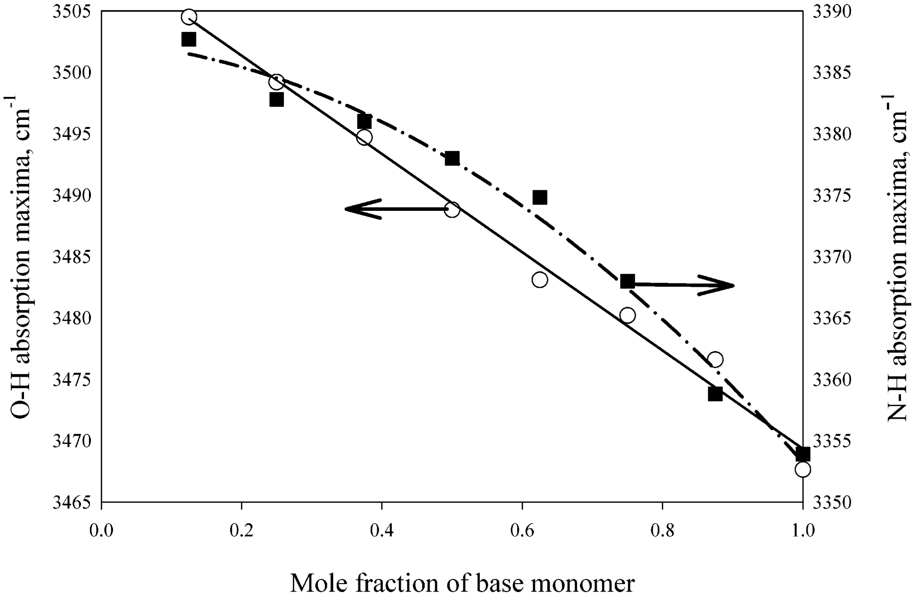

Figure 7. Shift of the O−H and N−H absoption maxima to lower wavenumbers of the resin mixtures with TEGDMA and Bis-GMA (open circles) or UDMA (filled squares), indicating an increase in the hydrogen-bonding activity with increasing amounts of the base monomers. The residual standard deviations to the fitted lines (as a measure of uncertainty) are 1 cm^{-1} for the Bis-GMA series and 3 cm^{-1} for UDMA series, respectively. (The arrows point toward the respective ordinates.)

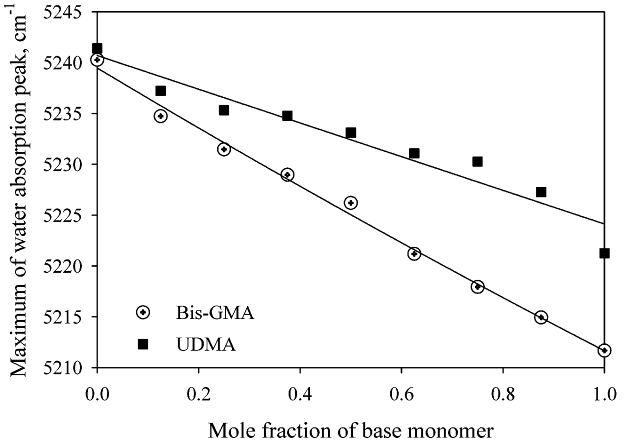

Figure 8. Shifts in the near-infrared position of the water absorption peak maxima (cm^{-1}) due to hydrogen-bonding activities of the O−H and N−H groups in Bis-GMA- and UDMA-based resins. The standard errors of the estimate as a measure of uncertainty are 1 and 2 cm^{-1} for the Bis-GMA- and UDMA-based resins, respectively.

further before it becomes diffusion-controlled, and thus a much higher conversion of about 53% is achieved in this formulation and throughout the entire UDMA series. For example, the most striking difference between Bis-GMA and UDMA occurs in the homopolymerization of these two base resins, in which UDMA reaches a conversion of 43%, in contrast to about 7% in the Bis-GMA polymer.

Hydrogen Bonding and Effects of the Initial Viscosity. To better understand the interaction between resin structures and reactivities, the hydrogen-bonding interactions in Bis-GMA and UDMA resin series were examined by analysis of the respective O−H and N−H absorption regions in the mid-IR (Figure 7) and in the NIR (Figure 8). The respective overlaid mid-IR O−H and N−H absorptions of Bis-GMA/TEGDMA and UDMA/TEGDMA resins demonstrate a clear transition to lower wavenumbers (longer wavelengths), and thus to greater hydrogen-bonding interactions, as the base monomer content in the resin is increased. For comparison, in dilute carbon tetrachloride solutions, the free, non-hydrogen-bonded absorptions of OH in Bis-GMA and NH in UDMA are found as sharp peaks at 3593 and 3461 cm^{-1}, respectively, along with broader hydrogen-bonded absorptions at lower wavenumbers. However, in the neat resins, only hydrogen-bonded OH and NH groups are observed. For both the Bis-GMA and the UDMA resin series, overlapping hydrogen-bonded absorptions are observed based on interactions with the different hydrogen-bond acceptors present. Generally O−H···O bonds are stronger than N−H···N bonds.[32] For Bis-GMA, weaker hydrogen bonds are formed between the OH group and methacrylate carbonyls ($O-H\cdots O=C_M$ at 3508 ± 3 cm^{-1}), while stronger hydrogen-bonding interactions arise between Bis-GMA hydroxyl groups (O−H···O−H at 3427 ± 4 cm^{-1}). In the UDMA-based resin series, NH hydrogen-bonded interactions can be differentiated into weaker associations with the methacrylate carbonyls ($N-H\cdots O=C_M$ at 3389 ± 3 cm^{-1}) and stronger bonds formed with the more electron-rich urethane carbonyls ($N-H\cdots O=C_U$ at 3336 ± 4 cm^{-1}). Deconvolution over this region of the IR spectra provides the relative contributions of each type of hydrogen-bonding interaction. However, the state of hydrogen bonding can also be displayed with the simple plot of the OH or NH absorption maxima as a function of resin composition. As shown in Figure 7, the shift toward the stronger O−H···O−H hydrogen bond is linear with Bis-GMA content. Molecular modeling studies (CAChe Group, version 4.4; Fujitsu America) indicate that the rigid aromatic core structure of Bis-GMA precludes intramolecular hydroxyl−hydroxyl interactions. The urethane $NH\cdots O=C_U$ hydrogen bonds vary as a nonlinear function of the UDMA concentration since a combination of intra- and intermolecular associations is possible with the more flexible aliphatic UDMA structure.

The extent of hydrogen bonding with increasing Bis-GMA or UDMA concentration is also indicated by a significant shift of the water peak (Figure 8) associated with trace amounts of moisture in the resins. The NIR water peak at about 5200 cm^{-1} in Bis-GMA resins shifts considerably more to lower wavenumbers with increasing hydrogen-bonding activity than that in the UDMA series, which indicates stronger hydrogen-bonding interactions in the Bis-GMA series.

Viscosity. The extremely high viscosity of Bis-GMA resin (note logarithmic scale in Figure 3) due to hydrogen bonding requires the addition of substantial amounts of TEGDMA as a reactive diluent to provide a mixture that has practical use as a dental composite matrix material. While the resin viscosity of UDMA is also influenced by hydrogen bonding, contributions from intramolecular hydrogen bonding may significantly decrease the viscosities of UDMA and its TEGDMA-diluted resins as well as affect its diffusion potential during polymerization compared with the Bis-GMA analogues. Typical Bis-GMA/TEGDMA resin compositions contain mass fractions of Bis-GMA in the range 50%−92%.[33,34] For comparison with the data presented here, this range corresponds to Bis-GMA mole fractions of 36%−86%, respectively. Higher diluent concentrations up to mass fractions of 61% may be required for sealants and adhesives.[35] Thus, the three series of resins studied not only provide a good practical representation of dental restorative materials but also give a very broad range of resin viscosities for examining resin reactivities. To evaluate these reactivities in more detail, the normalized maximum rate of polymerization and final conversion of each resin in the EBADMA, Bis-GMA, and UDMA series are shown as functions of resin composition and initial intrinsic viscosity in Figures 9 and 10, respectively.

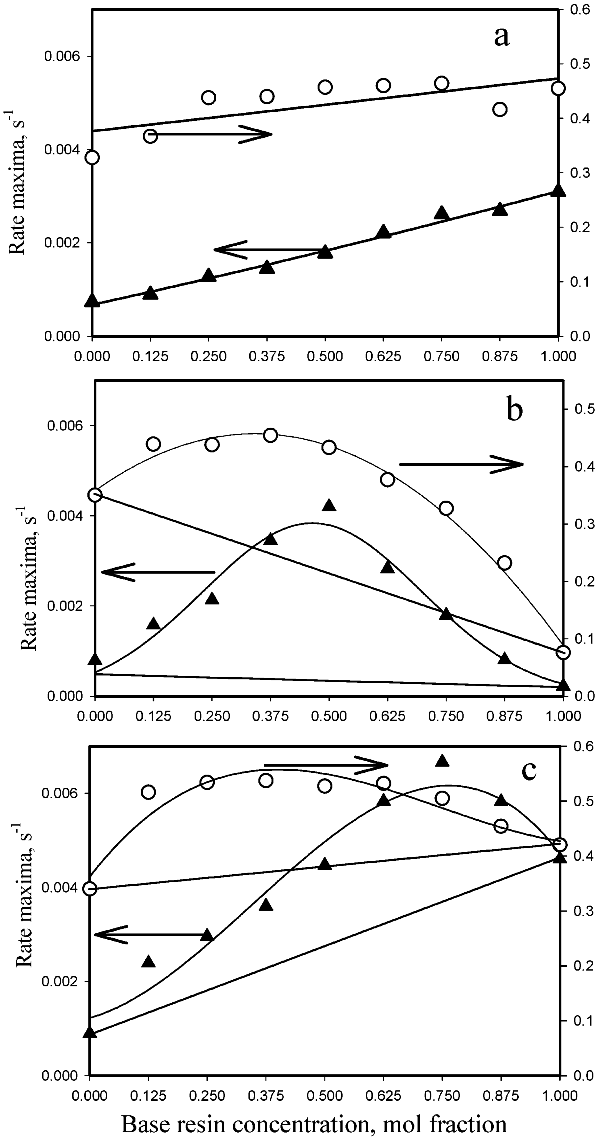

Figure 9. Rate maxima (triangles; left ordinate) and final conversion (circles; right ordinate) vs base resin concentration of the resin series based on EBADMA (a), Bis-GMA (b), and UDMA (c). The thick solid lines indicate the progression of reactivities if additive behavior had occurred. The arrows point toward the respective ordinates. The standard errors of the estimate as a measure of the uncertainty for the regression curves for rate maxima and fractional conversion are (a) 0.0001 s^{-1}, 0.04; (b) 0.0006 s^{-1}, 0.02; and (c) 0.0007 s^{-1}, 0.04, respectively.

The comparison of $R_{p,max}$ and conversion as a function of composition of the three resin series (Figure 9) shows that in EBADMA resins (Figure 9a) the reactivity rates increase monotonically along with the EBADMA content following an additive pattern. Although the conversion data in the EBADMA series show a slight deviation from the projected additive data, statistically no differences in the conversion of the individual resin mixtures was found (Kruskal−Wallis one-way analysis of variance on ranks, $p > 0.05$). In contrast, the Bis-GMA/TEGDMA and the UDMA/TEGDMA mixtures, which can hydrogen bond (Figure 9b,c), exhibit synergistic effects having both higher reaction rates and final conversion than expected from simple additive behavior. Contrary to the strong synergistic behavior in the Bis-GMA/TEGDMA series caused by the relatively low conversion of TEGDMA, which was obtained when using a narrow band filter and low light intensity, in various other studies monotonic trends in the conversion of similar data series have been reported. The higher conversion of TEGDMA in these studies was attributed to using medium[7,13] or high[16] light intensity, differing wavelengths,[7] and/or the absence of a wavelength narrowing band filter.[13,16] While for a given resin mixture an increase in light intensity leads to a corresponding increase in final conversion,[7,10,12] the increase is different for different monomers and/or resin compositions. Hence, TEGDMA when exposed to 0.1 mW/cm^2 (narrow band filter) achieved 34% conversion, while when exposed to 12 mW/cm^2 (no narrow band filter) reached 60% conversion. In contrast, the equimolar mixture of Bis-GMA and TEGDMA reached under similar conditions 43% and 53% conversion, respectively. A similar trend was observed for the conversion at maximum reaction rates (i.e., TEGDMA: 0.1 mW/cm^2 at 18% conversion; 12 mW/cm^2 at 27% conversion; equimolar Bis-GMA/TEGDMA mixture: 0.1 mW/cm^2 at 10% conversion; 12 mW/cm^2 at 9% conversion). Corroborating these findings, it has been reported that with increasing light intensity the conversion at maximum rate changed by nearly 20% for the low-viscosity tetraethylene glycol dimethacrylate and only a few percentages for ethoxylated bisphenol A dimethacrylate.[10,12] This effect was associated with the influence of initiation rate on radical chain length.

In contrast to the Bis-GMA/TEGDMA series (Figure 9b), the UDMA-rich resins produced the highest normalized $R_{p,max}$ and conversion observed in this study. It may be significant that there are certain structural similarities between UDMA and some ultrafast curing acrylate monomers that have been shown to provide

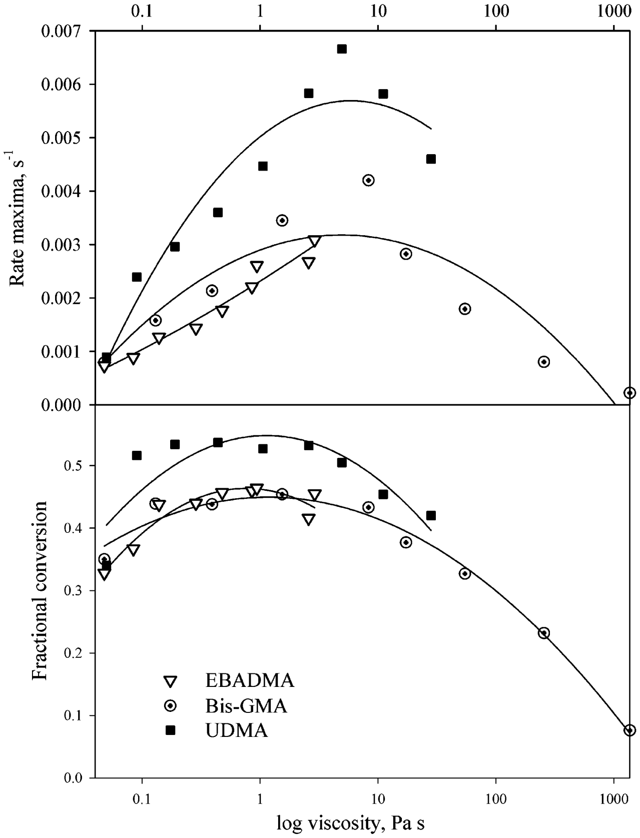

Figure 10. Rate maxima (a) and fractional conversion (b) vs the initial viscosity. The standard errors of the estimate as a measure of the uncertainty for the regression curves for rate maxima and conversion are for (EBADMA) 0.0002 s^{-1}, 0.04; (Bis-GMA) 0.001 s^{-1}, 0.04; and (UDMA) 0.001 s^{-1}, 0.07, respectively.

unusually rapid photopolymerization rates, which were attributed to a reduction in the termination rate constant process.[36] Therefore, beyond differences in resin viscosity, pendant group mobility, and diffusion potential that may influence reactivity, other possible factors such as hydrogen abstraction or other alternate polymerization pathways may be involved in the higher reactivity of UDMA compared to that of Bis-GMA and EBADMA. Hydrogen abstraction from the tertiary amine used in combination with camphorquinone could be in competition with hydrogen abstraction from monomer structures. These events could then be considered a component of a mechanism to enhance radical initiation or cause an alternate polymerization pathway. Exploring the role of hydrogen abstraction by using non-hydrogen abstractable photoinitiators could be the subject of further studies, as will be intramolecular cyclization, the amount of pendant double bonds, and the resulting network structure, which will be presented in detail elsewhere.

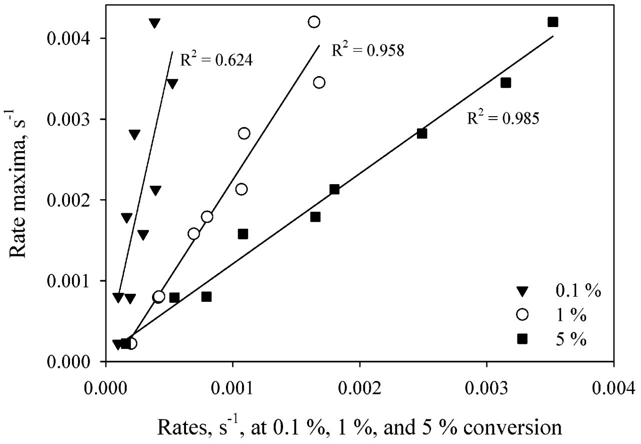

Figure 11. Polymerization rate maxima (s^{-1}) vs reaction rates at 0.1%, 1%, and 5% conversion of Bis-GMA/TEGDMA resin mixtures. The standard errors of the estimate as a measure of the uncertainty for the regression lines 0.1%, 1%, and 5% are 0.0009, 0.0003, and 0.0002 s^{-1}, respectively.

The plots in Figure 10 demonstrate the influence of the initial resin viscosity on the photopolymerization reactivity, i.e., rate maxima and fractional conversion. It is apparent that for all the resins examined relatively sharp increases in polymerization rate accompany the fairly minor initial increases in resin viscosity as the various base monomers are added to TEGDMA. In all three resin series, the maximum polymerization rate increases steadily as the base resin concentration increases leading to a maximum. However, increases beyond 0.5 mole fraction Bis-GMA and 0.75 mole fraction UDMA result in a decrease of the $R_{\mathrm{p,max}}$. The highest reaction rates were observed for resins with initial viscosities in the range of about 3−5 Pa s (measured at 30 °C). While this study has not investigated the rheology of the forming network and no simple and universal relationship exists between initial viscosity and the development of complex viscosities beyond the early gelation, Figure 11 demonstrates a significant correlation between the rate maxima, $R_{\mathrm{p,max}}$, which occur at such different conversion values ranging from 2.7% to 21%, and the polymerization rates at 0.1%, 1%, and 5% conversion (Pearson product moment correlation, $p < 0.01$). Since the gel point in dimethacrylate systems does not occur until about 1%−2%[37] and since the polymerization rate at 0.1% conversion (below the gel point) was strongly correlated to the maximum rate, which is generally assumed to occur after the gel point, it is suggested that the initial viscosity also influenced the reaction rates up to the point when autoacceleration stopped. A strong influence from the initial resin viscosity of a diacrylate system similar in structure to the Bis-GMA/TEGDMA resins in our study on the normalized polymerization rate has been reported by Scherzer and Decker,[5] who attributed changes in polymerization rates largely to changes in initial viscosity. As the initial viscosity can be readily controlled by the monomer selection, this appears to be a convenient way to influence the rate.

The undiluted EBADMA monomer has a viscosity that appears to be in the optimum range for maximum reactivity. The range of resin viscosities where optimum reactivity is observed is likely that which allows significant monomer diffusion but inhibits macroradical translation and termination. In this situation, the autoacceleration or Tromsdorff effect commences almost immediately with the onset of the polymerization reaction.[30] It is clear from the significant differences observed among the various resin systems in Figure 10 that the initial resin viscosity is a major factor in controlling polymerization kinetics and the final conversion, especially at the lower monomer viscosity ranges, but not the only one that controls resin photopolymerization reactivity. For example, comparing the fractional conversion and polymerization rates at various matching initial viscosities (Figure 12), it becomes obvious that the two bisphenol A core containing resins, Bis-GMA

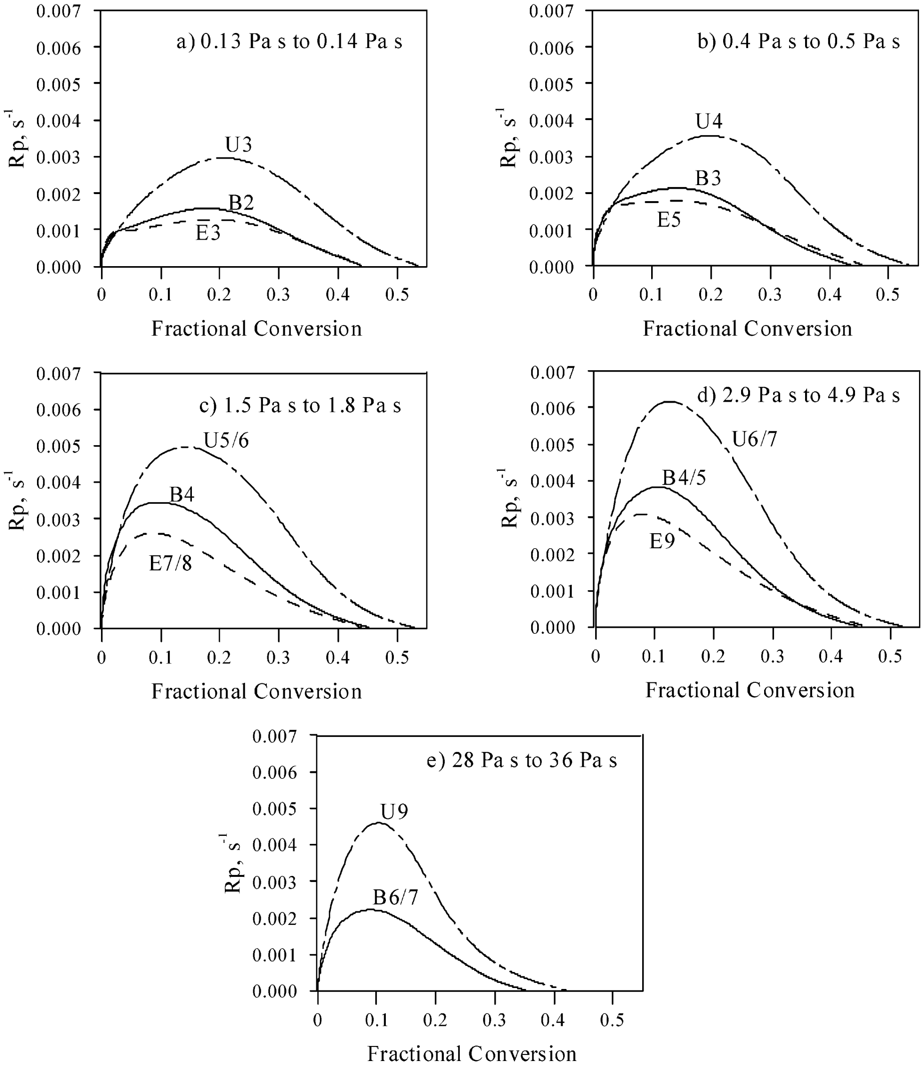

Figure 12. Polymerization rates and fractional conversion at various matching initial viscosities.

and EBADMA, have approximately the same conversion and are also fairly comparable in their reaction rates, especially at low base resin concentrations (Figure 12a,b). The slightly higher reactivity of resins B4 and B4/5 compared with that of EBADMA resins E7/8 (Figure 12c) and E9 (Figure 12d) may have been caused by the higher diluent content in the Bis-GMA-based formulations. (The term B4/5 indicates that average polymerization rates and fractional conversion values were calculated from resins B4 and B5.) The fairly similar reactivities of the bisphenol A-containing resins at a given (initial) viscosity range is contrasted by the considerably higher reaction rate and conversion of the UDMA-containing resins. Thus, these plots indicate that similarities in initial viscosity resulting in similar reactivities are overcome by structural parameters as indicated by the higher reactivity of a composition with a higher concentration of the more mobile, more flexible diluent monomer, and the much higher reactivity of the UDMA resins. The latter may have been enabled by both greater flexibility of the UDMA molecular structure and possible hydrogen abstraction and a chain transfer reaction mechanism.

Comparing Bis-GMA- and EBADMA-based resins at similar diluent concentrations, it can be concluded that the bisphenol A core structure on its own does not appreciably contribute to monomer viscosity. It is, however, conceivable that the relatively short 2-hydroxypropyl group in Bis-GMA contributes to a further decrease in flexibility compared to the multiple ethoxy groups in EBADMA. The moderate viscosity of UDMA monomer compared with the high viscosity of Bis-GMA is a clear indication that hydrogen-bonding interactions are the main factor controlling the viscosity. A direct comparison of hydrogen-bonding interactions within hydroxyl- or amide-terminated polybutadienes showed that the hydroxyl interactions were somewhat stronger than those of the secondary amide functionalized materials.[32] Thus, it can be expected that the intermolecular hydrogen-bonding interactions in Bis-GMA are stronger than the urethane hydrogen-bonding interactions in UDMA. This, along with the potential for intramolecular hydrogen bonding in UDMA, may explain why the viscosity of pure UDMA was more than an order of magnitude lower than that of Bis-GMA.

Effects of T_g. The potential limiting conversion of a photocured resin can be predicted on the basis of the monomeric T_g (shown in Figure 2) and the assumption that vitrification of the cured resin will limit its polymeric T_g to an approximation of the cure temperature.[38] Therefore, resins with higher monomeric T_g, such as much of the Bis-GMA/TEGDMA resin compositions, would be expected to produce relatively low degrees of conversion due to the limited dynamic range available

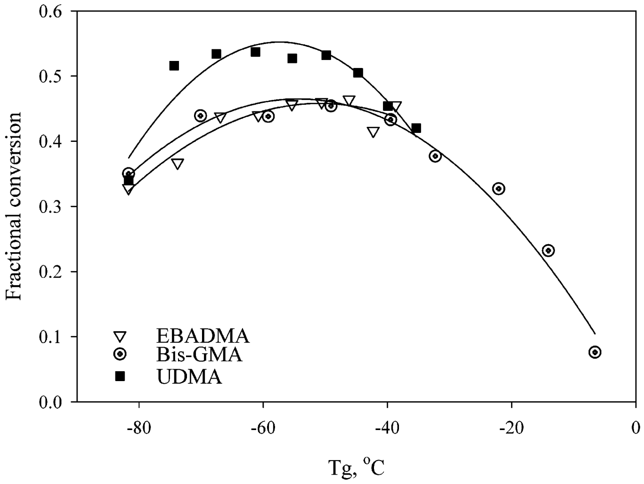

Figure 13. Fractional conversion vs monomeric T_g. The standard errors of the estimate as a measure of the uncertainty for the regression curves are for the resin series based on EBADMA, Bis-GMA, and UDMA 0.02, 0.02, and 0.03, respectively.

between the monomeric and polymeric T_g's under ambient curing conditions. While this is true in general,[16,39] when comparing the Bis-GMA-rich resins to the other base resin-rich mixtures, the correlation between the monomeric T_g's within each of the resin series and the corresponding final conversion data (Figure 13) is nonmonotonic, reflecting essentially the relationship between initial resin viscosity and conversion. In photopolymerizations of resins used in typical dental applications, a large sample size leads to greater heating effects and higher conversion. Higher irradiation intensities also increase sample heating and higher final degrees of conversion, which will be further augmented by the free volume generated through the delay between conversion and shrinkage.[30] Thus, larger sample size and higher irradiation intensities would likely result in higher polymeric T_g's and, therefore, higher final degrees of conversion than those observed here.

The polymerization of low-viscosity dimethacrylate monomers, e.g., diethylene glycol dimethacrylate or TEGDMA, leads to a significant amount of cyclization,[26] which in turn enhances the formation of microgels.[27,40−42] These can entrap pendant double bonds, unreacted monomer, and even radicals. As polymerization proceeds, the microgel regions become interconnected to form the macrogel,[40] but the heterogeneity remains in the final polymer network even though the majority of conversion occurs in the gelled state. Pendant double bonds, particularly those in the microgel regions, have reduced reactivities compared with free monomer. This differential reactivity, combined with cyclization reactions that limit effective cross-linking, causes a delay in the gel point conversion.[26,43] Therefore, resins with high base monomer contents, which, due to the stiffer structural properties, tend to engage in fewer cyclization reactions than TEGDMA, may undergo gelation at earlier stages of the polymerization process. If early cyclization plays a significant role in the polymerization kinetics of TEGDMA- and TEGDMA-rich formulations, the bimodal course of the rate/conversion profile should be emphasized in the presence of a nonreactive species.[27,42]

To test this hypothesis and to further probe the influence of monomer structure on resin photopolymerization kinetics, nonreactive, hydrogenated analogues of both Bis-GMA and TEGDMA were added as the minor components (0.125 mole fraction) in model resin mixtures and compared with the fully reactive resins of the same composition (Figure 14). The resin mixtures containing the hydrogenated analogues were homogeneous solutions, without any visible signs of phase separation before and after polymerization. The viscosities of the fully and partially reactive resin pairs were indistinguishable. These experiments, performed at a power density of 250 μW/cm^2, showed that while both resins B8 and B8* with either reactive or unreactive TEGDMA achieved much higher maximum polymerization rates and conversion than the neat Bis-GMA, their kinetic profiles are very similar with only moderately higher reactivities in the resin containing the hydrogenated TEGDMA due to its solvating effect. This effect is obviously concentration dependent, and thus, greater increases in maximum reaction rate and conversion have been reported when a higher amount (0.37 mole fraction) of hydrogenated TEGDMA was added to Bis-GMA.[8] When yet higher amounts of hydrogenated TEGDMA are present (0.84 mole fraction of nonreactive TEGDMA), the competing effects of enhanced reaction in a solvent-like environment and slowed reaction from dilution separating the reactive double bonds lead to a smaller increase of reactivity.[8] The photopolymerization

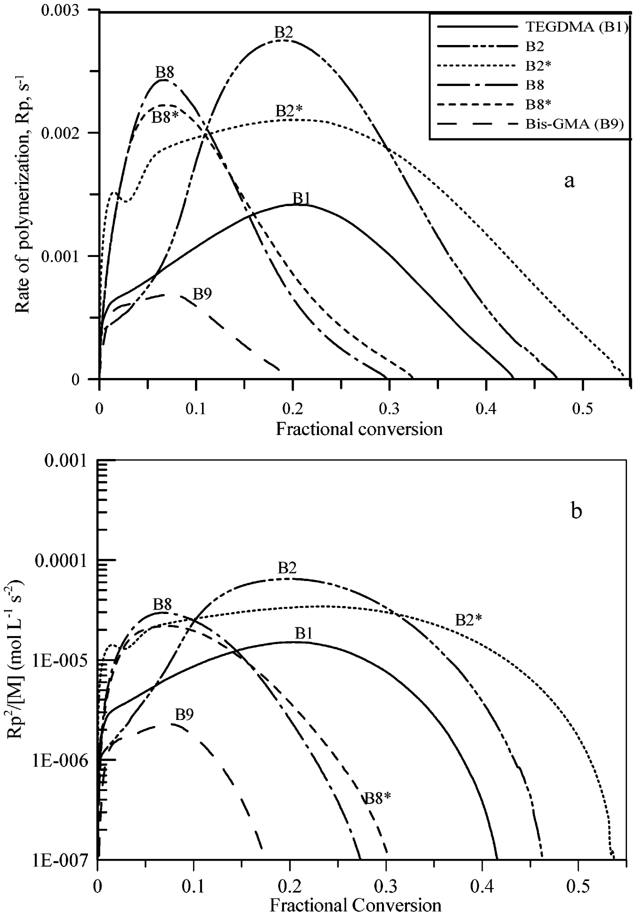

Figure 14. Rates of polymerization (a) of the resin formulations Bis-GMA (B9), Bis-GMA with 0.125 mole fraction TEGDMA (B8), Bis-GMA with 0.125 mole fraction hydrogenated TEGDMA (B8*), Bis-GMA with 0.875 mole fraction TEGDMA (B2), Bis-GMA with 0.875 mole fraction hydrogenated TEGDMA (B2*), and TEGDMA (B1). The squared rates divided by the molar concentration of double bonds (b) are shown to demonstrate the various stages in the polymerization process, as discussed in the text.

of resin B2*, in which the 0.125 mole fraction Bis-GMA was replaced with its nonreactive hydrogenated analogue, resulted in dramatically different kinetic profiles. Here, the model resin (B2*) reached a considerably lower maximum rate of polymerization, yet showed a much more rapid increase in polymerization rate compared to that of its fully reactive analogue. This as well as the more pronounced bimodal profile and the greater conversion seen in resin B2* may indicate that cyclization played a far bigger role in the photopolymerization of the resin despite the hydrogenated Bis-GMA, due to its limited mobility, being a relatively "poor solvent". This hydrogenated resin study indicates that TEGDMA, whether in the free monomer or reacted state, imparts mobility to the cross-linking polymerization process that allows high reactivity. It is also apparent that the active participation of the Bis-GMA component, even in minor amounts, is required to achieve high resin reactivity.

Conclusions

From this work it suggested that the main factors to obtain optimum reactivity are the initial resin viscosity and, within a given range of viscosities, structural effects allowing for molecular mobility. However, while maximum reactivity and optimum conversion are most valuable material properties, the impact of choosing materials based for example on low-viscosity resins requires careful balancing of other material properties such as overall volume shrinkage, toughness, wear resistance, and strength.

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