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Crosslinking copolymerization of epoxy methacrylates as studied by Fourier transform Raman spectroscopy

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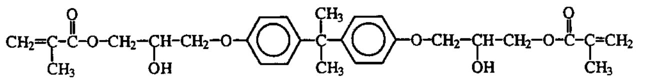
Bisphenol-A-bis(2-hydroxypropyl methacrylate) (BisGMA) was copolymerized with methyl derivatives of styrene initiated by di-tert-butyl peroxide in the presence of 76 wt% of silica filler at 150°–200°C. The Raman bands of the C=C stretching vibrations at 1630 and 1637 cm^{-1} were found to be suitable for determining the conversion of C=C double bonds of the styrene and the methacrylate monomer simultaneously in dependence on the copolymerization time. The C=O Raman band of the BisGMA monomer at 1702 cm^{-1} vanishes during the copolymerization, whereas the intensity of the C=O band at 1718 cm^{-1} decreases. Copyright © 1996 Elsevier Science Ltd.

(Keywords: methacrylates; crosslinking; *FT* Raman spectroscopy)

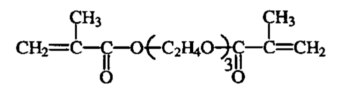
INTRODUCTION

The addition product of the diglycidyl ether of bisphenol A (DGEBA) with methacrylic acid (MAA) or of bisphenol A with glycidyl methacrylate (GMA), the so called BisGMA as introduced by Bowen[1] is a well known crosslinking monomer. It is of importance for dental applications like restorative composite materials, sealants, adhesives etc.

The free radical polymerization reaction of BisGMA is characterized by a low conversion of the pendant C=C double bonds[2]. This results in a relatively small polymerization shrinkage which is advantageous for most purposes. However, the high viscosity of BisGMA necessitates the use of a diluent monomer, e.g. tri(ethylene glycol)dimethacrylate (TEGDMA) which again enhances the polymerization shrinkage.



BisGMA



$$CH_2{=}\overset{CH_3}{C}-\underset{\overset{\|}{O}}{C}-O\left(C_2H_4O\right)_3\underset{\overset{\|}{O}}{C}-\overset{CH_3}{C}{=}CH_2$$

TEGDMA

The nearly constant polymerization shrinkage of 22.4 $cm^3\,mol^{-1}$ C=C double bond of methacrylic esters of aliphatic alcohols[3] can be used to determine dilatometrically the conversion of C=C double bonds during the polymerization reaction of methacrylates. Similarly, the molar polymerization heat of various methacrylates was found to be nearly constant with $\Delta H_p \approx 60\,kJ\,mol^{-1}$ C=C double bond[4]. The conversions of C=C double bonds of the copolymerization of BisGMA with TEGDMA (7/3 wt/wt) at 30°–60°C lay in the range of only 40–60% as determined by differential scanning calorimetry (d.s.c.)[5].

Kloosterboer *et al.*[6] found non-corresponding C=C double bond conversions during the photopolymerization of 1,6-hexandiol diacrylate by shrinkage and d.s.c. measurements. The discrepancy was explained by the delay of shrinkage with respect to the reaction of C=C bonds at the glassy state where propagation reactions of monomer molecules with trapped radicals were possible, but the corresponding volume shrinkage was impossible.

Therefore, direct monitoring of the decrease of the C=C double bond absorption at 1640 cm^{-1} in the i.r. spectrum of the polymerizing monomer mixture may be a more suitable method to analyse the polymerization course. The free radical copolymerization of the dimethacrylate of a low molecular epoxy resin (number-average molecular weight was 1100 $g\,mol^{-1}$) with styrene redox initiated at room temperature in bulk, was studied by *FT* i.r. spectroscopy[7].

Ruyter and Svendsen[8] applied multiple internal

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reflection (MIR) spectroscopy to determine the remaining unreacted methacrylate C=C double bonds quantitatively in polymerized commercial dental composites. Since MIR spectroscopy is essentially a surface measuring technique, the specimens have to be prepared for analysis in such a way that the surface properties simulate the bulk properties. The MIR spectra in the region of 1500–1700 cm^{-1} are representative for only 0.5 μm on the top of the material using a germanium crystal as an internal reflection element. Therefore, special precautions have to be taken to minimize the inhibiting effect of oxygen on the polymerization reactions.

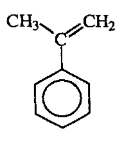
On the other hand, it is well known that the non-polar C=C double bond gives rise to a strong Raman band owing to the C=C stretching vibration[9]. For that reason, the Raman spectroscopy has an obvious potential for determining the conversion of C=C double bonds. The usefulness of this technique has been demonstrated for the polymerization of methyl methacrylate (MMA)[10–12]. In the past, the occurrence of fluorescence, either as intrinsic to the sample or present due to impurities, has severely inhibited the general application of Raman spectroscopy. With the introduction of highly stable near-i.r. lasers used in conjunction with Fourier transform (*FT*) instrumentation, fluorescence problems could finally be overcome. As Raman spectroscopy is a scattering technique, samples are simply placed in the laser beam and the backscattered radiation is analysed. Moreover, glass and water give only weak Raman signals, so that in most cases, a sophisticated sample preparation is not necessary. For *in situ* monitoring of the conversion of C=C double bonds at room temperature, we have shown that a time resolution of less than 10 s is possible without much experimental effort[13].

We have been interested to study the copolymerization of BisGMA with methyl derivatives of styrene, i.e. with α-methyl styrene (αMS), *p*-methyl styrene (pMS) and vinyl toluene (VT) which is a mixture of 60 wt% *m*-methyl styrene (mMS) and 40 wt% pMS, at polymerization temperatures higher than the glass transition temperature $T_g = 130$–140°C of poly(BisGMA)[14] to find out which maximum conversion of C=C double bonds can be achieved. Relationships between the latter and changes of the Raman band intensities of the C=O stretching vibrations as well as the conversion of monomers determined by extraction were also of interest.

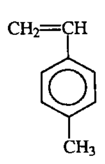
EXPERIMENTAL

Materials

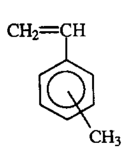
The synthesis of BisGMA from DGEBA (EPILOX 17.01, Leuna-Werke GmbH; epoxy value (groups): 5.81 eq. kg^{-1}, $M = 344$ g mol^{-1}) and MAA (Röhm Chemische Fabrik GmbH; 99.9 wt% acid, stabilized with 200 ppm hydroquinone monomethyl ether (HQME)) catalysed with 0.8 mol% 1-methylimidazole (Fluka Chemie AG; p.a. > 99%) was carried out by the method described by Sandner and Schreiber[15].



αMS



pMS



VT

α-Methyl styrene (αMS, Laborchemie Apolda), 4-methyl styrene (pMS, Aldrich-Chemie; 98%, stabilized with 50 ppm 4-tert-butylbrenzcatechin), and 3(4)-methyl styrene (VT, Aldrich-Chemie; 98%, stabilized with 50 ppm 4-tert-butylbrenzcatechin) were destabilized with 10% aqueous NaOH solution, washed with water, dried and distilled under vacuum.

Quartz powder (Keradenta-Werk Radebeul, average diameter = 20 μm) was silanized with 0.8 wt% 3-trimethylsilylpropyl methacrylate before use. The silanized quartz powder was mixed with fumed silica (Wacker HDK) (74/2 wt/wt).

Di-tert-butyl peroxide (DTBP, Peroxid-Chemie GmbH, techn. pure) was used as received.

Curing process

BisGMA and 10 wt% of a styrene derivative (αMS, pMS or VT) were mixed with 0.5 wt% DTBP and 76 wt% silanized quartz powder. The pastes obtained were poured into Teflon moulds (diameter: 5 mm, depth: 3 mm) between glass discs and then placed in an air oven for curing.

Samples with α-methyl styrene were cured 90 min at 150°C, the other samples for 45 min at 150°C and then 45 min at 200°C. The curing process was stopped by cooling the samples to 0°C in ice at different times to determine the conversion of monomers as well as C=C double bonds.

Analysis

The conversion of monomers was determined gravimetrically by extraction of 0.1–0.5 g milled samples in 40 ml acetone.

The ratio of comonomers in the extract was determined after extraction with tetrahydrofuran. The chromatograms of the extracts were recorded on a gel permeation chromatography (g.p.c.) apparatus (Knauer Wissenschaftliche Geräte KG) equipped with a Waters Styragel HR 1 column (eluent: THF, flow rate: 1 ml min^{-1}).

The conversion of double bonds was determined by *FT* Raman spectroscopy. The depolarized Raman spectra were recorded with a Bruker Fourier transform infra-red spectrometer IFS 66 equipped with the FT Raman module FRA 106. A diode pumped Nd:YAG laser which emits radiation at 1064 nm was used as the excitation source. The scattered radiation was collected at 180° to the source. Typical spectra were recorded at a laser power of 300 mW at sample location and a resolution of 4 cm^{-1}. In order to obtain a good signal to noise ratio, typically, 200 scans were co-added for the spectra. The manipulation and evaluation of the spectra were carried out using the Bruker OPUS software package. Generally, Raman intensities were determined as integrated band intensities. The quartz band at 465 cm^{-1} was used as a reference. The intensity of the $>$C=C$<$ stretching vibration was calculated after decomposition of the overlapping bands in the range of 1540–1670 cm^{-1}. The 'Levenberg–Marquardt'-strategy was used for fitting the function to the experimental Raman intensity.

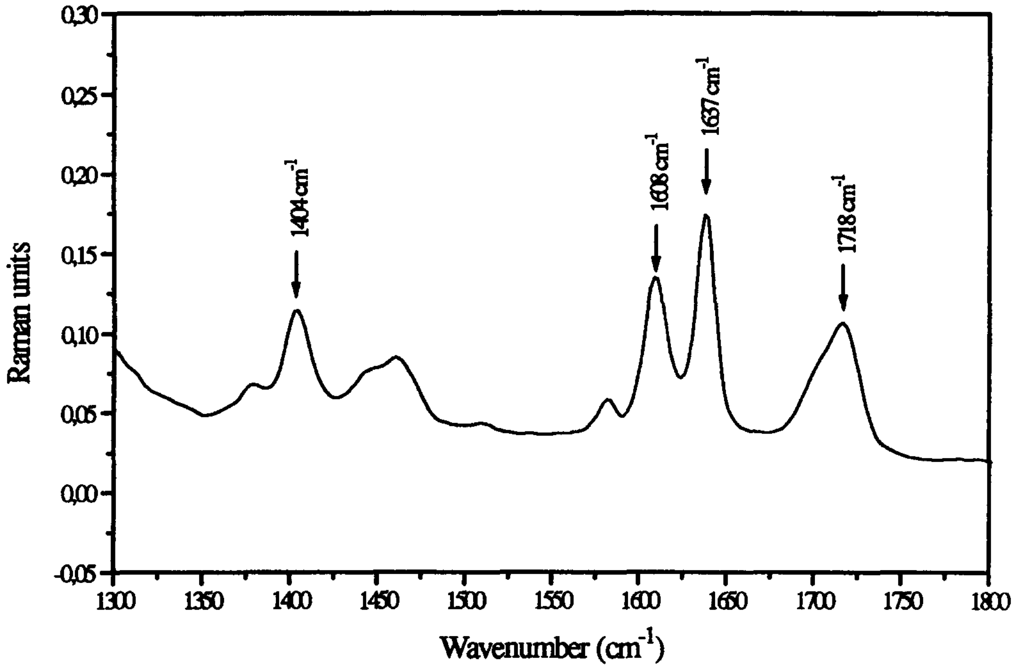


Figure 1 Raman spectrum of BisGMA

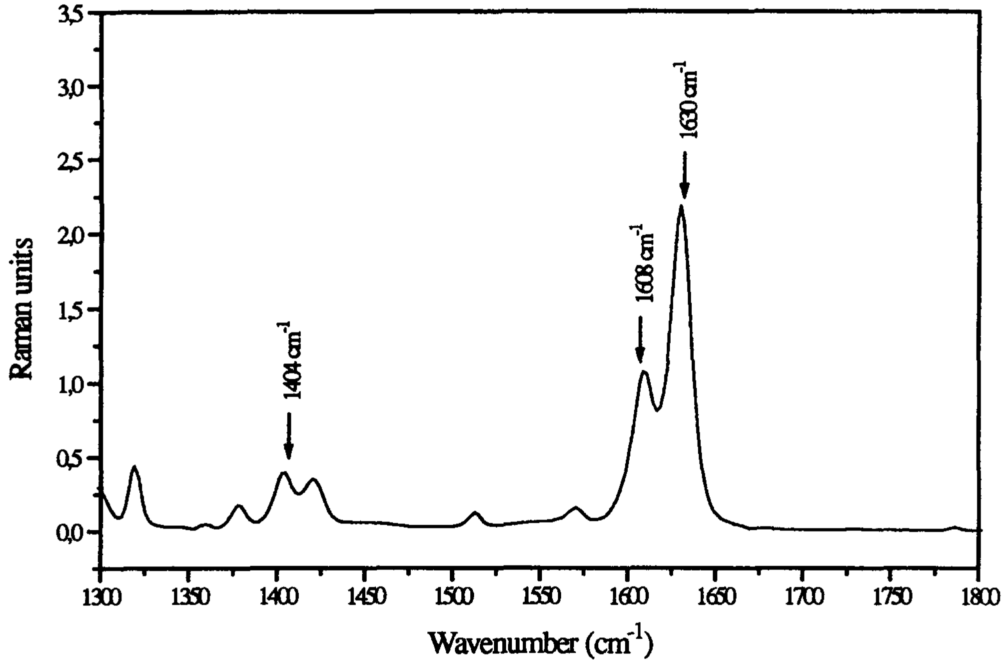


Figure 2 Raman spectrum of pMS

RESULTS AND DISCUSSION

Raman spectra of the monomers

The Raman spectra of the monomers BisGMA and pMS are shown in *Figures 1* and *2*, respectively. The vibration bands of interest listed in *Table 1* are those of the C=C and C=O stretching modes as well as that of the $H_2C=$ bending mode. The latter did not prove to be quite suitable for determining the conversion during the polymerization of MMA[12].

Of course, the C=C stretching modes of the styrene derivatives at 1630 cm^{-1} and of BisGMA at 1637 cm^{-1} overlap in the Raman spectrum of the monomer mixture. Their decomposition shown in *Figure 3* enables to determine the conversion of both kinds of C=C bonds separately.

It is also clear from *Figure 1* that the C=O stretching mode of BisGMA at 1718 cm^{-1} is an unsymmetrical

Table 1 Assignment of the bands from the Raman spectrum of *Figures 1* and *2*

Observed wavenumber (cm^{-1})	Assignment[9]
465	quartz band, used as reference
1404	$>C{=}CH_2$ stretch
1608	in plane deformation of phenyl ring
1637/1630	$>C{=}C<$ stretch
1718	$>C{=}O$ stretch

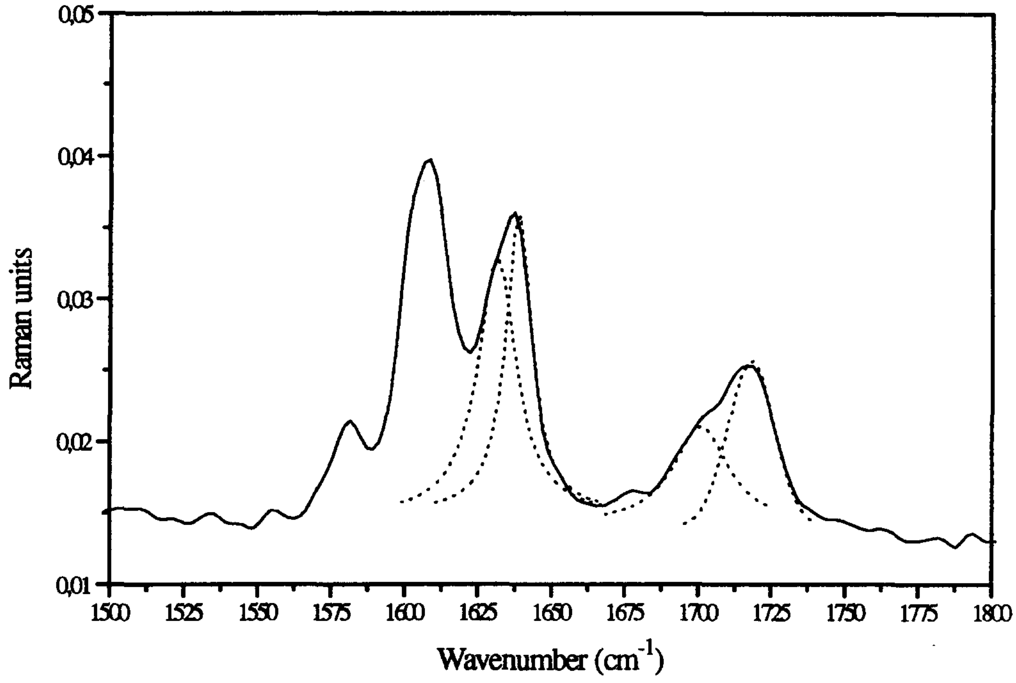


Figure 3 Decomposition of the C=C band and the C=O band in the Raman spectrum of an uncured monomer formulation based on BisGMA, αMS (9/1 wt/wt), 0.5 wt% DTBP and 76 wt% silanized quartz powder

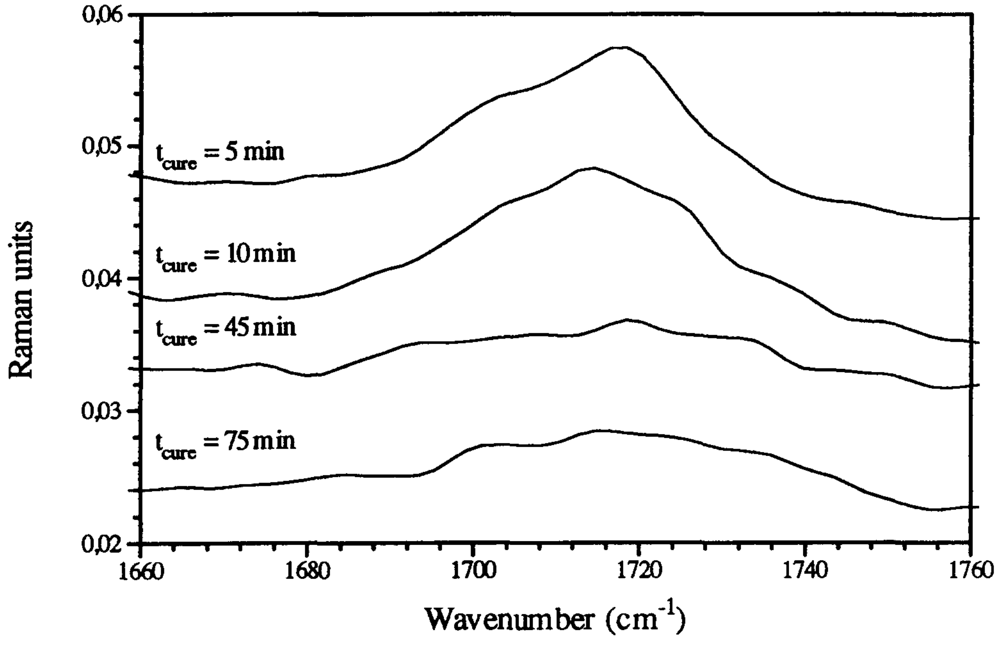


Figure 4 Decrease of the intensity of the C=O band with the curing time (BisGMA/αMS = 9/1 wt/wt, 0.5 wt% DTBP, 76 wt% silanized quartz powder, curing temperature 150°C)

one. The decomposition of this mode results in a band at 1718 cm^{-1} which is 100% Gaussian and one at 1702 cm^{-1} which is about 1/1 Lorentzian/Gaussian. The ratio of their integrated intensities is 1/1 (*Figure 4*).

The frequency of the C=O mode at 1718 cm^{-1} corresponds nearly to that of 1721 cm^{-1}[12] and 1722 cm^{-1}[11] reported for MMA. The C=O band of BisGMA at the lower frequency of 1702 cm^{-1} may be caused by hydrogen bond interactions with the hydroxyl groups which are in the β-position to the C=O group.

Copolymerization of BisGMA with styrene derivatives

BisGMA was copolymerized with 10 wt% of a styrene derivative as a diluent comonomer in the presence of 76 wt% of quartz filler initiated by DTBP. Samples with αMS were prepared only at 150°C for 90 min because this monomer evaporates to a slightly larger extent already at this temperature than pMS and VT at 200°C in the second stage of polymerization (*Figure 5*). Furthermore, initial degradation of the αMS copolymers was

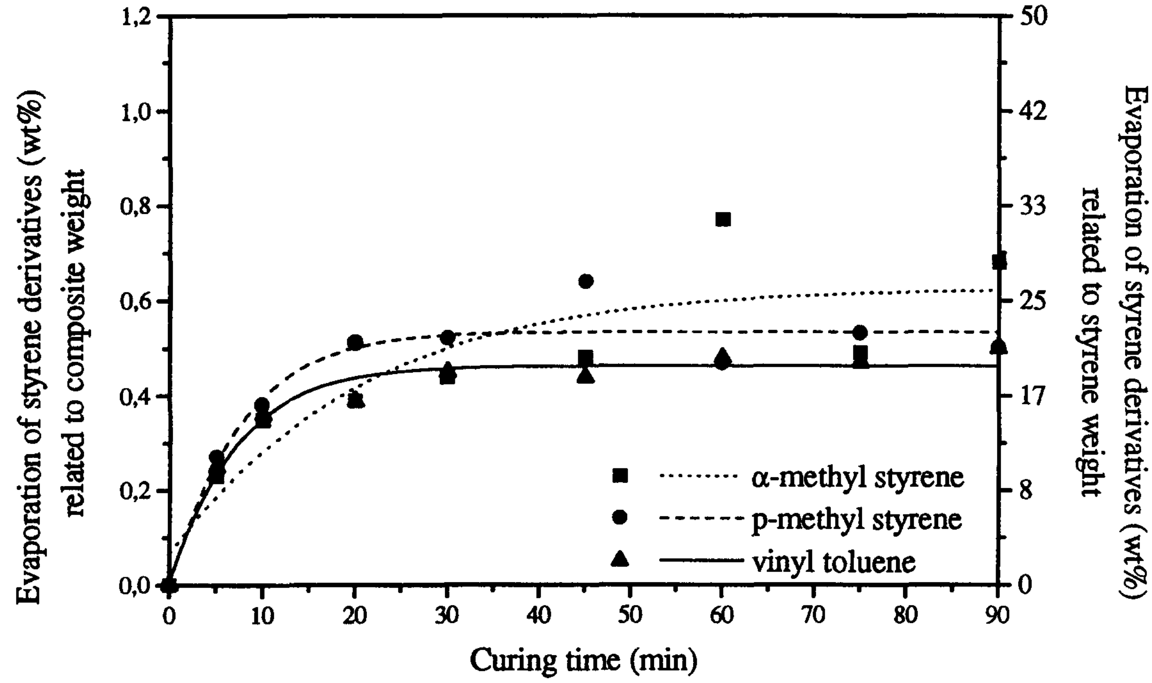


Figure 5 Evaporation of styrene comonomers during the curing (BisGMA/styrene derivative = 9/1 wt/wt, 0.5 wt% DTBP, 76 wt% silanized quartz powder, curing temperature for αMS 150°C, for pMS and VT 45 min 150°C and 45 min 200°C)

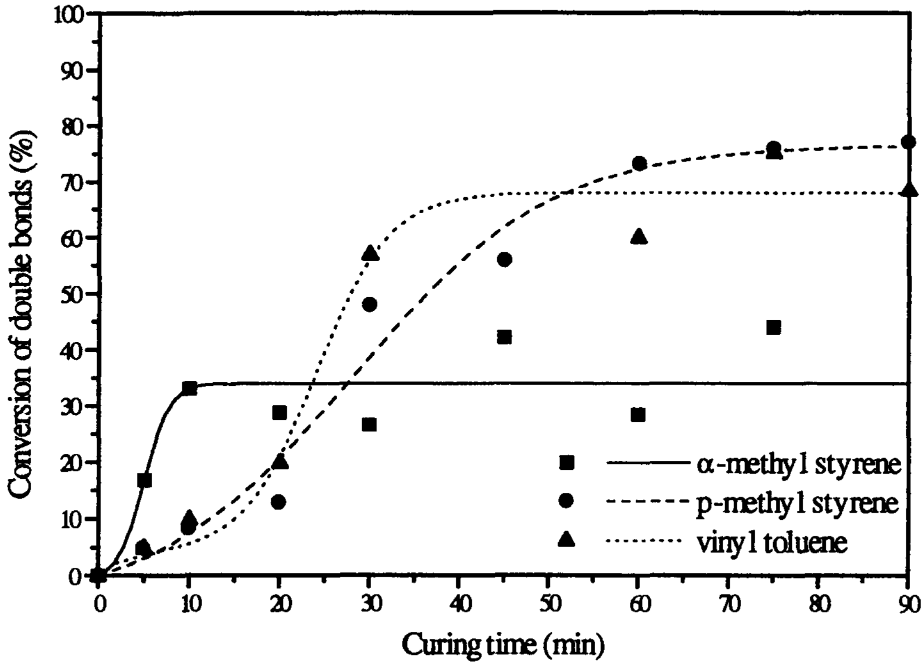


Figure 6 Dependence of the conversion of C=C double bonds of styrene comonomers on the curing time with BisGMA (BisGMA/styrene derivative = 9/1 wt/wt, 0.5 wt% DTBP, 76 wt% silanized quartz powder, curing temperature for αMS 150°C, for pMS and VT 45 min 150°C and 45 min 200°C)

observed at 200°C obviously caused by the depolymerization reaction.

The conversion of C=C double bonds of the styrene derivatives during the curing process was calculated considering the fraction of evaporated styrene monomers as determined from the mass loss of the samples shown in *Figure 5*.

The conversion–time curves of the C=C double bonds from pMS and VT in the copolymerization reaction are very similar as expected (*Figure 6*). However, the copolymerization with αMS attains a relatively low ultimate conversion quickly owing to the lower polymerization temperature (150°C during 90 min compared with 200°C during the second 45 min in the copolymerization with pMS and VT, respectively) which is lower than the glass transition temperature ($T_g \approx 166$°C) of the composite. The decrease of the intensity of the C=C double bond mode at 1637 cm^{-1} of BisGMA during its copolymerization with αMS is also only visible up to a reaction time of 45 min at 150°C (*Figure 7*).

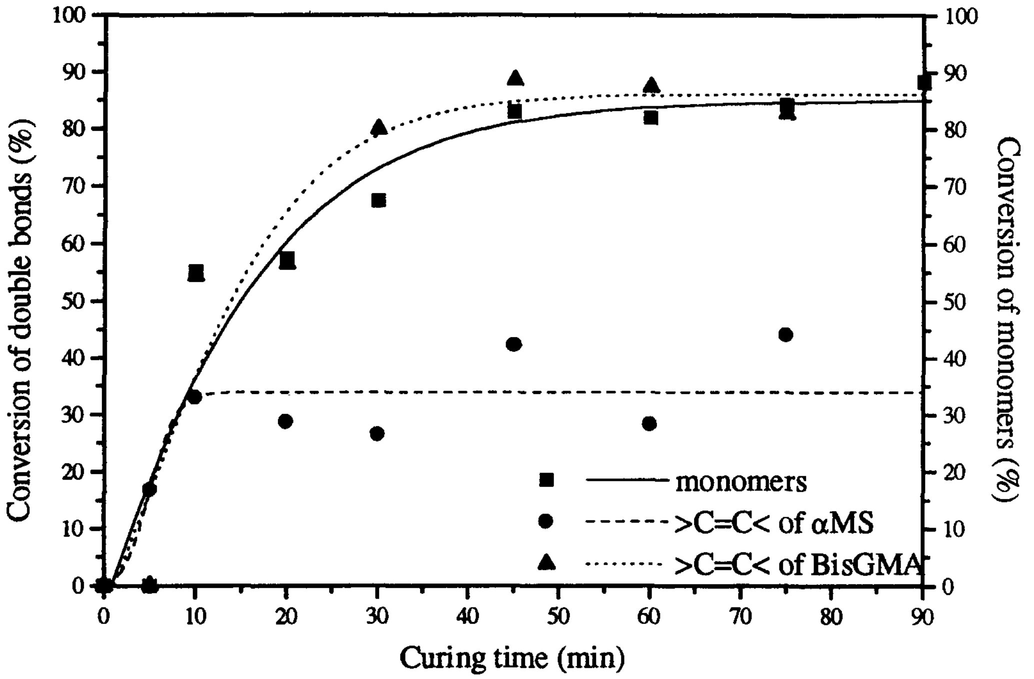


Figure 7 Dependence of the conversion of monomers and C=C double bonds on the curing time for αMS and BisGMA (BisGMA/αMS = 9/1 wt/wt, 0.5 wt% DTBP, 76 wt% silanized quartz powder, curing temperature 150°C)

Table 2 Copolymerization of BisGMA with VT (9/1 wt/wt = 67.5/32.5 mol mol^{-1} = 80.6/19.4 mol mol^{-1} C=C) in the presence of 76 wt% quartz filler initiated by 0.5 wt% DTBP at 150°C for 45 min and at 200°C for an additional 15 min

	Curing time (min)		
	10	45	60
Loss of VT (%)	15.9	17.8	19.7
Conversion of monomers to copolymer (%)	17.8	85.3	96.2
BisGMA/VT in extract (wt/wt)	11.8	22.4	37.8
Conversion (%) of			
BisGMA monomer	15.5	84.4	95.6
VT monomer	24.1	63.2	80.3
BisGMA C=C bonds	8.3	54.9	89.0
VT C=C bond	7.3	54.8	75.3
BisGMA pendant C=C bonds	7.1	30.1	86.2
BisGMA content of copolymer (mol%) calculated from			
copolymerization parameters with pMS	66.7		
with mMS	51.1		
conversion of			
monomers	57.2	73.5	71.2
C=C bonds			82.5
complete conversion of monomers, 20% loss of VT, infinite curing time			72.2

The overall conversion of monomers, as determined by extraction of composite samples after different curing times, attains about the same level as the C=C double bond conversion of BisGMA (*Figure 7*). Therefore, almost the whole part of the second C=C double bond of BisGMA should have reacted.

The relationship between the conversion of C=C double bonds and monomers may also be derived from the results of the copolymerization of BisGMA with VT grouped in *Table 2*. The conversion of BisGMA and VT was calculated from the content of both monomers in the extract solution determined by g.p.c. The comparison of BisGMA monomer and C=C double bond conversion for the short curing time of 10 min suggests that at this time, almost all of the BisGMA units in the copolymer contain a pendant C=C double bond,

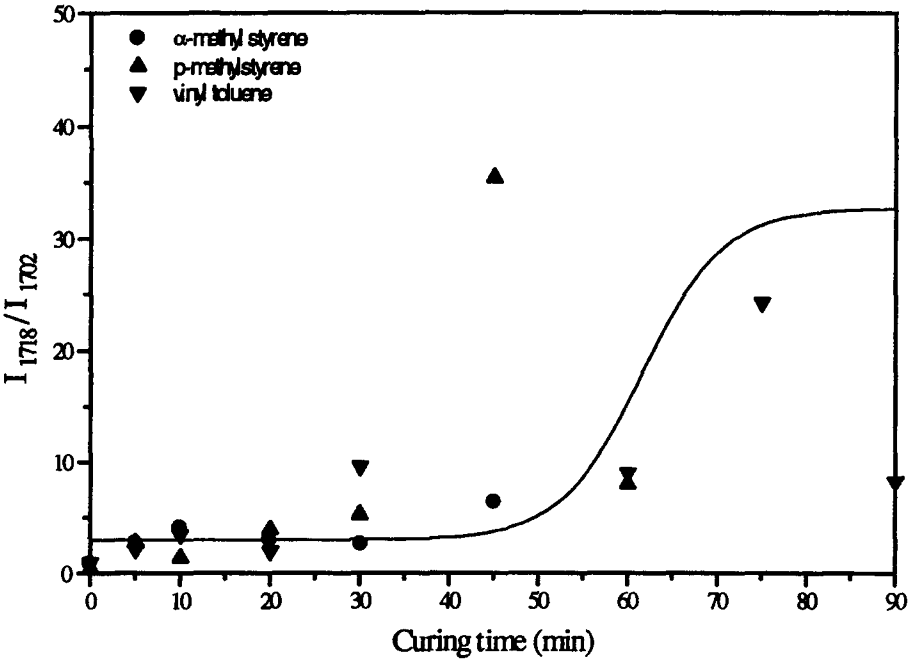


Figure 8 Change of the intensity ratio of both BisGMA C=O modes with the curing time for several comonomers (BisGMA/styrene derivative = 9/1 wt/wt, 0.5 wt% DTBP, 76 wt% silanized quartz powder, curing temperature for αMS 150°C, for pMS and VT 45 min 150°C and 45 min 200°C)

i.e. 15.5% conversion of BisGMA monomer would correspond to 7.75% conversion of BisGMA C=C double bonds, from which 7.1% conversion of pendant C=C double bonds can be calculated by comparison with 8.3% total conversion of BisGMA C=C double bonds as found by Raman spectroscopy.

An increasing approach of the conversions of BisGMA monomer and its C=C double bonds can be observed at longer curing times, corresponding to a decreasing fraction of pendant C=C double bonds in the copolymer network (70% after 45 min and 14% after 60 min) (*Table 2*).

The error of the determination of VT conversion results in a disagreement between both types of VT conversion for 10 and 45 min reaction time, whereas the agreement for 60 min is acceptable (*Table 2*). Besides, the copolymer composition after curing for 60 min (71.2 mol% BisGMA content) calculated from the content of BisGMA and VT in the extract, agrees with that (72.2 mol% BisGMA) calculated from the composition of the monomer mixture considering 20% loss of VT and assuming a complete overall conversion of monomers.

The content of BisGMA in the copolymer was also evaluated using the copolymer composition equation (1) for neglectable conversion of monomers:

$$\frac{M_{\mathrm{BisGMA}}}{M_{\mathrm{pMS}}} = \frac{r_1 \frac{[\mathrm{BisGMA}]}{[\mathrm{pMS}]} + 1}{r_2 \frac{[\mathrm{pMS}]}{[\mathrm{BisGMA}]} + 1} \qquad (1)$$

where M_{BisGMA} and M_{pMS} are the molar fractions of BisGMA and pMS, respectively, in the copolymer, [BisGMA] and [pMS] are the molar concentrations in the monomer mixture and the copolymerization parameters r_1 are the ratios of the propagation constants $k_{\mathrm{p}11}/k_{p12} = r_1$ of a BisGMA terminated macroradical with BisGMA and pMS, respectively, and $k_{\mathrm{p}22}/k_p12 = r_2$ are those of a pMS terminated macroradical with pMS and BisGMA, respectively, assuming that only one C=C double bond of BisGMA reacted. r_1 and r_2 were calculated from the reactivity parameters Q_i and the polarity parameters e_i of the monomers according to the Alfrey-Price[16] scheme where $r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)]$ and $r_2 = Q_1/Q_2 \exp[-e_2(e_2 - e_1)]$. $Q_{\mathrm{BisGMA}} = 6.22$ and $e_{\mathrm{BisGMA}} = -2.74$ were obtained from copolymerization parameters of BisGMA with *N,N*-bis(2-methacryloyloxyethyl)-*p*-toluidine (BMAT) as well as $Q_{\mathrm{BMAT}} = 4.29$ and $e_{\mathrm{BMAT}} = -0.73$[17]. *Q*- and *e*-parameters of pMS and mMs are given in the literature: $Q_{\mathrm{pMS}} = 1.10$, $e_{\mathrm{pMS}} = -0.63$; $Q_{\mathrm{mMS}} = 1.57$, $e_{\mathrm{mMS}} = -0.03$[18]. The formation of relatively homogeneous copolymers may be concluded comparing the calculated contents of about 60–73.5% BisGMA at different curing times (*Table 2*).

Changes of the methacrylate ester carbonyl bands at 1702 and 1718 cm^{-1} were observed during the crosslinking copolymerization of BisGMA (*Figure 4*) like those similarly reported for the polymerization of MMA[10–12] and also the copolymerization of oligo(lactide) macromonomers prepared from BisGMA[13].

Figure 4 shows that the total intensity of the C=O mode decreases at increasing polymerization time. The decomposition of this mode reveals that the band with the lower wavenumber of 1702 cm^{-1} vanishes during the copolymerization reaction whereas the intensity of the mode at 1718 cm^{-1} only decreases. The intensity ratio J_{1718}/J_{1702} of both modes increases from 1 to *ca* 30 (*Figure 8*).

The mode at 1718 cm^{-1} has to be assigned both to C=O vibrations of the copolymer and of residual BisGMA monomer as well as pendant methacrylate groups at the copolymer network. The wavenumber ($\nu = 1718$ cm^{-1}) of the C=O mode attributed to polymerized methacrylate units, is lower than that of the C=O mode of PMMA ($\nu \approx 1723$ cm^{-1})[11]. This finding can again be interpreted by hydrogen bonding between C=O groups and hydroxyl groups in the β-position. Some signs of an additional C=O mode at about $\nu = 1730\,\mathrm{cm}^{-1}$ are slightly discernible (*Figure 4*). However, it has not been possible quantitatively to analyse this mode until now.

CONCLUSIONS

Thermally fast curing materials can be prepared from BisGMA with pMS and VT, respectively. *FT* Raman spectroscopy has been proved as an outstanding method to characterize the course of the copolymerization reaction in the presence of quartz filler. Determination of the conversion of C=C double bonds of the styrene derivative and of BisGMA is simultaneously possible by a suitable decomposition of the C=C stretching vibration modes at 1630 and $1637\,\mathrm{cm}^{-1}$, respectively.

Conversions of about 95% of the C=C double bonds were obtained by curing at 150 to 200°C for 90 min corresponding to the conversion of monomer molecules as determined by extraction of the composites. These copolymer networks distinguish from those prepared with styrene at room temperature[7] by a relatively high homogeneity concerning their chemical composition.

The C=O stretching vibration mode of BisGMA at $\nu = 1718\,\mathrm{cm}^{-1}$ changes both in shape and intensity during the copolymerization reaction. Therefore, this mode is in no case suitable as an internal standard for analysing the conversion of C=C double bonds.

A more detailed analysis of the changes of the C=O stretching mode of various methacrylates during their polymerization reaction is in preparation.

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