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Polymerization of hydroxyalkyl methacrylates characterized by combination of FT-Raman and step-scan FT-i.r. photoacoustic spectroscopy

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Abstract

The homopolymerizations of bisphenol-A-bis(2-hydroxypropyl methacrylate) (BisGMA) and 2-hydroxyethyl methacrylate (HEMA) were monitored using FT-Raman spectroscopy and those of BisGMA also by FT-i.r. photoacoustic spectroscopy. Raman spectroscopy was applied to quantify the conversion of C=C double bonds of the monomers. Changes of intensity and wavenumber of the carbonyl band observed in the Raman spectra during the polymerizations were complementally studied by use of FT-i.r. photoacoustic spectroscopy. The carbonyl vibrational band at 1700 cm^{-1} was identified as the vibrational mode of the carbonyl group with hydrogen bonds and those at 1717 cm^{-1} (Raman) as well as 1725 cm^{-1} (i.r.) as the modes of the ‘free’ carbonyl group. Localization of the π-electrons of the carbonyl group and decreasing strength of the hydrogen bonds caused by the polymerization reaction result in a decrease of the Raman intensity and an increase of the i.r. intensity as well as of the wavenumber of the carbonyl i.r. vibrational mode at 1700 cm^{-1}. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyalkyl methacrylates; Polymerization; Carbonyl vibration

1. Introduction

(Meth)acrylic polymers and copolymers are broadly used as adhesives, coatings, lacquers and for medical applications. The conversion degree of C=C double bonds and the content of pendent C=C double bonds and/or of residual monomers after finishing the polymerization influence the thermal and mechanical properties of the final products. A wide range of analytical techniques is available for pursuing the course of polymerization. Extraction and analysis of the extracted sol by chromatography provide the content of residual monomers [1,2] and the content of soluble polymers.

Direct monitoring of the decrease of the intensity of C=C double bonds by vibrational spectroscopy was reported to be a suitable method for analysing the polymerization course [1–7]. Whereas the C=C double bonds give rise to a weak i.r. band, it is well known that this non-polar functional group shows a strong Raman band. For simple preparation of samples and the feasibility of on-line monitoring of the polymerization course, Raman spectroscopy has gained acceptance as a valuable qualitative as well as quantitative technique for analysing radical polymerizations [1,2,4–7].

Dywan et al. [8] used the C=O band as a reference for the quantitative determination of the content of methyl methacrylate in poly(methyl methacrylate), whereas other literature reports [9–14] and our own studies [1] pointed out that the carbonyl vibrational band changes its position and intensity during the polymerization.

In the Raman spectra of methyl methacrylate, two carbonyl vibrational bands were found by Rousseau et al. [14]. During the polymerization, the intensity of the carbonyl band at 1740 cm^{-1} increases, whereas that of the mode at 1725 cm^{-1} decreases. The authors explain these two carbonyl bands as a result of different dipole–dipole interactions between carbonyl qroups of the two configurations A and B in the polymer:

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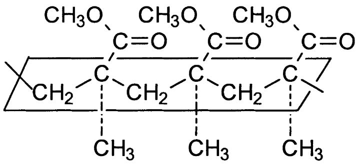
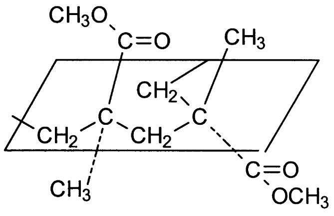


A

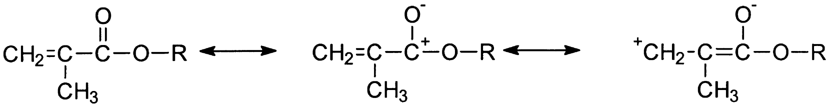


B

The weaker dipole–dipole interaction between two neighbouring C=O groups above and below the plane of the syndiotactic configuration B leads to a band at higher wavenumber. The band at 1725 cm^{-1} was attributed to overlapping modes resulting from methyl methacrylate monomer and the configuration A.

Based on ab initio MO calculations Faria et al. [15] predicted a more stable s-*cis* rotational conformer of poly(methyl acrylate) than the s-*trans* conformer, and assigned the stronger carbonyl band in the spectra at a wavenumber of 1722 cm^{-1} to the s-*cis* rotational conformer.

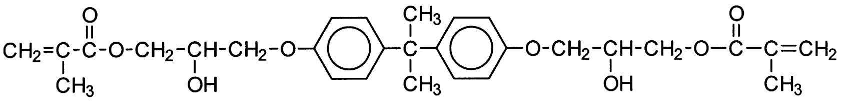
It is also known that the resonance effect in methacrylates influences the position and intensity of the carbonyl vibrational band [16].



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}R \longleftrightarrow CH_2{=}C(CH_3){-}\overset{+}{C}(O^{-}){-}O{-}R \longleftrightarrow {}^{+}CH_2{-}C(CH_3){=}C(O^{-}){-}O{-}R$$

This effect is enhanced due to hydrogen bonds. Xu et al. [11] observed two carbonyl vibrational bands at 1701 and 1727 cm^{-1} in the i.r. spectra of copolymers from various mixtures of 4-vinyl phenol with *n*-alkylmethacrylates. The band at the lower wavenumber was identified as a mode of the carbonyl group with hydrogen bonds and the other one as the mode of the 'free' carbonyl group. Measurements of the temperature dependency of the band intensities confirmed these assignments.

In our former publication [1], we have also reported on changes of carbonyl bands during the polymerization of BisGMA. In the case of the copolymerization of BisGMA with various styrene derivatives in the presence of quartz powder as filler, the intensity of the Raman band of the carbonyl group is rather weak and, therefore, a quantitative analysis is difficult. However, in the i.r. spectra a strong carbonyl vibrational band can be expected. For the traditional i.r. technique it is necessary to grind the samples. On the other hand, FT-i.r. spectroscopy combined with very sensitive photoacoustic (PA) detection does also offer the advantage of the simple non-destructive sample preparation as in the case of Raman spectroscopy. Applying both spectroscopic techniques it is now possible to record i.r. and Raman spectra of one and the same sample without time-consuming and faulty sample preparation.



BisGMA

The alterations in the spectral region of the carbonyl vibration in the course of the homopolymerization of BisGMA reported in Ref. [1], were examined in more detail by using both FT-Raman and FT-i.r. photoacoustic spectroscopy (PAS). These results will be compared with the alterations observed during the polymerization of 2-hydroxyethyl methacrylate (HEMA). Relationships between positions and intensities of the C=O stretching vibrational bands monitored by i.r. PAS and conversions of C=C double bonds determined by Raman spectroscopy were of interest.

2. Experimental

2.1. Materials

The synthesis of BisGMA from diglycidyl ether of bisphenol-A (Epilox 17.01, Leuna-Werke GmbH; epoxy value (groups): 5.81 eq kg^{-1}, $M = 344\ g\ mol^{-1}$) and methacrylic acid (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 as described by Sandner and Schreiber [17].

HEMA (Röhm Chemische Fabrik GmbH; 99.6%, stabilized with 100 ppm HQME), di-*tert*-butyl peroxide (DTBP, Peroxid-Chemie GmbH; techn. pure) the photoinitiator 1-phenyl-2-hydroxy-2-methylpropan-1-on (Darocur 1173; Merck) and glycerol (99.5%, Aldrich) were used as received.

2.2. Polymerization

BisGMA was mixed with 0.5 wt% DTBP, ca. 10 mg of the mixture were poured into aluminium pans (diameter 5 mm, depth 2 mm), placed for curing in an air oven at 150°C for 45 min and then at 200°C for 45 min. The polymerization was stopped by cooling the samples to 0°C in ice at different times.

Eight–10 mg of a mixture of 4.52 mol kg^{-1} HEMA in glycerol with 0.55 mol% Darocur 1173 referred to HEMA were photopolymerized in aluminium pans (diameter 4.8 mm, depth 1 mm) in the differential scanning calorimeter DSC 220 C (Seiko Instruments Inc.) with a photomodule containing a Hg–He lamp (UXM-200 YA), monitoring the polymerization heat at 30°C [18]. The photopolymerization was terminated by quenching the samples in the pans in liquid nitrogen at different reaction times. The samples were then directly used for the Raman spectroscopic studies.

2.3. Analysis

The conversion of C=C double bonds and the changes of the carbonyl bands were studied by FT-Raman spectroscopy. The Raman spectra were recorded with a Bruker Fourier transform infrared 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 in plane deformation of the p-substituted phenyl ring at 1608 cm^{-1} for BisGMA and the bending mode of the ethoxy group at 606 cm^{-1} for HEMA were used as internal references for the polymerizing monomers.

The FT-i.r. PA spectra were collected on a Bruker FT-IR spectrometer IFS 28 equipped with a MTEC Photoacoustics model 200 photoacoustic cell. The pans with the samples were placed into the PAS sample holder. Using the Bruker OPUS software package, the step-scan experiments were conducted by applying the phase modulation technique with a modulation frequency of 25 Hz and a modulation amplitude of $2\lambda_{HeNe}$ (1.25 μm) and 10 coadditions. In this option the moving mirror of the interferometer oscillates sinusoidally about the stopping position with the desired modulation frequency and amplitude. In this manner the sinusoidal phase modulation of the radiation is provided. The demodulation of the PA signal with reference to the i.r. beam modulation is provided by the acquisition processor and results in the ‘inphase’ (I) and ‘in-quadrature’ (Q) components. The PA spectra were recorded using the strong Norton–Beer apodization function and Mertz phase correction. A delay time of 120 ms was chosen for stabilizing the step-scan position. Before measuring each sample the PA cell was purged with helium. The magnitude spectrum $M = (I^2 + Q^2)^{1/2}$ was calculated from the two signal components I and Q. All spectra were normalized proportioning the sample spectrum with a carbon black spectrum. The intensities and wavenumbers of the C=O and the OH stretching bands were determined after

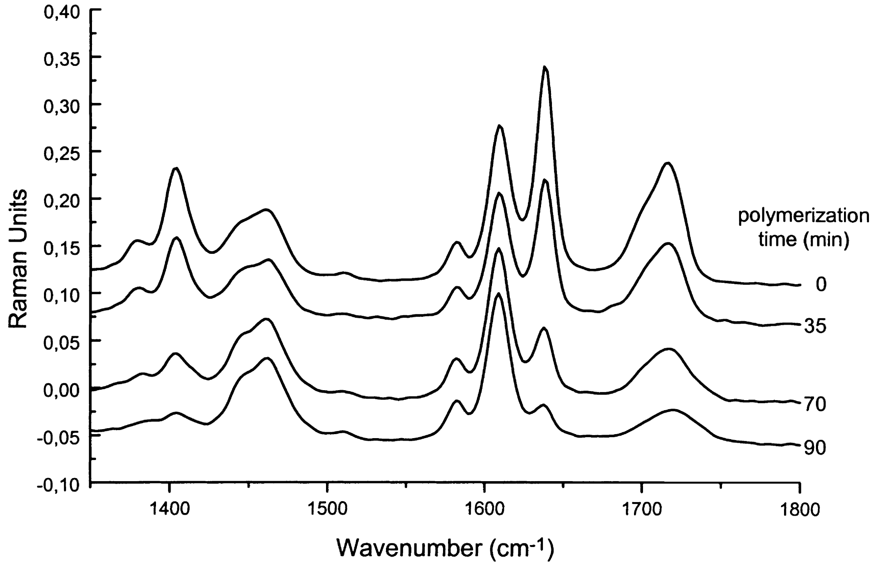


Fig. 1. Variation of Raman spectra of BisGMA with the polymerization time.

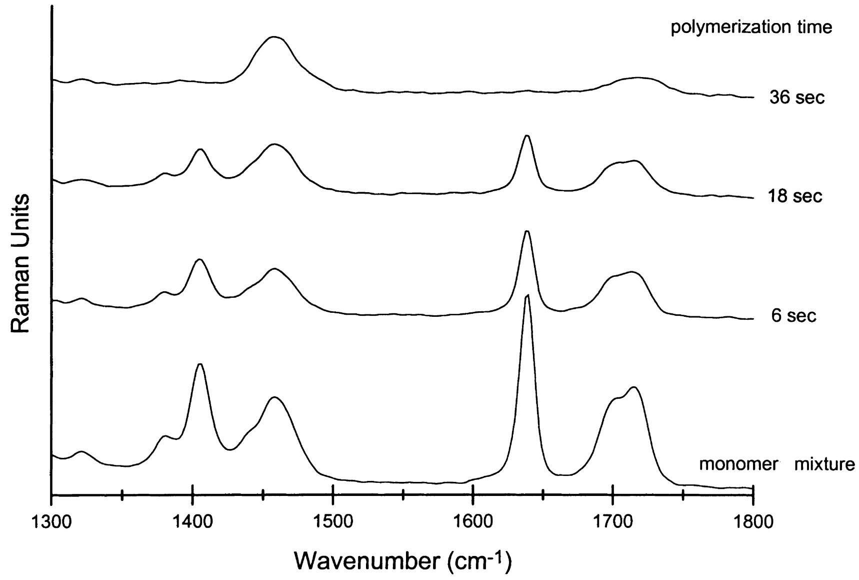


Fig. 2. Variation of Raman spectra of HEMA in glycerol with the time of photopolymerization.

Table 1
Assignment of the bands of interest in the FT-Raman spectra of Figs 1 and 2 and the FT-i.r. PA spectrum of Fig. 3

Wavenumber (cm^{-1})		Assignment
Raman	I.r.	
606		$-O-CH_2-CH_2 <$ used as reference for HEMA
1404		$> C{=}CH_2$ stretch
1608	1608	In-plane deformation of phenyl ring, used as reference for BisGMA
1637	1637	$> C = C <$ stretch
1710	1710	$> C{=}O$ stretch
	3470	$-OH$ stretch

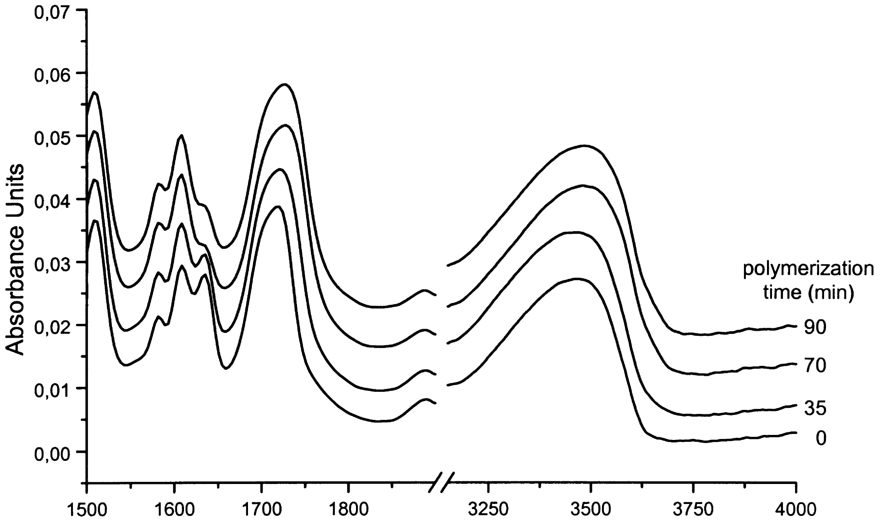


Fig. 3. Variation of step-scan FT-i.r. PA magnitude spectra of BisGMA with the polymerization time.

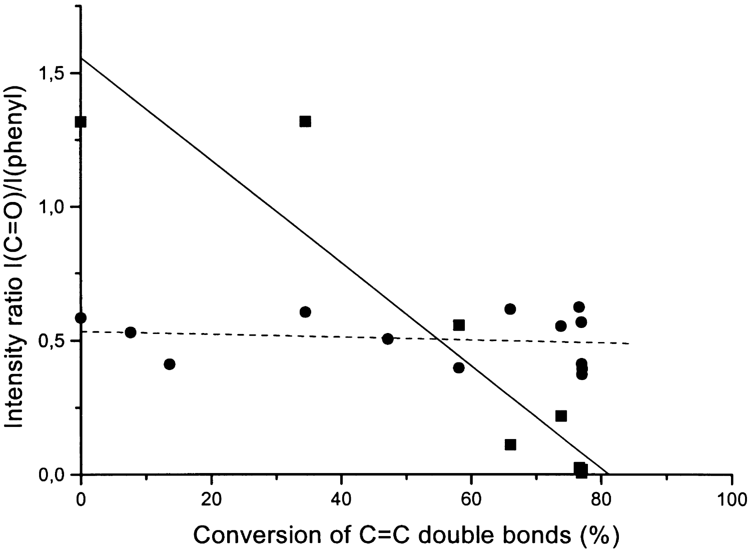


Fig. 4. Intensity of the carbonyl Raman bands versus conversion of C=C double bonds during the homopolymerization of BisGMA (0.5 wt% DTBP, polymerization temperature: 45 min 150°C, then 45 min 200°C); (■) band 1, $\nu = 1700\ \mathrm{cm}^{-1}$; (●) band 2, $\nu = 1717\ \mathrm{cm}^{-1}$.

decomposition of the overlapping bands in the ranges of 1650–1850 and 3230–3750 cm^{-1}, respectively. The ‘Levenberg–Marquardt’ strategy was used for fitting the function to the experimental data.

3. Results and discussion

The Raman spectra of BisGMA and HEMA monitored during their homopolymerization are presented in Figs 1 and 2, respectively. Fig. 3 shows the i.r. PA magnitude spectra of polymerizing BisGMA. Table 1 contains the vibrational bands of interest. The spectra exhibit an excellent signal to noise ratio. The conversion of the C=C double bonds during the polymerization was determined from the decrease of the C=C stretching Raman band intensity at 1637 cm^{-1} with respect to that of the phenyl ring at 1608 cm^{-1} for BisGMA and with respect to that of the ethoxy group at 606 cm^{-1} for HEMA. Variations of the C=O vibrational bands were studied after fitting and normalizing to the reference bands in the Raman and PA spectra, respectively.

3.1. Raman spectroscopy

It is evident from Figs 1 and 2 that the carbonyl vibration around 1710 cm^{-1} exhibits a non-symmetric bandshape.

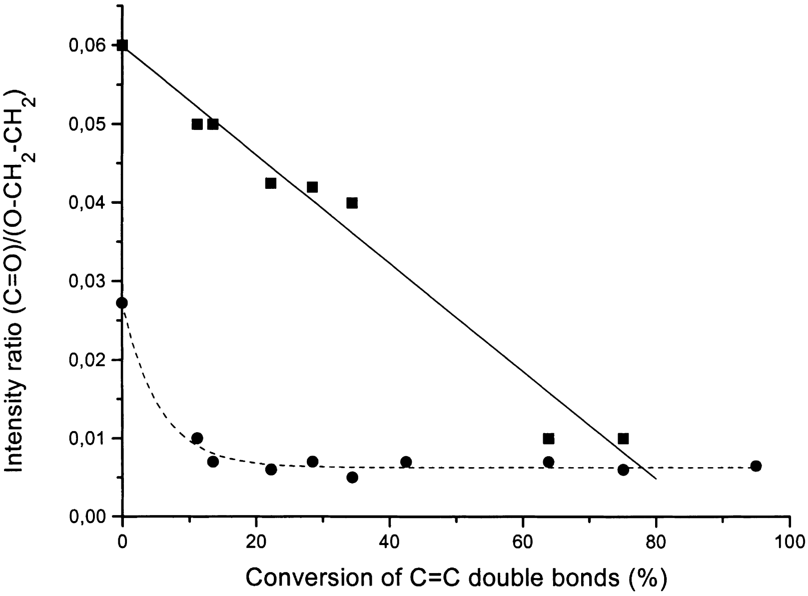


Fig. 5. Intensity of the carbonyl Raman bands versus conversion of C=C double bonds during the polymerization of 4.52 mol kg^{-1} HEMA in glycerol (0.55 mol% photoinitiator related to HEMA; polymerization temperature, 30°C); (■) band 1, $\nu = 1700\ \mathrm{cm}^{-1}$; (●) band 2, $\nu = 1717\ \mathrm{cm}^{-1}$.

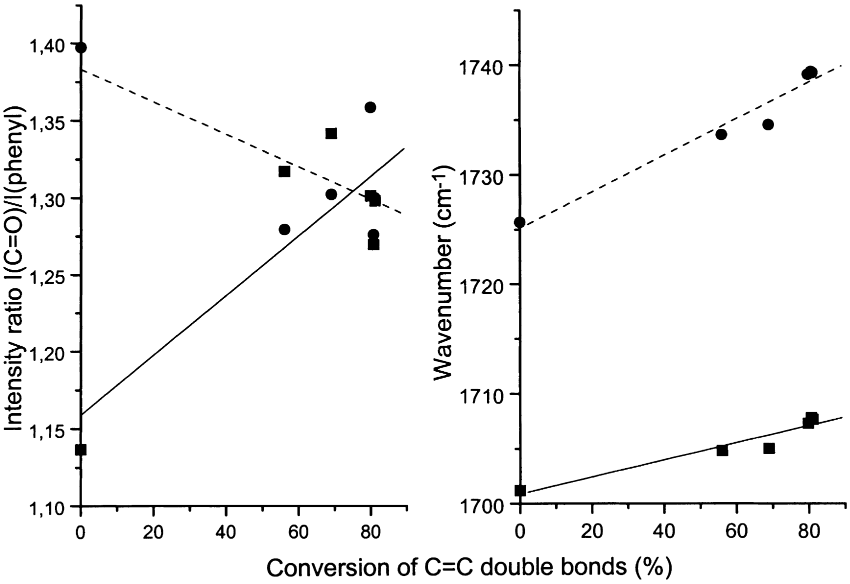


Fig. 6. Intensities and positions of the i.r. PA carbonyl bands of BisGMA during its homopolymerization (0.5 wt% DTBP; polymerization temperature, 45 min 150°C then 45 min 200°C); (■) band 1; (●) band 2.

After decomposition of this spectral feature, two Raman bands appear at 1700 and 1717 cm^{-1} where the first one is of ca. three-fold intensity for both monomers (Figs 4 and 5). In accordance with Ref. [11], the first band at 1700 cm^{-1} can be identified as the mode of the carbonyl groups with strong hydrogen bonding and the second one as vibrations of the ‘free’ carbonyl groups.

As shown in Figs 4 and 5, the intensity of the C=O band at 1700 cm^{-1} decreases with increasing conversion of C=C double bonds, whereas that of the C=O band at 1717 cm^{-1} is nearly constant. Variations of the band intensities caused by changes of the viscosity or optical properties during the polymerization can be neglected. Measurements between 0 and − 20°C, the range of the glass transition temperature of BisGMA monomer (about − 8°C), did not indicate any changes. The C=C double bond of the methacrylate group is transformed into a single bond by polymerization, and thus the delocalization of the π-electrons of the carbonyl group is diminished. For that reason the intensity of hydrogen bonding between carbonyl and hydroxyl groups, and with that the intensity of the vibrational band at 1700 cm^{-1}, decrease approximately linearly with the conversion of the monomers.

3.2. FT-i.r. photoacoustic spectroscopy

It is clear from Fig. 3 that the non-symmetrical i.r. bandshape of the carbonyl vibration can be decomposed into two

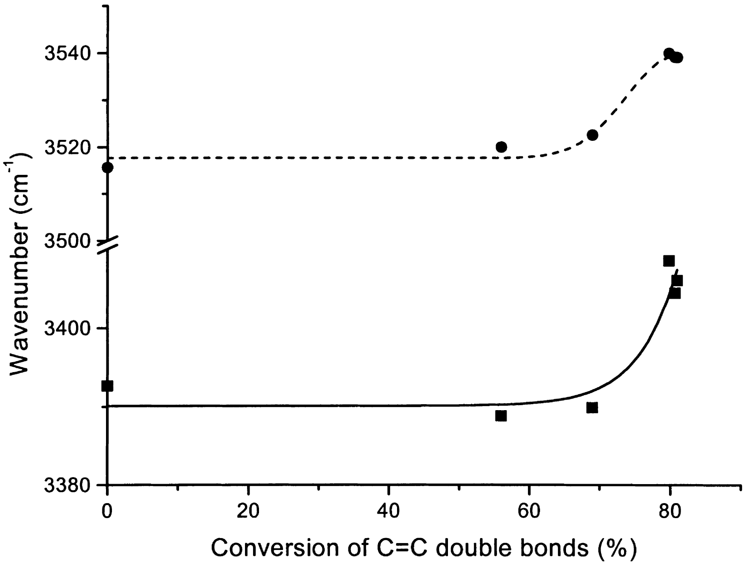


Fig. 7. Wavenumbers of the i.r. PA hydroxyl bands of BisGMA during its homopolymerization (0.5 wt% DTBP; polymerization temperature, 45 min 150°C, then 45 min 200°C; step-scan modus, He); (■) band 1; (●) band 2.

vibrational bands at 1701 and 1725 cm^{-1}, as reported for the Raman band. The better signal-noise ratio of these i.r. bands than that of the Raman bands, enabled to determine also the shifts of their positions caused by the polymerization reaction.

The wavenumbers of the two bands increase during the polymerization (Fig. 6). Effects due to changes of the viscosity and optical properties during the polymerization can be neglected since the position of the aromatic vibrational band remains constant during the whole polymerization course.

An increase in the intensity of the carbonyl band at the lower wave number of 1701 cm^{-1} is clearly shown. The π-electrons of the carbonyl group are localized increasingly by polymerization because their conjugation with the C=C double bond of the methacrylate disappears, and hydrogen bonds between hydroxyl and carbonyl groups are weakened. Therefore, increasing polarization of the carbonyl group by decreasing delocalization of the π-electrons and decreasing strength of the hydrogen bonds lead to increasing intensities and an increasing wavenumber of the first carbonyl band (Fig. 6).

Changes in the strength of hydrogen bonds can also be observed in the region of the hydroxyl vibrations from 3100 to 3700 cm^{-1}. Only vibrations of hydroxyl groups with hydrogen bonds are observable as shown in Fig. 3.

The broad hydroxyl vibrational band can be decomposed into one at 3393 cm^{-1} and another one at 3516 cm^{-1}. These two vibrational bands result from inter- and intramolecular interactions between hydroxyl groups and between hydroxyl and carbonyl groups.

The wavenumbers of the hydroxyl bands are constant up to a conversion degree of C=C double bonds of nearly 70% (Fig. 7). Pendant C=C double bonds and the flexible ester groups still allow the formation of hydrogen bonds. The increase of the wavenumbers of hydroxyl vibrations with increasing C=C double bond conversion above 70% indicates the decreasing strength of the hydrogen bonds caused by the low content of residual BisGMA monomer and pendant C=C double bonds in the rigid BisGMA polymer network.

4. Conclusions

The combination of FT-Raman and FT-i.r. photoacoustic spectroscopy is very useful for monitoring the free radical polymerization course of methacrylates. Using Raman spectroscopy it is possible to determine the conversion of the C=C double bonds exactly. The i.r. PA spectroscopy supplements the Raman spectroscopy by elucidating changes of the vibrational bands of polar groups like those of the carbonyl and the hydroxyl group. The alterations of the carbonyl band at 1700 cm^{-1} observed by Raman spectroscopy, during the polymerization of two hydroxyalkyl methacrylates, can be interpreted as alterations of the strength of the hydrogen bonds between carbonyl and hydroxyl groups and localization of the π-electrons of the carbonyl group of the polymer. The increasing intensity of the i.r. carbonyl band at 1701 cm^{-1} results from the localization of the π-electrons and the increasing polarization of the carbonyl groups with increasing conversion of double C=C bonds. The reduced strength of the interactions between hydroxyl and carbonyl groups in poly(BisGMA) manifests itself by increasing wavenumbers of the hydroxyl vibrational bands.

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