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# On the heterogeneous structure of thermally cured bis-GMA/TEGDMA resins

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In this paper we report on the morphogenesis of dental resins formed by a thermally initiated radical cross-linking copolymerization of model dental resins. These systems were considered reasonable model simplifications of the actual resins used in commercial filling composites, veneers, etc. Effect of bis-GMA content varying from 0 to 100% on the degree of conversion and morphology of the cured resin was investigated. Dynamic scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical thermal analysis (DMTA) and high temperature solvent extraction experiments were performed in order to determine the nature and location of unreacted unsaturations in relation to bis-GMA concentration. The interval of cure temperatures, ranging from 23 to 250 °C, may seem irrelevant from the clinical point of view but is instrumental for an understanding of the processes involved.

Single glass transition temperature (Tg) found in DMTA experiments showed that the copolymerization process between bis-GMA and TEGDMA is random in nature, however, the overall cure reaction is inhomogeneous and this inhomogeneity is increasing with increasing bis-GMA molar fraction. Heterogeneous character of the cure was reflected into the network morphogenesis characterized by microgellation preceded by cyclization and, following connection of microgels. These cure kinetics resulted in a heterogeneous morphology of the cured resin. Moreover, it was shown that the cure kinetics controls to a great extent the degree of conversion of the reactive vinylidene C═C bonds in a fully cured resin. A decrease in bis-GMA concentration in the resin mixture led to a higher degree of conversion, however, even a neat TEGDMA homopolymer did not exhibit C═C conversion greater than 65–70% under the cure conditions used. Leaching out tests, consisting of an extraction of unreacted monomer from a finely ground cured resin in boiling cyclohexanone at 160 °C over a period of 5 d, revealed total weight loss of the order of 3.2–5.6 wt % regardless of the total conversion. No uncured monomer was detected in the extract solution using FTIR spectroscopy, however, the method used is not sensitive to the presence of oligomers. It was concluded that the remaining unreacted double bonds are the inevitable result of the diffusion controled heterogeneous cure reaction. The low rate of diffusion in the resin beyond its gel point is controlled by high monomer rigidity, low mobility and radius of gyration of the monomers. The unreacted C═C bonds exist in the form of pendant, side groups chemically attached to the network. In addition, a hypothesis has been proposed that for concentrations of rigid bis-GMA monomers above 50 wt %, preferably only one methacrylate group of its molecule has reacted on the time span of the experiment performed and has been incorporated in the cured network. Hence, a substantial part of unsaturation exists in the solid polymer in the form of pendant groups formed by mechanically ineffective bis-GMA monomers. The results are in good qualitative agreement with computer simulations based on the kinetic gelation model.

## 1. Introduction

Commonly utilized dental filling composites are mostly based on rapidly curing mixtures of dimethacrylate monomers such as 2,2-bis[4–(2–hydroxy–3–methacryloyloxypropoxy)phenyl]propane (bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) [1]. These monomers form, after a proper chemical or light initiation, three dimensional tetrafunctional networks by radical cross-linking polymerization of vinylidene C═C double bonds of methacrylate end-groups of the monomers used [2-5]. The morphogenesis of a tetrafunctional network produced by radical polymerization of dimethacrylate monomers exhibits a number of interesting and yet not well understood features resulting in several morphological peculiarities which are not commonly seen in less functional networks or networks produced by other polymerization mechanisms [6]. Moderate degrees of conversion, ranging commonly from 50–85%, of the vinylidene C═C groups in cured resins as well as large numbers of mechanically ineffective side chains affect mechanical response of commercial dental resins as well as their hydrolytic and color stability. It is now generally accepted that there is a direct correlation between the total degree of conversion and mechanical and wear properties and color stability of the dental resins [7].

In an excellent survey, Ruyter [1] pointed out several important features of cure of various dental resins. It has been shown that during a copolymerization of a linear methyl methacrylate (MMA) and ethyleneglycol dimethacrylate (EGDMA), linear PMMA chains are cross-linked by EGDMA linkages. However, only one third of EGDMA formed cross-links [8]. For the remaining two thirds of EGDMA monomer, only one methacrylate group of each EGDMA molecule entered the co-polymerization reaction. Hence, about 30% of the total amount of C═C bonds remained unreacted in the form of pendant groups. The amount of unreacted C═C bonds increases substantially in the case of co-polymerization of two dimethacrylates such as bis-GMA and TEGDMA. It has been shown that the quantity of unreacted unsaturations in the bis-GMA/TEGDMA system can be qualitatively correlated with the amount of bis-GMA in the polymerizing system [9–11] and that neat TEGDMA exhibits about a 10% higher degree of conversion than neat bis-GMA [9, 12].

Theoretically, the reactivity of vinylidene C═C bonds in methacrylate groups of various dimethacrylate monomers used in commercial dental composites, veneers, luting resins and adhesives, is more or less the same. This suggests that the mechanism of resin cure does not change for various resin mixtures [13]. On the other hand, Simon *et al.* [4], Allen *et al.* [29] and Wang [14] have shown that in various resins higher rigidity and reduced mobility of a monomer molecule affects kinetics of resin cure substantially. This results in a formation of morphologically heterogeneous solid resin of broadly varying degrees of unsaturation. In addition, the morphology and properties of the cured resin will depend to a greater extent on the kinetic parameters of the cure.

One of the typical features of radical polymerization of a monofunctional monomer, such as polymerization of methylmethacrylate into linear polymethylmethacrylate (PMMA), is its addition character, i.e. reaction proceeds via stepwise adding of a monomer to the growing polymer chain. High molecular weight polymer is formed immediately at very low monomer conversion. Hence, the reacting system always contains high molecular weight polymer and monomer species at the same time [15]. Published data suggest that the kinetics of radical cross-linking reactions, resulting in formation of a three dimensional solid network, differ from the above mentioned scheme typical for linear dental polymers significantly, even though the individual reaction mechanism may remain unchanged [4,6].

In tetrafunctional cross-linked dental resins, a typical feature is an extremely low degree of conversion at a gel point [1, 4, 15] resulting in a heterogeneity of the cured resin. Gelation proceeds by a mechanism completely different from those leading to the traditional Flory-Stockmayer trees. It rather resembles some kind of chemical aggregation of colloidal particles [6]. Theoretically, conversion of 0.1 wt % at the gel point was predicted assuming no cyclization. Experimentally, conversions of 1–2 wt % at the gel point have been found, confirming a strong role of cyclization at the very early stages of the cure [6]. Reduced mobility of growing radicals results in a substantial reduction of the rate of termination even at very low conversions, resulting in the presence of a relatively large number of ''living'' radicals in a completely cured system [4,16]. This obscures effects of primary initiation, i.e. the initiator concentration on the degree of conversion. It also greatly complicates any kinetic analysis of this polymerization process. Theoretical approaches for treating these difficulties have been published by Dusek [6], Boots and Dotson [17] and recently by Kinney and Scranton [18].

The relatively moderate degree of C═C bonds conversion achieved commonly in thermally or light-cured commercial dental resins (typically 50–85%) may be of concern for both mechanical performance of a cured resin application and for possible toxicity and tissue irritation by untreated, leaching out dimethacrylate monomers [2]. Attempts have been made to determine the nature and location of these unsaturations [2-5, 19–21]. Unfortunately, most of these attempts have been made using either proprietary resins or commercial resin materials containing various additives. This makes the results almost useless for any rigorous interpretation of kinetic data. In order to shed some light on the mechanisms of network formation and the nature and location of unreacted double bonds, simple model resin mixtures have to be employed [4, 9, 29] before considering more complex materials such as dental composites. Presence of solid filler particles of large specific surface area can alter resin cure significantly, as shown by Connelly [22] and Shieh and Hsu [23] by radical immobilization and de-activation. These effects are expected to play an important role in many heavily filled restorative composites [24].

It has been suggested [6, 25] that formation of a radically polymerized network of multifunctional monomer can proceed in two steps. In the first step, microgellation occurs which is followed by connection of microgels in the second step resulting in an inhomogeneous network morphology. It has also been suggested that depending on the molecular weight and flexibility, microgellation can be preceeded by cyclization at the oligomer level. The reactivity of pendant double bonds is strongly affected by spatial correlations, by increased probability of cyclization and by its decreased reactivity due to steric effects. Generally, cyclization is more effective at the early stages of cure while the steric excluded volume effects operate at the later stage of the cure. Kinetic gelation model is used to describe these type of cross-linking reactions [17, 18, 26]. When considering kinetics of network formation one can estimate conversion of reactive groups at the gel point, which is an important threshold in reaction kinetics. For tetrafunctional dimethacrylates the gel point occurs at 2–4.6 wt % conversion of C=C groups [1, 18, 27, 28], i.e. at a very early stage of the cure compared to the usual 16–20% conversion for a typical radically cured unsaturated polyester [6]. This extremely low conversion at the local gel point is caused by the monomer being its own cross-linking agent and a high probability of cyclization at low conversions. The cyclization causes increased compaction of the microgel particles resulting in an increased heterogeneity of the cured resin.

Above the gel point, the termination becomes a diffusion controled process, resulting in a growing number of secondary radicals existing in the system as shown by Burtscher [3] and Kloosterboer *et al.* [26]. Within a microgel particle, diffusion of monomer or radical units is much slower than outside of it making diffusion rates of free monomers and radicals the primary variables of the process [17]. Primary initiation affects mainly the early stage of cure, i.e. concentration and spatial arrangement of microgels, which corresponds to the generally observed weak dependence of the total degree of conversion on initiator concentration. Later in the cure, both termination and growth may become diffusion controled. Kloosterboer *et al.* [30] have demonstrated that in highly cross-linked systems displacement of radical functions by transfer reactions may become dominant.

In this paper we report on the morphogenesis of resin mixtures based on two dimethacrylate monomers used to model commercial restorative composites, veneers, luting resins, adhesives, etc. In the resin mixtures investigated, concentration of bis-GMA in TEGDMA was systematically varied from 0 to 100%. Dynamic scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical thermal analysis (DMTA) and high temperature solvent extraction experiments were performed in order to characterize the nature and location of unreacted unsaturations. Needless to emphasize that the cure reaction was studied under dynamic thermal conditions and no standard kinetic data were obtained. The temperature interval used may seem irrelevant from the clinical point of view but it is instrumental for an understanding of the processes involved.

## 2. Experimental

Bis-GMA ($M_w = 512$) and TEGDMA ($M_w = 286$) monomers have been obtained from Esschem (Essington, PA, USA) and were of the same molecular structure as those used in commercially available dental resins. The peroxide initiators, di-benzoyl peroxide (DBP) and t-butyl peroxymaleic acid (TBPA), were supplied by Atochem North America (Buffalo, NY, USA).

Reaction mixtures were prepared by dissolving the initiator in TEGDMA monomer by means of magnetic stirring at room temperature for 1 h at 23 °C. Then, bis-GMA was added to obtain its required concentration in the resin mixture and was stirred for 1 h at 23 °C to obtain homogeneous mixture of the high viscosity monomer and the initiator in TEGDMA. In order to dissolve peroxides in the pure bis-GMA sample, the monomer was heated to 45 °C to reduce its viscosity and then peroxide was mixed with the monomer by means of magnetic stirrer for 20 min. The reaction mixtures were sealed in aluminum pans and placed in the DSC equipment. Cured samples from DSC experiments were used to collect FTIR spectra. In order to prepare specimens for DMTA measurements, reaction mixtures were poured into silicon rubber molds with $25 \times 10 \times 0.5\,\mathrm{mm}^3$ cavities and cured in a vacuum oven at 120 °C for 1 h and then post-cured at 250 °C for 1 h. Specimens were allowed to cool to room temperature at a cooling rate of approximately 5 °C/min, carefully removed from the molds, mold overflows were trimmed and specimens were left for one to two d at a room temperature prior the measurements.

Total heats of reaction, Δ H, were measured using a Perkin-Elmer System 7 DSC (Perkin-Elmer, USA) in dynamic experiments at a heating rate of 5 °C/min. Presented data are averaged from three measurements. The standard deviation of 5% was calculated for these experiments. Glass transition temperature, $T_g$, storage modulus, E′, and tan δ were measured using a DMTA spectrometer (Polymer Laboratories, UK) at 1 Hz and at a heating rate of 3 °C/min. Standard deviation of 5% was determined for the DMTA data using five measurements for each point. Infrared spectra were been collected using an FTIR spectrometer (Nicolet, USA) at room temperature. In average, two spectra were taken for each sample.

Extraction experiments were carried out in order to determine the content of unreacted unconstrained monomer in the cured resin. Samples cured according to the above described procedures were characterized by FTIR in order to measure the degree of unsaturation, then finely ground in a ball mill under liquid nitrogen and placed in a very fine stainless steel mesh. The weight of the mesh containing the ground sample was measured using standard analytical scale and then immersed in a boiling cyclohexanone. The refluxing aperture was closed and left at 160 °C for 5 d. Then the mesh was removed, thoroughly dried at 100 °C in the vacuum oven and weighed. The difference between its original and post-extraction weight was divided by its original weight in order to determine the percentage weight loss reported in this paper. An average of three measurements for each copolymer composition have been used and the average of these measurements is presented. Standard deviation of the measurement was 10%. The extracting solvent was placed in the FTIR spectrometer in order to determine the presence of monomer species.

## 3. Results and discussion

### 3.1. Network formation

Increasing the concentration of bis-GMA in the resin mixture resulted in a change of the DSC exotherm structure from a single peak exotherm for neat TEGDMA to a double peak exotherm for resins containing more than 25 wt % bis-GMA (Fig. 1). In agreement with Simon *et al.* [4], Dusek [6] and Allen *et al.* [29], this can be considered as evidence for increasing inhomogeneity of the cure reaction. The first major peak at about 100 °C

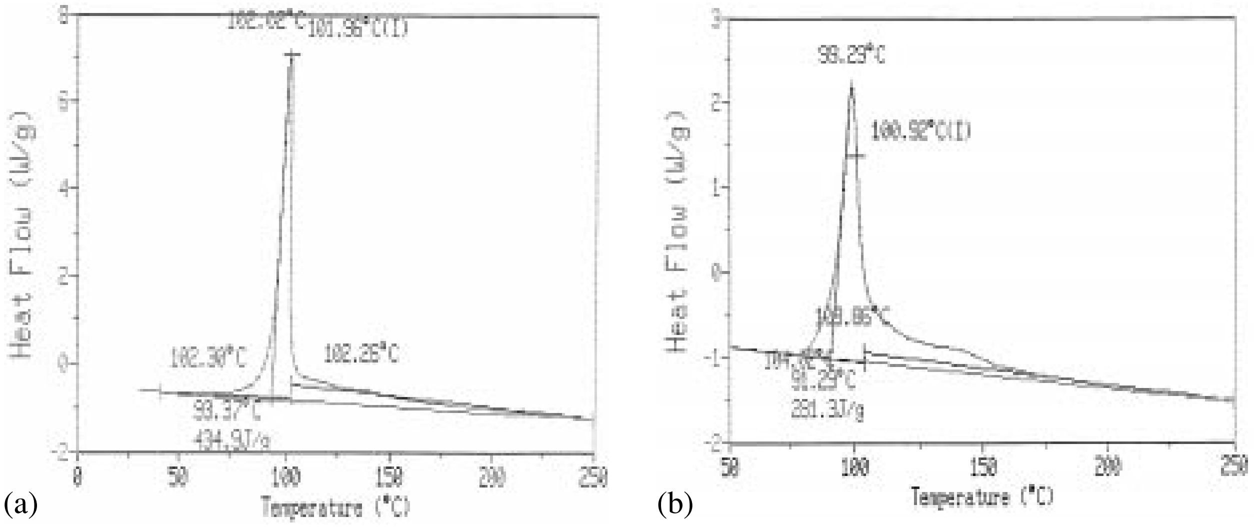

*Figure 1* (a) Temperature dependence of the heat flow during a cure reaction of the neat TEGDMA monomer as measured in a dynamic DSC experiment showing only one reaction exotherm; (b) temperature dependence of the heat flow during a cure reaction of 70 wt %/30 wt % bis-GMA/TEGDMA mixture as measured in a dynamic DSC experiment showing a substantial heat flow after reaching the peak reaction temperature and a secondary exotherm at about 140°. Reaction onset temperature is 91 °C, reaction peak temperature is 99 °C.

was related to a relatively homogeneous oligomerization and cross-linking of TEGDMA in microgels. This process proceeds theoretically up to 12% C=C conversion. In this step, compaction of the microgels occured due to cyclization of a highly flexible monomer. Low viscosity of the TEGDMA allowed for even distribution of the peroxide initiator, resulting in relatively homogeneous initiation within the whole specimen. High mobility of flexible TEGDMA molecules allowed for recombination of secondary radicals from neighboring microgels and imminent connectivity among them. In the process of connecting the microgels, pendant double bonds, presented mostly on the microgel surface, played a dominant role. For C=C conversions above 40%, phase inversion in the curing resin occurred transforming the system from microgels in monomer to monomer pools within the network of linked microgels. At this conversion, monomer and radicals become trapped among microgels and immobilized [4, 6]. In the cured TEGDMA resin, relatively high degrees of conversion were attained and finely heterogeneous morphology with small compacted domains was formed.

Increasing concentration of the rigid and bulky bis-GMA monomer in the resin mixture caused an increase in the viscosity of the resin mixture. This resulted in a less homogeneous initiation and a cure proceeding preferentially in coarse microgels with rigid bis-GMA molecules congregated on their surface [4, 6]. The actual size of these domains and their density depends on the bis-GMA concentration, on the homogeneity of initiator distribution within the resin mixture and its initial concentration. Similarly to neat TEGDMA, this stage of the resin cure occurred at approximately constant temperature of 100 °C independently of bis-GMA concentration. It was suggested that this stage is controlled by the formation of primary peroxide radicals, i.e. initiation. Compaction of the molecules in domains by cyclization became less likely due to increasing presence of the rigid bis-GMA monomer. The second step in the cure reaction was the connection of microgels, which is a diffusion controled process. Computer simulations and nuclear magnetic resonance (NMR) spectroscopy [4, 31] suggested that the microgels were connected most probably by the pendant bis-GMA unsaturations presented preferentially on the microgel surface. Since the inter-microgel connection is a diffusion controled process, with a diffusion coefficient differing from that for intra-microgel diffusion, an increase in reaction temperature was required in order to increase monomer and radical mobility at the given time span of the experiments. At temperatures around 140 °C, a second peak ascribed to a reaction between the radicals and monomers on the surface of microgels and in the remaining monomer pools has been observed reproducibly. While the presented data do not suggest any detailed description of the actual kinetics of this process, the above hypothesis is in agreement with the predictions based on the kinetic gelation model predicting enhancement of pendant C=C groups concentration at the interface between microgel and unreacted monomer pools [4, 32–35]. It seems worthwile to note that similar results were obtained by Kloosterboer *et al.* [30] for photo-cured dimethacrylate resins based on higher oligo(ethylene glycols) and by Simon *et al.* [36] for copolymerization of long and short chain oligo(ethylene glycol). An alternative hypothesis assuming formation of an interpenetrating network (IPN) of two polymers of different comonomer composition in the course of cure has been ruled out, since only a single $T_g$ existed for any resin composition investigated (Fig. 2).

The DSC experiments were carried out at two initiator concentrations of 0.5 and 0.75 wt % in order to investigate the effect of primary initiation of the C=C conversion. At the benzoyl peroxide (BP) concentration of 0.5 wt %, the total heat of reaction per mole of reacting species, Δ H, measured in a dynamic DSC experiment, performed within a temperature interval ranging from 23 °C to 150 °C (Fig. 3), was 20% lower for neat bis-GMA in comparison to the system containing neat TEGDMA. This apparently corresponds to about 10%

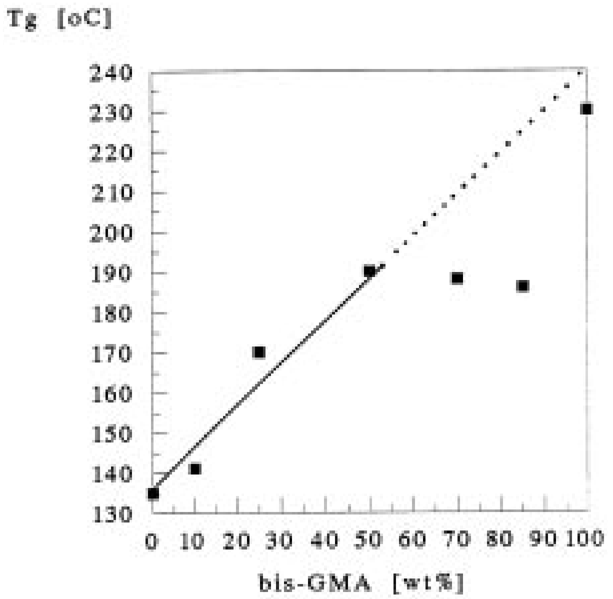

*Figure 2* Composition dependence of the glass transition temperature, $T_g$, of the cured dimethacrylate copolymers as determined from tanδ versus T plots. Tanδ was measured using a DMTA spectromoter (heating rate 3/min, 1 Hz). Viscoelastic spectra exhibited only a single relaxation peak for all the bis-GMA concentrations investigated. Plotted line is depicting the dependence for an ideal random copolymer network with all the monomers mechanically effective.

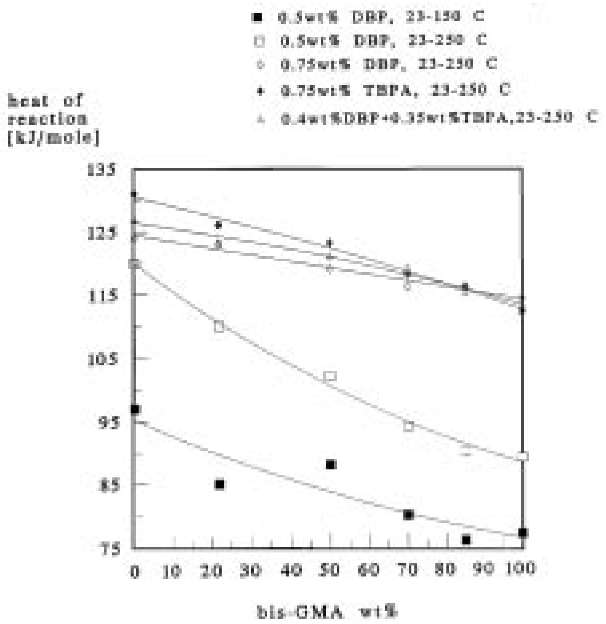

*Figure 3* Molar heat of reaction measured in a dynamic DSC experiment plotted versus weight fraction of bis-GMA monomer in the reaction mixture. Initiator concentration and composition is the parameter of the dependences. Except for the filled squares (reaction conducted from 23 °C to 150 °C), all the experiments were carried out from 23 °C to 250 °C at a heating rate of 5 °C/min.

reduction in the degree of conversion in bis-GMA compared to TEGDMA [9, 12]. Increasing the upper limit of the temperature interval to 250 °C, the total heats of reaction increased by 20% regardless of the bis-GMA concentration, hence, the difference between total heats of reaction between bis-GMA and TEGDMA homopolymers remained unchanged.

Increasing the BP concentration to 0.75 wt %, the difference in ΔH between bis-GMA and TEGDMA homopolymers became less pronounced due to about a 15% increase in ΔH for neat bis-GMA, while essentially no increase has been observed for neat TEGDMA. Moreover, this effect appears to be unaffected by initiator composition (Fig. 3). More massive initiation, i.e. larger number of microgels being formed at very low conversions, is the proposed interpretation. This resulted in a substantial increase in the microgel surface area. Since the bis-GMA monomer is preferentially located on the surface of microgel particles, more rigid bis-GMA monomers can be incorporated in the network in the early stages of massively initiated resin cure. This finding is in agreement with the results of Burtscher [3] and Lapcik *et al.* [16], suggesting that the half-life of primary and secondary free radicals in cured dental resins can be extremely long and enough free radicals exist in a cured system at room temperature over a period of several days after primary initiation. Low radical and monomer mobility preventing recombination, further cross-linking or other decay processes were the reasons for long half-life of radicals in the cured resins.

FTIR spectra of uncured and cured monomer mixtures revealed little variation in the content of remaining unreacted double bonds in respect to bis-GMA concentration (Table I). Apparently, increasing concentration of bis-GMA monomer in the resin mixture resulted in a 10% reduction of total conversion of C═C bonds compared to neat TEGDMA. In order to quantify the amount of remaining unsaturations, the C═C peak at 1634 cm$^{-1}$ was related to the peak at 1716 cm$^{-1}$ which should not change due to cure reaction. While the method used to quantify FTIR absorption spectra was based on simplifying assumptions of constant absorption coefficient of the liquid monomer mixture and solid resin, the findings were supported by independent DSC data described above. The results are in good agreement with the data reported in the literature for similar resins [1, 4, 12].

Even when a post-cure up to 250 °C was employed [35], the total degree of conversion remained within an interval 55–70%. In this regard, one has to keep in mind that a ceiling polymerization temperature, $T_p^c$, of methyl methacrylate is about 220 °C [38]. One can expect an increase in $T_p^c$ for dimethacrylate polymer due to a two-fold increase in reaction enthalpy, however, increase in entropy partly compensates for this increase. Thus, it seemed reasonable to assume that the dimethacrylate $T_p^c$ did not differ from that of MMA substantially. The upper temperature limit of our experiment was very close to $T_p^c$ for the monomers used and, thus, a more complete reaction could not be expected by further increasing the reaction temperature, since de-polymerization was expected to start.

## 3.2. Network morphlogy

In order to characterize the morphology of cured resins, the nature and location of unreacted unsaturations was investigated. In order to determine whether the polymer consists of a dense three dimensional network swollen by entrapped monomer and immobilized withinin microgels

TABLE I Degree of C=C conversion ($\Delta_{C=C}$) in bis-GMA/TEGMA copolymers from DSC and FTIR data and results of extraction experiments

| TEGMA [wt %] | $\Delta^{***}_{C=C}$ (DSC) [%] | $\Delta^{\dagger}_{C=C}$ (FTIR) [%] | $\Delta w$ [wt %] | $\Delta^{*}_{C=C}$ [%] |
|---|---|---|---|---|
| 0 | 45 | 42 | 3.6 | — |
| 20 | 59 | 48 | 3.4 | 41**-45 |
| 30 | 65 | 53 | 5.4 | 51**-53 |
| 40 | — | — | — | 36**-63 |
| 50 | 63 | 54 | 2.9 | 25**-59 |
| 60 | — | — | — | 26**-56 |
| 70 | 64 | 56 | 3.5 | — |
| 80 | — | — | — | 14**-55 |
| 90 | 67 | 54 | 3.8 | — |
| 95 | 65 | 57 | 5.2 | — |
| 100 | 69 | 55 | 3.4 | 9**-48 |

*DSC measured $\Delta_{C=C}$ taken from [12].

**Lower limiting data from cure in air, upper limiting data from curing in argon.

***Cured under nitrogen flow, $\Delta_{C=C}$ calculated from (12):

$$\Delta_{C=C} = \frac{100.\Delta Q}{\Delta Q_t}$$

$\Delta Q_t$ is the heat of reaction for 100% C=C conversion, ΔQ is the measured heat of reaction.

†Cured in DSC under nitrogen flow, $\Delta_{C=C}$ calculated from the respective FTIR C=C and C=O absorbances $A_{C=C}$ and $A_{C=O}$:

$$\Delta_{C=C} = \frac{100.\left(\frac{A_{C=C}}{A_{C=O}}\right)_{cured}}{\left(\frac{A_{C=C}}{A_{C=O}}\right)_{uncured}}.$$

or whether the unreacted double bonds exist as pendant groups in a more or less ideal network, extraction experiments were conducted.

Extraction in cyclohexanone at 160 °C for 5 d resulted in weight loss ranging from 3–5.6%, i.e. substantially less than expected if loose monomers were present in the system of about 50% degree of conversion (Table I). This suggests that the unreated double bonds exist in cured dental resins mostly in the form of pendant groups which is in good agreement with published data [3, 4, 6]. Further support for this interpretation was provided by FTIR analysis of the extract solution exhibiting no detectable amount of monomer. Needless to say, however, that the method used is not sensitive to the presence of larger three dimensional oligomers which may exist in the cured polymer due to the inevitable distribution of $M_w$ obtained in addition polymerization. The measured weight loss has been attributed to the loss of submicron size particles from the stainless steel mesh used to hold the specimen in the solvent bath.

In order to evaluate the macroscopic heterogeneity of the cured resins, DMTA measurements of tensile storage modulus, E′, and loss factor, tanδ, over a temperature interval ranging from 30–250 °C were performed. Glass transition temperature, $T_g$, was determined as the position of the maximum on tanδ vs. T plot. Dependence of $T_g$ of the cured resin on bis-GMA concentration was measured (Fig. 2). A single $T_g$ existed for every bis-GMA concentration, suggesting a more or less random incorporation of the two monomers in the cured resin network. DMTA measurements of viscoelastic moduli and tanδ can be visualized as an averaging of contributions from local domains of various conformational mobility [29, 39]. The measured property is proportional to the volume fractions of various local structures, hence, it does not allow one to distinguish local variations in the structure from a single DMTA experiment. When two components of substantially different $T_g$ are mixed and cured resulting in a solid network exhibiting only one $T_g$, one can interpret such an observation with a great deal of confidence as the formation of a random copolymer [29, 36, 41]. No information on preferred spatial arrangement of bis-GMA and TEGDMA monomers in the formed network can be obtained from these data.

Below concentrations of 50 wt % bis-GMA, the observed increase in $T_g$ with increasing rigid bis-GMA content followed a simple free volume additivity equation derived for linear copolymers [36]:

$$T_g = \frac{kw_2}{(1-w_2)}\left[T_{g2} - T_g\right] + T_{g1} \qquad (1)$$

where $T_g$ is the glass transition temperature for the copolymer, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures for the respective comonomers, $w_2$ is the weight fraction of comonomer two in the resin mixture and $k$ is a constant related to the expansion coefficients of the specimens in glassy and rubbery states. For bis-GMA concentrations above 50%, $T_g$ remained essentially unchanged at about 186 °C, being substantially less than expected for an ideal copolymer network. Neat bis-GMA exhibited $T_g$ of around 230 °C, and neat TEGDMA possessed $T_g$ of 140 °C which is in agreement with published data [29, 36]. The resulting network consists of flexible TEGDMA members and rigid, bulky bis-GMA members. Significant local variations in resin mixture composition can be attained due to two orders of magnitude lower viscosity of TEGDMA compared to that for bis-GMA. Hence, the linear increase in $T_g$ up to 50 wt % of bis-GMA can be explained and as formation of a random copolymer TEGDMA/bis-GMA with a substantially greater portion of flexible TEGDMA members incorporated by reacting both unsaturations compared to rigid bis-GMA. Greater TEGDMA mobility, flexibility and diffusion coefficient and lower viscosity resulted in a higher degree of total C=C conversion. Moreover, the incorporation of both methacrylate groups of bis-GMA into the network structure is quite probable.

With bis-GMA concentration increasing above 50 wt %, i.e. about 30 mol%, viscosity of the system increases substantially. The probability of the second dimethacrylate group of bis-GMA to enter polymerization reaction is reduced substantially after the first one has been reacted. Thus, preferentially only one methacrylate group of bis-GMA reacts during the cure and most of the bis-GMA molecules formed apparently pendant groups located preferentially on the surface of the microgels. This is in agreement with computer simulations based on the percolation concept and kinetic gelation model [4, 18, 30, 31, 34]. Further increases in bis-GMA concentration caused gradual replacement of flexible TEGDMA by rigid bis-GMA in the inner space of the microgels, thus reducing the microgel density. Since a portion of the rigid, bulky bis-GMA molecules within the microgels are mechanically ineffective due to very low probability to become incorporated into the network compared to those presented on the microgel surface, the bis-GMA rich microgel has greater segmental mobility resulting macroscopically in the observed reduction of $T_g$ compared to an ideal copolymer described by Equation 1. This hypothesis is also supported by the observed reduction of the storage modulus, $E'$, with increasing bis-GMA concentration measured in the rubbery plateau zone above $T_g$ (Fig. 4). In analogy, one could use the Flory correction accounting for a reduction of the elastic modulus in rubbery zone caused by mechanically ineffective chain ends in order to describe the observed decrease in rubbery elastic modulus with increasing bis-GMA concentration [39, 41]:

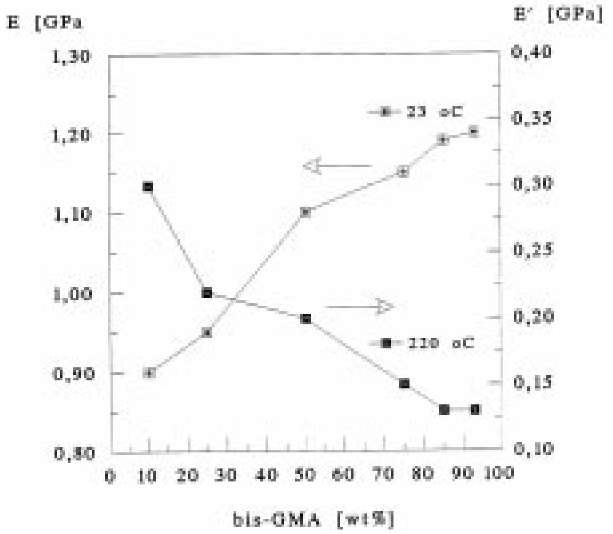

*Figure 4* Composition dependences of the elastic modulus, E, in a glassy state (23 °C) and in a rubbery state, E′, (220 °C). E is more sensitive to the monomer rigidity and increases with bis-GMA concentration, while E′ reflects the behavior of the whole network and decreases with increasing concentration of mechanically ineffective bis-GMA monomer.

$$E = 3\frac{\rho RT}{M_c} f \left[1 - \frac{2M_c}{M}\right] \qquad (2)$$

where $\rho$ is the polymer density, $R$ is the gas constant, $T$ is temperature in Kelvins, $f$ is the front factor, $M_c$ is the molecular weight between cross-links and $M$ is the molecular weight of the cross-linked chain. This is in agreement with the data of Korolev *et al.* [40] for similar systems both light-and thermally-cured and those published by Simon *et al.* [36] and Priyawan *et al.* [41] for dimethacrylate monomers extended with urethane linkages.

## 4. Conclusions

In order to establish relationships between the network morphology and important physico-chemical properties in the resin-based dental materials, a simplified model resin system based on thermally cured TEGDMA/bis-GMA mixture has been used in this initial study. DSC, FTIR, DMTA and leach-out experiments have been utilized to determine the nature and location of unreacted double bonds in relation to resin mixture composition. Previously suggested heterogeneous character of the cure reaction in dimethacrylate copolymers, i.e. microgelation step followed by interconnection of the microgels, has been confirmed. The heterogeneity of the cure reaction was increased with increasing concentration of bulky, rigid bis-GMA monomer in the resin mixture. Presence of unreacted C=C bonds in the cured resin was, thus, an inevitable result of this heterogeneity. No unreacted monomer has been extracted from the cured solid resin under the conditions used. Measurements of the storage viscoelastic moduli of the cured resin in both glassy and rubbery states were performed. Compositional dependences of $E_{\text{plateau}}$ and $T_g$ were interpreted using hypothesis proposing that the unreacted double bonds belong mostly to pendant bis-GMA groups inside the microgels. Experimental observations and theoretical predictions of Kloosterboer *et al.* [30] and preliminary results of the authors [16] support the hypothesis that there is a close correlation between the cure kinetics of thermally and photo-cured dimethacrylate resin mixtures. This investigation will continue in order to study resin cure in the vicinity of a solid surface simulating presence of inorganic fillers.

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