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Quantitative determination of unsaturation in photocured halogenated acrylates and methacrylates by FT-IR and Raman-spectroscopy and by thermal analysis

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Abstract

The photo-polymerization of tetrachloroethylacrylate (TeCEA), pentafluorophenylacrylate (PFPA) and pentafluorophenylmethacrylate (PFPMA) was examined by quantitative FT-IR and FT-Raman spectroscopy and by thermal analysis. The agreement between the FT-Raman results and thermal analysis was good for all monomers. The FT-IR measurement yielded higher percentages of unsaturation than the two other techniques in the slowly reacting PFPMA polymer, which can be attributed to oxygen quenching effects. Calculations of unsaturation based on spectroscopic measurements were carried out using the relative band ratio method. The influence of the choice of the internal reference band on the unsaturation calculation was examined. The photo-polymerization of the acrylates reached conversions of 95%–99% after irradiation of only a few minutes, samples which contained PFPMA reached conversions of about 85% after 1.5 h of irradiation. Volatile compounds in the resulting polymers were quantified and identified by thermogravimetic analysis (TGA) and thermal desorption followed by gas chromatography with mass spectrometric detection (TD-GC-MS), respectively. Glass transition temperatures of the resulting polymers as determined by differential scanning calorimetry (DSC) vary from 70°C to 125°C. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Halogenated acrylates; Quantitative infrared spectroscopy; Quantitative Raman spectroscopy

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1. Introduction

Fluorine and chlorine containing acrylates and methacrylates find a variety of applications. Special interest in highly halogenated poly(meth)acrylates is based on their strongly reduced optical absorption in the near-IR (NIR) [1–4]. This makes the polymers of these (meth)acrylates very useful for application in optical telecommunication where information is transported in the so-called transmission windows around 1310 nm and 1550 nm.

In the POPCORN approach optical components are fabricated by photo-curing of liquid halogenated (meth)acrylates which were applied on moulded PMMA substrates [5–7]. With regard to the long term chemical, thermal and optical stability of fabricated components the knowledge of monomer conversion and polymer glass transition temperature is essential.

IR and Raman spectroscopy are intensively used in polymer analysis to study branching, cross-linking, crystallinity, composition and residual monomer content [8–15].

In this paper quantitative determination of residual unsaturation in photocured (meth)arylates was carried out by thermogravimetric analysis (TGA) and also by FT-Raman and transmission-FT-IR spectroscopy using the relative band ratio method [16,17]. By the used spectroscopic methods not only monomer unsaturation but also for instance end group unsaturation were measured and therefore the volatile compounds in the polymers were characterized by TD-GC-MS.

For the unsaturation determination by vibrational spectroscopy using the relative band ratio method, the intensity decrease of the vinylic-bond-vibrations resulting from polymerization is determined with reference to vibrations which do not directly take part in the polymerization reaction (internal standard method). An assumption for the application of this method is that the relative absorptivity or Raman

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activity of the reference vibrations are the same in the monomer and in the polymer. Typical acrylate bands which can be used to follow polymerization are, for example, the 1635 cm^{-1} band with the typical shoulder at 1625 cm^{-1} resulting from the C=C stretching vibration (methacrylates do not have the 1625 cm^{-1} shoulder) and the 1407 cm^{-1} band caused by the CH_2= bond moiety. As starting point (100% unsaturation) the relative band ratio of typical acrylate band intensities to internal standard band intensities in the monomers was used.

2. Experimental

2.1. IR spectroscopy

FT-IR measurements were carried out on a Bruker IFS 28. The spectral resolution was set at 4 cm^{-1}. Sixty-four interferograms were added for each spectrum. A Bleckman–Harris three-term function was used for apodization. Samples were prepared by doctor-blading of monomers on KBr-pellets. To prevent vaporization of monomers during irradiation (under Ar stream) they were covered by a 15 μm FEP-foil (Du Pont). After irradiation the FEP-foil was removed and substituted by a second KBr-pellet. The typical resulting polymer layer thickness was measured to be about 10 μm.

2.2. Raman spectroscopy

FT-Raman measurements were performed using a Bruker RFS 100. Excitation source was a Nd:YAG-Laser (1064 nm), at an intensity of 1000 mW. Raman samples were prepared by filling monomers in quarz-tubes with inner diameters of 2 mm, flushed with Ar and finally cured by UV-irradiation.

2.3. Spectral calculation

For evaluation of the spectra and calculations the Bruker software OPUS 2.0 was used. Integral band intensities in IR and Raman were calculated by curve fitting procedures based on the Levenberg–Marquardt algorithm. The lineshape was a parameter of the curve-fitting procedure.

2.4. Thermal analysis

TGA analysis were done under nitrogen on a TA Instruments TGA 2950 and DSC analysis on a Seiko RDC 220. The instrument used for TD-GC-MS was a GC8165-Trio 1000. The GC column was a 5 μm DB-1, 30 m × 0.32 mm. Ionisation was realized by EI^+ and CI^+ with CH_4, NH_3 and isobutane and CI^- using CH_4-NH_3.

2.5. Polymerization conditions

Polymerization experiments were performed under argon atmosphere at room temperature with 1 wt% of photo-initiator Darocur 1173™ (Ciba-Geigy) which has its absorption maximum at 365 nm. Irradiation source was a high-pressure mercury-vapour lamp (Osram HPK 125) with an additional WG 360 optical filter to prevent monomers/polymers from photochemical damage. Intensity of this lamp at the sample position (8 cm distance to lamp surface) at 365 nm was measured to be 2.80 mW cm^{-2}.

2.6. Chemicals

TeCEA was synthesized by the method of F. Hrabák and H. Pivcová [21], PFPMA was received from University of Versailles [22] and PFPMA was synthesized in accordance with the procedure described by B. Boutevin et al. [23]. All monomers had a purity of $>$ 99.9% (GC). Photoinitiator Darocur 1173™ was purchased from Ciba–Geigy.

3. Theory

The absorption ratio of two bands in infrared spectroscopy (acrylate band χ and internal standard band δ) in a one monomer system based on the Lambert–Beer law is given by:

$$\frac{A_\chi}{A_\delta} = \frac{\epsilon_\chi \cdot c_\chi}{\epsilon_\delta \cdot c_\delta} = X_{\mathrm{Monomer}} \tag{1}$$

where ϵ is the absorptivity, c the concentration and A the absorption.

If by polymerization of this monomer band χ is decreased in intensity, the relative concentration of χ' (acrylate band in the polymer) and δ' (internal standard band in the polymer) in the polymer leads to Eq. (2):

$$\frac{A_{\chi'}}{A_{\delta'}} = \frac{\epsilon_{\chi'} \cdot c_{\chi'}}{\epsilon_{\delta'} \cdot c_{\delta'}} = X_{\mathrm{Polymer}} \tag{2}$$

By dividing X_{Polymer} and X_{Monomer} results Eq. (3):

$$\frac{X_{\mathrm{Polymer}}}{X_{\mathrm{Monomer}}} = \frac{\epsilon_\delta \cdot c_\delta \cdot \epsilon_{\chi'} \cdot c_{\chi'}}{\epsilon_\chi \cdot c_\chi \cdot \epsilon_{\delta'} \cdot c_{\delta'}} \tag{3}$$

Assuming that $\epsilon_{\delta'} = \epsilon_\delta$ and $\epsilon_{\chi'} = \epsilon_\chi$ as well as $c_{\delta'} = c_\delta$ Eq. (3) simplifies to Eq. (4):

$$\frac{X_{\mathrm{Polymer}}}{X_{\mathrm{Monomer}}} = \frac{c_{\chi'}}{c_\chi} \tag{4}$$

With Eq. (4) the content of unsaturation can be directly calculated.

Quantitative measurements using IR spectroscopy can be carried out as absolute measurements (by using a double-beam spectrometer or taking a background spectrum) and results between different users on different instruments are quantitatively comparable. This is not the case for Raman measurements.

The quantitative relations of intensities in Raman spectroscopy as developed by Plaszek [18] are not suitable for practical application. So the more convenient Eq. (5) for

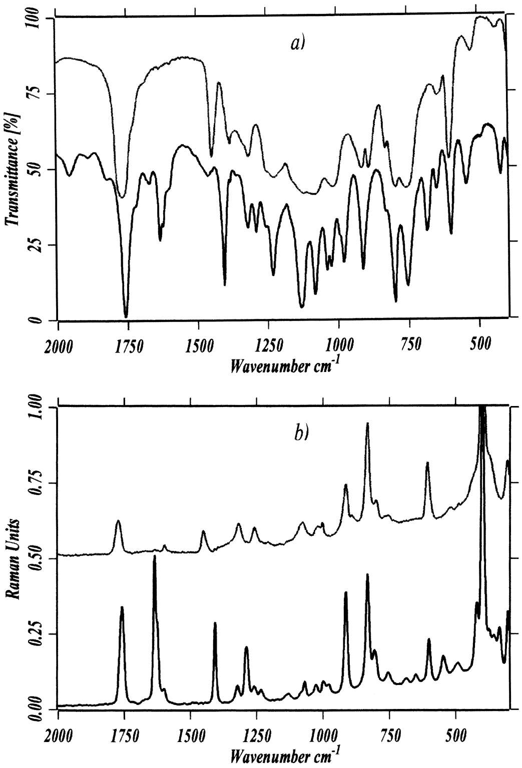

Fig. 1. (a) FT-IR spectra of TeCEA monomer and TeCEA polymer; and (b) FT-Raman spectra of TeCEA monomer and TeCEA polymer.

the Raman intensity (I_{Raman}) which is very similar to the Lambert–Beer law was used:

$$I_{\text{Raman}} = K \cdot \alpha \cdot C \tag{5}$$

K in this equation means the scattering cross-section of the acrylate bonds and C is the concentration of the acrylate bonds. The factor α depends upon the experimental setup and the sample morphology. α is determined by the laser source intensity and the laser wavelength, the collection and detector efficiency, the illuminated sample volume, the sample properties (scatter, attenuation, refractive index) and the sample position [19]. Therefore a standard has to be used in quantitative Raman measurements. For measurements of solutions, for instance, commonly the solvent is used as standard [20], alternatively the external standard method is applied by addition of one or more reference substances in known concentration. For a pure sample, an internal standard band can be used. The experimental conditions and sample preparation then have to be kept constant during the quantitative measurements. In this case α can be considered as constant and K and I in Eq. (5) correspond to ϵ and A in the Lambert–Beer law. This is of course an approximation for the observation of a polymerization reaction because, for example, the refractive index of the sample and the specific intermolecular interactions change. In this paper for unsaturation calculations based on quantitative Raman measurements Eq. (4) is used.

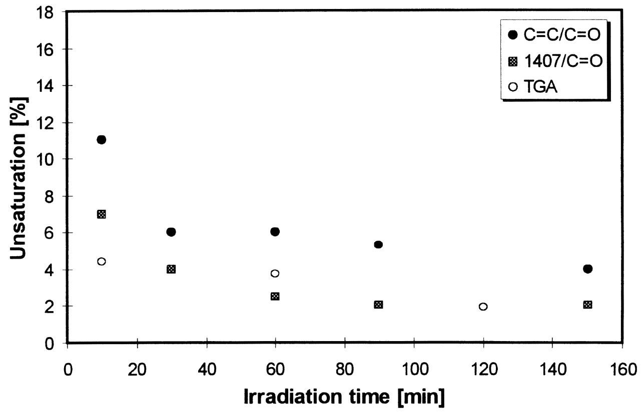

Fig. 2. FT-IR spectroscopy of photo-polymerization of TeCEA. Unsaturation as a function of irradiation time. C=C means the sum of intensity of 1625 cm^{-1} and 1635 cm^{-1} bands (for comparison TGA results are shown).

For unsaturation measurements in poly(meth)acrylates the Raman technique is more applicable than the IR technique because of the very high intensities of the acrylate bands.

4. Results

4.1. Tetrachloroethylacrylate

4.1.1. Unsaturation determination by vibrational spectroscopy in TeCEA polymer

Fig. 1 shows the monomer and polymer infrared and Raman spectra of TeCEA. In quantitative infrared spectroscopy of TeCEA (Fig. 1a) only the carbonyl band at 1758 cm^{-1} (monomer) and 1771 cm^{-1} (polymer), respectively, can be used as an internal standard band. Quantification with other theoretically possible internal standard bands (e.g. $\nu_{\text{C–Cl}}$ or $\delta_{\text{C–Cl}}$ between 200 cm^{-1} and 800 cm^{-1}) is not possible because of the strong overlap with other bands. Decreasing intensity can be observed for the acrylate specific weak double band caused by C=C stretching vibration at 1635 cm^{-1} and 1625 cm^{-1}, respectively. Calculation of integral absorption can be done accurately (no overlap). For unsaturation calculation the strong 1407 cm^{-1} band is also used. This band is caused by the CH_2=C deformation vibration. Intensity calculation of this band has to be done by curve-fitting to remove the influence of overlapping bands.

The C=C stretching vibration leads in Raman spectra to very intensive bands at 1635 cm^{-1} and 1625 cm^{-1}. Further, bands resulting from the unsaturation in acrylates at 1407 cm^{-1} and 1290 cm^{-1} were applied for calculation of the unsaturation. As reference bands for quantitative calculations the C–Cl stretching and deformation vibrations in the wavenumber area from 244 to 834 cm^{-1} were used. For intensity calculation of bands in this area curve-fitting was applied.

The unsaturation determined for the photo-polymerization of a mixture of TeCEA with 1 wt% of photoinitiator

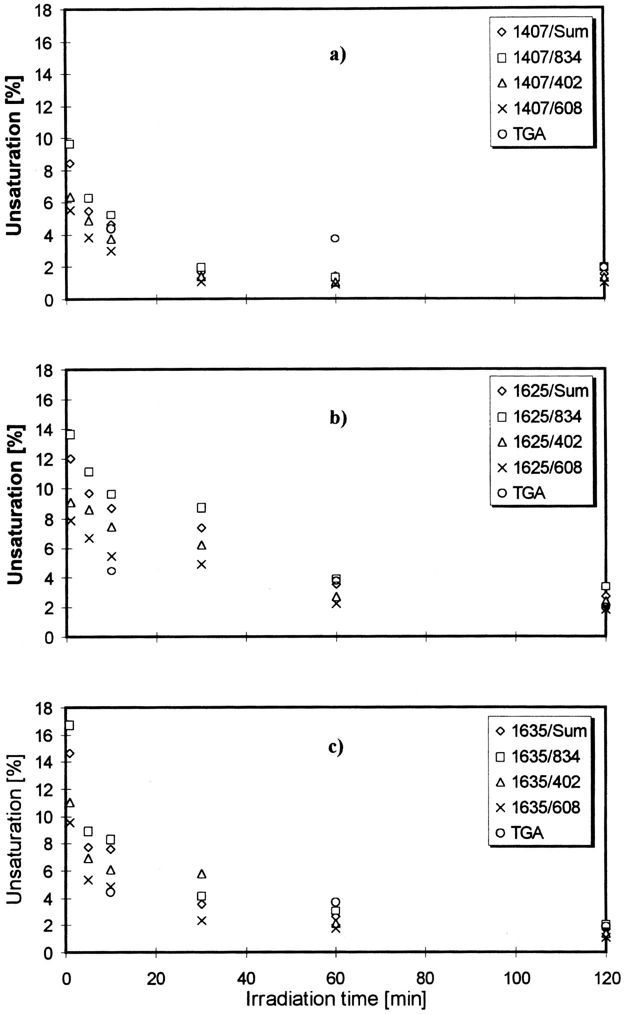

Fig. 3. FT-Raman spectroscopy of photo-polymerization of TeCEA. Unsaturation as a function of irradiation time. (a) 1290 cm^{-1} band relative to internal standard bands at 402 cm^{-1}, 608 cm^{-1}, 834 cm^{-1} and 244–305 cm^{-1} (Sum), respectively. (b) 1407 cm^{-1} band relative to internal standard bands. (c) 1635 cm^{-1} band relative to internal standard bands.

(Darocur 1173™) followed by FT-IR spectroscopy is shown in Fig. 2. This figure illustrates the high polymerization ratio. After an irradiation time of only 10 min about 95% conversion is reached.

In Raman spectroscopy the use of different internal standard bands was examined as well. The high conversion in photochemically initiated polymerization of TeCEA as determined by FT-Raman spectroscopy is shown in Fig. 3. Observed differences in unsaturation values in Fig. 3 are mainly caused by the choice of the internal standard bands. These bands at 834 cm^{-1}, 608 cm^{-1}, 402 cm^{-1} and in the range 244–305 cm^{-1} are attributed to C–Cl deformation and stretching vibrations. To compare the influence of the choice of the internal standard band on the measured results, the relative changes of these bands with respect to each other during the polymerization were examined.

When the ratio of the intensities of the 834 cm^{-1} reference band before and after polymerization is set to 1, the following results are obtained for the different bands:

$$1.77_{608\mathrm{cm}^{-1}} > 1.41_{402\mathrm{cm}^{-1}} > 1.16_{244\text{–}305\mathrm{cm}^{-1}} > 1_{834\mathrm{cm}^{-1}} > 0.44_{\mathrm{C=O}}$$

The magnitude of the decrease is reflected in the results shown in Fig. 3. The carbonyl band is not used as an internal standard band in the Raman spectra because the intensity decrease of this band during the polymerization is, as quantified previously, 2–4 times higher than that of the internal standard bands used for this determination.

Relative standard deviations of TeCEA unsaturation determinations and the deviations derived from these results with regard to an adopted unsaturation content of 5% in the resulting polymer measurements (given between brackets) are listed in Table 1. As a consequence of the curve-fitting process in which the 1625 cm^{-1} band is a shoulder of the 1635 cm^{-1} band, values calculated using this line show

Table 1
Standard deviations of band intensity ratios of FT-Raman monomer measurements. Failures in unsaturation calculations caused by deviations of monomer measurements for an unsaturation value of 5% are given in brackets

1407 cm^{-1}/Sum	1625 cm^{-1}/Sum	1635 cm^{-1}/Sum	1290 cm^{-1}/Sum
1.22% (± 0.06%)	17.05% (± 0.73%)	3.61% (± 0.17%)	1.35% (± 0.07%)
1407 cm^{-1}/832 cm^{-1}	1625 cm^{-1}/832 cm^{-1}	1635 cm^{-1}/832 cm^{-1}	1290 cm^{-1}/832 cm^{-1}
1.79% (± 0.09%)	16.36% (± 0.71%)	3.91% (± 0.19%)	0.74% (± 0.04%)
1407 cm^{-1}/402 cm^{-1}	1625 cm^{-1}/402 cm^{-1}	1635 cm^{-1}/402 cm^{-1}	1290 cm^{-1}/402 cm^{-1}
3.78% (± 0.18%)	15.47% (± 0.67%)	6.21% (± 0.30%)	3.68% (± 0.18%)
1407 cm^{-1}/608 cm^{-1}	1625 cm^{-1}/608 cm^{-1}	1635 cm^{-1}/608 cm^{-1}	1290 cm^{-1}/608 cm^{-1}
0.81% (± 0.04%)	17.62% (± 0.75%)	2.50% (± 0.12%)	1.01% (± 0.05%)

Table 2
Thermal analysis of TeCEA polymer

Irradiation time [min]	TGA weight loss [%]	Degradation [°C]	T_g [°C] 1. cycle[d]	T_g [°C] 2. cycle[d]
10	4.37[a] (30–168)[c]	210 [a]	—	—
60	3.74[b] (30–240)[c]	260 [b]	59–82	63–85
90	1.94 [a] (60–205)[c]	235 [a]	—	—

[a] Heating rate 1°C min^{-1}.
[b] Heating rate 20°C min^{-1}.
[c] Temperatures between weight loss is quantified.
[d] DSC onset and offset temperatures.

larger variations. The 1290 cm^{-1} and 1407 cm^{-1} bands are isolated bands and therefore the deviations obtained for the unsaturation are much lower when these bands are used.

4.1.2. Thermal analysis of TeCEA polymer

Results of TGA and DSC analysis of photocured TeCEA polymer samples are summarized in Table 2.

By thermal desorption GC-MS with different temperature steps (70°C, 170°C and 240°C) volatile components in TeCEA polymer (60 min UV irradiated 99 wt% TeCEA/ 1 wt% Darocur 1173™) were identified. At 70°C the major part of the volatile components was identified to be water, a small amount of TeCEA monomer and benzaldehyde and acetone as products of the degradation of the photo-initiator. At 170°C and 230°C main volatile components are free monomer, unreacted Darocur 1173™, water and a HCl-TeCEA-addition compound. Also small amounts of benzaldehyde, acetone and tetrachloroethylacetate were found. Only at 240°C was trichloroethanal detected. The formation of the HCl-TeCEA addition product can be explained by hydrolysis of the polymer. To prove the formation mechanism the ground TeCEA polymer (0.003 wt%) was mixed with water and stirred for three days at 35°C. This reaction leads to a strong decrease of the pH-value to 3.7 and by ion chromatography 7.3×10^{-4} mol l^{-1} Cl^- could be identified. One dominating reaction product, 1,1,1-trichloro-2,2-dihydroxy-ethane, a narcotic, was identified by GC-MS. The formation of this product can be explained by the reaction in Fig. 4.

4.2. Pentafluorophenylacrylate

4.2.1. Unsaturation determination by vibrational spectroscopy in PFPA polymer

Fig. 5 shows the monomer and polymer IR and Raman spectra of PFPA. Like in TeCEA, the acrylate double bond gives rise to vibrations at 1625 cm^{-1}, 1635 cm^{-1} and at

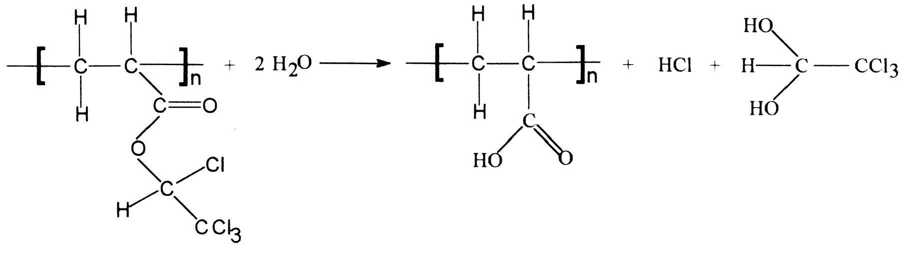

Fig. 4. Formation of 1,1,1-trichloro-2,2-dihydroxy-ethan from TeCEA.

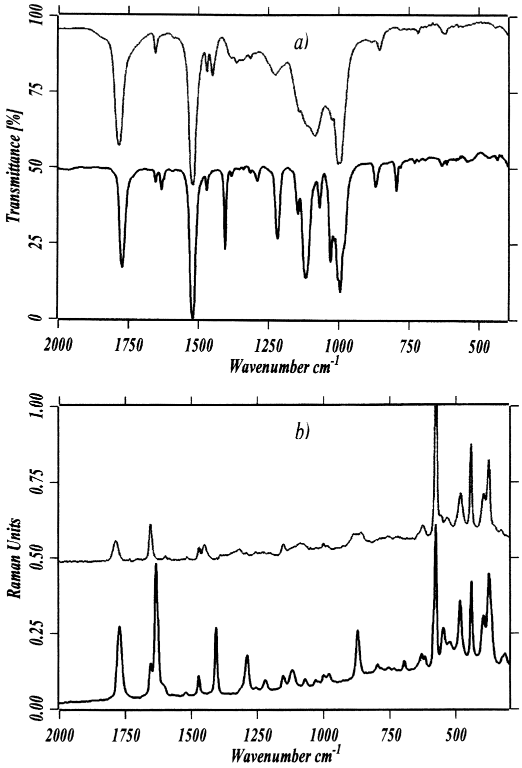

Fig. 5. (a) FT-IR spectra of PFPA monomer and PFPA polymer; and (b) FT-Raman spectra of PFPA monomer and PFPA polymer.

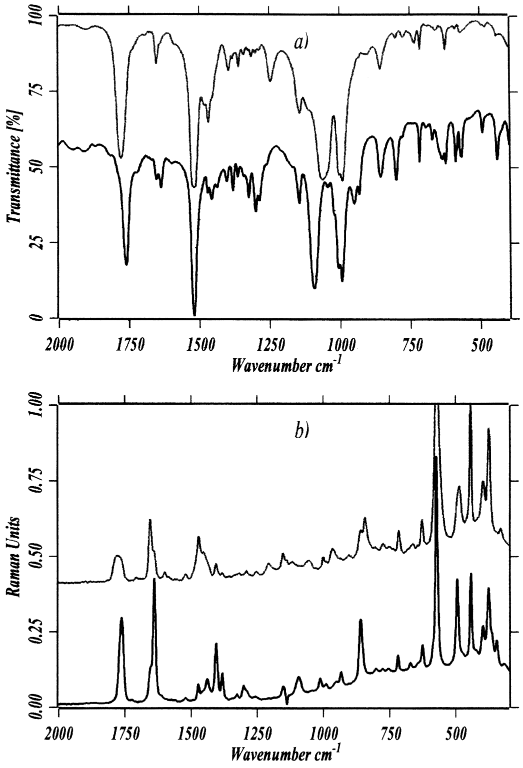

Fig. 7. (a) FT-IR spectra of PFPMA monomer and PFPMA polymer; and (b) FT-Raman spectra of PFPMA monomer and PFPMA polymer.

1407 cm^{-1} which can be used to follow the polymerization. In the IR spectra of the PFPA polymer two reference bands can be used, the C=O band (monomer at 1773 cm^{-1} and polymer at 1785 cm^{-1}) and also the very strong band at 1521 cm^{-1} which is caused by $(C\text{–}C)_{aryl}$ stretching vibrations. The intensity of the latter band has to be defined by curve-fitting.

In the PFPA Raman spectra again the typical very intensive 1625 and 1635 cm^{-1} combination of acrylate monomer bands and also the bands at 1290 cm^{-1} and 1407 cm^{-1} can be observed and used for unsaturation calculation. C–F deformation vibrations in the wavenumber range 399–578 cm^{-1} were used as reference bands.

The fast photo-polymerization of PFPA is illustrated in Fig. 6 which contains the results of IR measurements. After an irradiation time of only 5 min the conversion of the monomers is at least 95%. After an irradiation time of 60 min the conversion finally amounts to about 99%. This value also could be confirmed by TGA.

With Raman-spectroscopy the calculated conversion

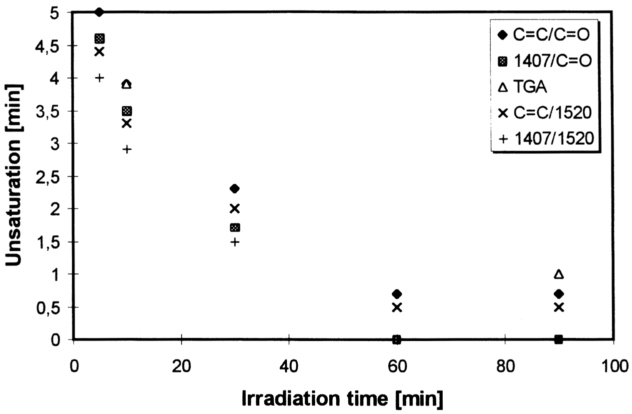

Fig. 6. FT-IR spectroscopy of photo-polymerization of PFPA. Unsaturation as a function of irradiation time. C=C means integral absorption of 1625 cm^{-1} and 1635 cm^{-1} bands.

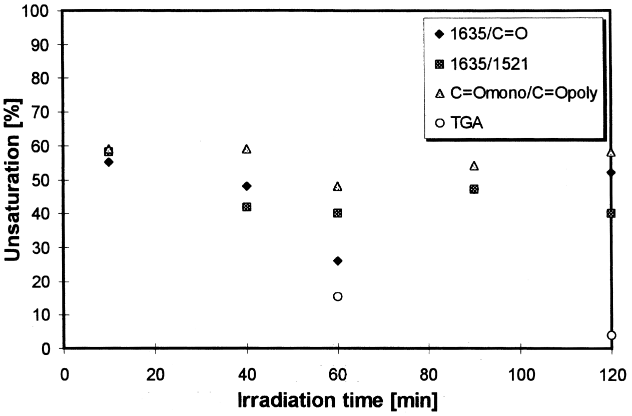

Fig. 8. FT-IR spectroscopy of photo-polymerization of PFPMA. Unsaturation as a function of irradiation time. C=C means the intensity of 1625 cm^{-1} and 1635 cm^{-1} bands.

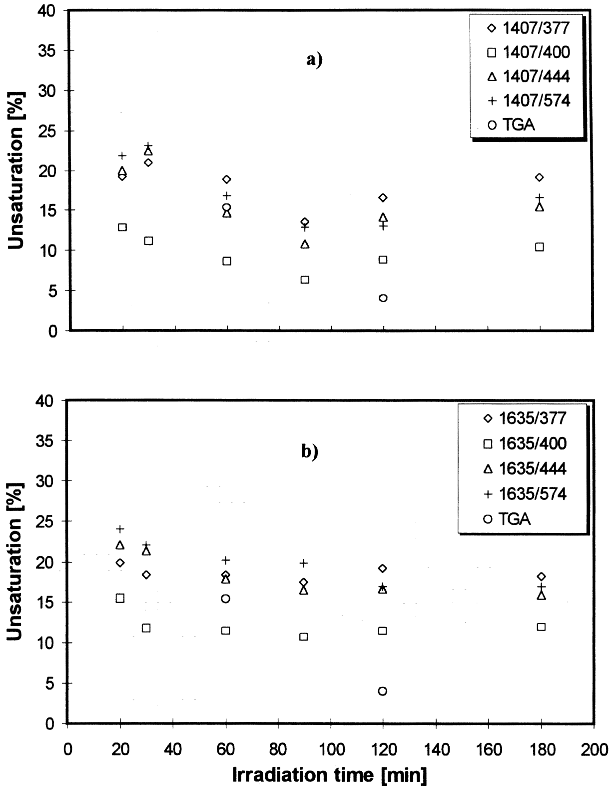

Fig. 9. FT-Raman spectroscopy of photo-polymerization of PFPMA. Unsaturation as a function of irradiation time. (a) 1407 cm^{-1} band relative to internal standard bands at 377 cm^{-1}, 400 cm^{-1}, 444 cm^{-1} and 574 cm^{-1}, respectively. (b) 1635 cm^{-1} band relative to internal standard bands.

(using acrylate bands 1407 cm^{-1}, 1625 cm^{-1} and 1635 cm^{-1}) already reached 99% after irradiation times of only 5 min.

Relative intensity changes of reference bands with respect to each other during polymerization of PFPA could not be observed within the measurement accuracy. All the reference bands used correspond to the pentafluorophenyl group. The relative intensity increase of the used reference bands to the carbonyl band resulting from polymerization is given by a factor of about 4. Therefore the carbonyl band is not used a as reference band. Values obtained by use of different acrylate bands and standard bands as well as by TGA are in very good agreement.

4.2.2. Thermal analysis of PFPA polymer

TGA of photo-cured PFPA (60 min irradiated 99 wt% PFPA/1 wt% Darocur 1173™) showed a weight loss of less than 1 wt%. Samples with 10 min irradiation time showed weight loss of 3.9% and 4.5% (30–150°C), respectively. Degradation temperature in all cases was 290°C. The glass transition temperature was 64°C. TD-GC-MS, carried out at 50°, 120°, 175° and 240°C, yielded as volatile components water, acetone, benzaldehyde, Darocur 1173™ and ethylpentafluorophenylether. Even at higher temperatures no additional products were formed. Main components at all temperatures were Darocur 1173™, water and the ether. The dominance of Darocur 1173™ in the volatile fraction (which is present before curing in only 1 wt% concentration) also indicates the very high conversion in PFPA polymerization.

4.3. Pentafluorophenylmethacrylate

4.3.1. Unsaturation determination by vibrational spectroscopy in PFPMA polymer

Fig. 7 contains the IR and Raman spectra of PFPMA monomer and polymer. In contrast to the acrylates, PFPMA does not give rise to a band at 1625 cm^{-1}, only one weak band at 1635 cm^{-1} is observed. Further this weak band overlaps with the 1654 cm^{-1} band caused by $(C–C)_{aryl}$ stretching vibrations. As reference bands for calculation of unsaturation the carbonyl band (monomer at 1761 cm^{-1} and polymer at 1778 cm^{-1}) and the strong 1521 cm^{-1} band were used.

The acrylate double bond leads in Raman spectra to bands at 1407 cm^{-1} and 1635 cm^{-1}. As reference bands for unsaturation calculation, C–F deformation vibration bands from 377 cm^{-1} to 574 cm^{-1} were applied.

Figs. 8 and 9 contain the results of PFPMA polymerization. As expected for methacrylates, the polymerization reaction proceeds at a much lower rate compared to the acrylates.

Of special interest is the marked difference of unsaturation observed in the samples measured by IR and Raman spectroscopy. Most probably these differences are caused by the sample preparation procedure. Preparation of the Raman samples could be realized in a completely oxygen free Ar atmosphere whereas during the preparation of the IR samples influence of air could not be fully excluded. Therefore the conversion values of about 50% as found in the infrared experiments are probably caused by inhibition of polymerization by oxygen. The TGA-samples were prepared in the same manner as the Raman samples. In addition to the internal standard band method the wavenumber shift of the carbonyl band during the polymerization reaction (1761–1781 cm^{-1}) was used to calculate the unsaturation in FT-IR samples. An advantage of this method is that no other band has to be used. As the measured C=O band is the sum of monomer and polymer-C=O bands, it can be separated by curve-fitting. Assumed that the same C=O absorptivity is obtained in the monomer and in the polymer the unsaturation U in % was directly calculated from Eq. (6):

$$U = \frac{I_{C=O,Monomer}}{(I_{C=O,Monomer} + I_{C=O,Polymer})} \cdot 100 \tag{6}$$

The quantitative Raman-measurements lead to higher conversions than obtained by IR. After an irradiation time of 60 min conversions of about 80%–85% were reached. The agreement between the values obtained by different internal standard bands (except the band at 400 cm^{-1}) is good.

The relative intensities of the reference bands in Raman spectra at 574 cm^{-1}, 444 cm^{-1} and 377 cm^{-1} are the same

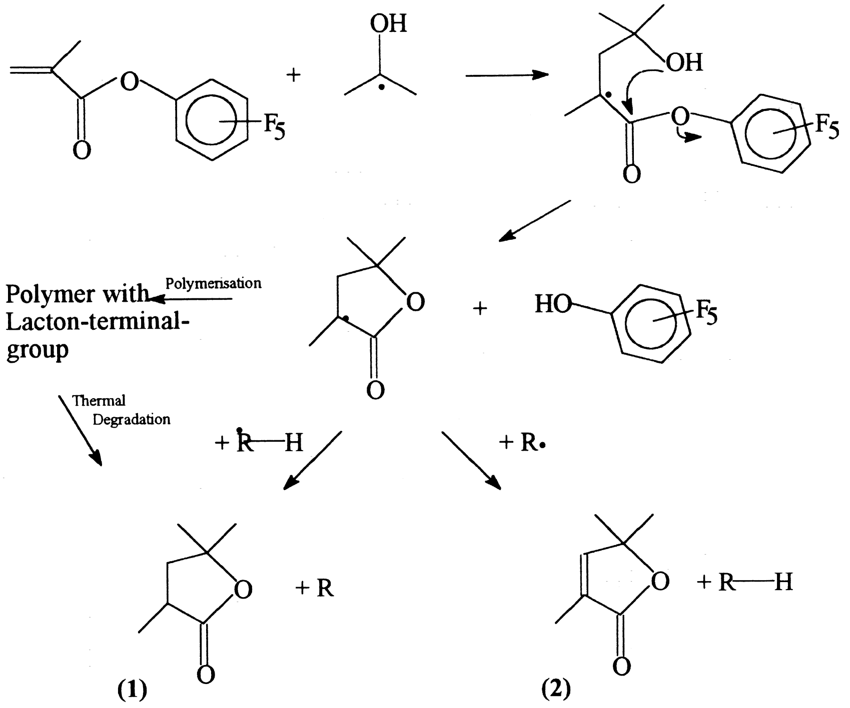

Fig. 10. Formation of lactones by reaction of 2-hydroxypropyl-radical with PFPMA.

within the measurement accuracy in the monomer and in the polymer. Only the 400 cm^{-1} band loses in intensity by a factor of 1.3 to 1.6 with respect to the intensities of the other reference bands as it is represented in the obtained unsaturation values in Fig. 9. The carbonyl band loses in relative intensity, with respect to the other reference bands, a factor of about 4.

4.3.2. Thermal analysis of PFPMA polymer

TGA of photocured PFPMA (60 min UV irradiated 99 wt% PFPMA/1 wt% Darocur 1173™) showed a weightloss of about 15% (30°C–200°C) and 6.8% after 120 min of irradiation time (60°C–216°C). Degradation temperatures were 210°C and 230°C, respectively. TD-GC-MS experiments were carried out at 100°C, 170°C, 205°C and 240°C. The main volatile component at all temperatures was free monomer, as expected and further: pentafluorophenol, water, benzaldehyde, Darocur 1173™, 2,4-dimethyl-γ-valero-lactone (1), 2,4-dimethyl-β-angelica-lactone (2) and in trace amounts some unidentified compounds. The lactones were only observed at $T > 100°C$. Formation of the lactones can be explained by reaction of the 2-hydroxypropyl-radical with PFPMA as illustrated in Fig. 10:

Comparable reactions in samples of PFPA could not be observed.

5. Conclusions

The high polymerization velocity in the radical photopolymerization of the acrylates TeCEA and especially PFPA leads to very high conversions (95%–99%) after irradiation times of only 5–10 min. The photochemically initiated polymerization of the methacrylate PFPMA is significantly slower. It reaches conversions of about 80% (Raman and TGA result) and about 50% (infrared result), respectively, after irradiation during 20 min. The marked differences between the applied techniques in the sample with PFPMA are attributed to differences in the sample preparation. Samples for Raman measurements were prepared in completely oxygen free Ar atmosphere. This could not be realized for the samples for FT-IR measurements, therefore the oxygen inhibition of the radical polymerization of PFPMA may lead to reduced conversion, which could not be increased by prolonged irradiation times. Therefore for photopolymerization of PFPMA a completely oxygen-free atmosphere has to be realized. The agreement of the Raman and TGA measurements is gratifying, since this implies that the error which might be caused by the fact that an internal standard band is used for quantification in the spectroscopic measurement (which may be influenced by the polymerization too!), is limited.

For determination of the unsaturation during TeCEA polymerization by Raman spectroscopy using the relative band ratio method, marked differences are obtained depending on the choice of reference bands. All reference bands used are caused by C–Cl vibrations in the tetrachloroethyl group in which the several C–Cl bonds are individually influenced by inductive effects caused by polymerization. This leads to marked differences in relative reference band intensities caused by polymerization. In PFPA and PFPMA all reference lines result from C–F vibrations in the resonance stabilized pentafluorophenylgroup. Relative intensity changes of the used reference bands caused by polymerization could not be observed within the measurement accuracy.

The wavenumber shift of the carbonyl band by polymerization could successfully be exploited for a very simple unsaturation calculation in PFPMA polymer.

The thermal stability of resulting polymers with respect to possible applications in optical telecommunications should be in the range of at least 80°C. This requirement is certainly fulfilled by PFPMA polymer but not by TeCEA and PFPA polymer with a T_g of only about 70°C and 64°C, respectively. Also the chemical stability of TeCEA polymer as suggested by the reaction with water seems to be problematic relating to technical application.

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