

UV-laser-assisted degradation of poly(methyl methacrylate)

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Received 30 July 2004; accepted 20 November 2004

Available online 2 March 2005

Abstract

Poly(methyl methacrylate) (PMMA) has been irradiated by UV-laser light with different wavelengths (193 nm, 248 nm and 308 nm) in order to investigate the photolytic degradation of the physical–chemical molecular structure. The photoinduced chemical reactions at the polymer surface have been investigated by QMS, XPS, FTIR and NMR in order to clarify the degradation mechanism. It was also shown that in the UV-illuminated area a modification of the refractive index can be achieved which strongly depends on the irradiation conditions.

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Keywords: UV-excimer laser; Poly(methyl methacrylate); X-ray photoelectron spectroscopy (XPS); Norrish reaction; Refractive index modification

1. Introduction

A number of articles have been published about the fundamental photochemical defragmentation reactions of poly(methyl methacrylate) PMMA by UV-illumination such as main chain scission, (in-) complete side chain cleavage and direct UV-depolymerization (unzipping) [1–6], but without specifying precisely the applied wavelength and irradiation dose. Melville [7], Kopietz et al. [8], Tsao and Ehrlich [9], Jónsson et al. [10] and Garnett [11] investigated the after-curing and direct UV-photopolymerization of PMMA at low irradiation dose in a wavelength range of 250 nm–280 nm. In the same wavelength range, but at medium irradiation dose Frank et al. [12] generally report about the side chain cleavage of PMMA. Küper and Stuke [13], Wochnowski et al. [14] and Scully et al. [15] examined the modification mechanism of PMMA (mainly side chain

cleavage) induced by excimer laser irradiation (193 nm, 248 nm) which is called incubation [13] or modification [14]. Sutcliffe and Srinivasan [16] and Küper and Stuke [13] examined the UV-laser assisted ablation mechanism of PMMA at high irradiation dose after the modification or incubation period has taken place.

Mass spectroscopic investigation of UV-illuminated PMMA (wavelength range below 250 nm and low irradiation dose) indicates a complete cleavage of the ester side chain [17] indicating that the above-mentioned classical photochemical degradation processes prevail [1–6] in this wavelength range. However, in the wavelength range > 250 nm and with a comparable irradiation dose no complete ester side chain cleavage occurs in the mass spectrum suggesting the dominance of molecular rearranging photochemical reaction like curing, crosslinking or photopolymerization [17,18].

Only few papers deal with the modification with excimer laser wavelengths at a relatively low irradiation dose [19,20]. Tomlinson et al. [19] proposed a photochemical crosslinking reaction after peroxidation triggered by Hg–Cd-laser irradiation, but no experimental evidence is given in the paper. Also Isaacs and Fox [21]

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suggest a photochemical curing or crosslinking between polyacrylate derivatives induced by UV-irradiation.

Many investigations of the photodegradation of PMMA by UV-irradiation below 250 nm (excimer laser, mercury lamp etc.) have been reported, showing the side chain scission as the main photodegradation mechanism [1–6,13]. However, the exact side chain scission mechanism was not clarified until now, e.g. it is not known by which wavelength and at which irradiation dose a complete or a partial side chain cleavage occurs. Additionally, photochemical molecular rearrangement reactions induced by UV-irradiation below 250 nm are not verified until now.

This paper reports on the occurrence of photochemical rearrangement reactions in PMMA under certain irradiation conditions (especially at very low irradiation dose at the beginning of a UV-illumination process) even below 250 nm before wavelength-specific degradation processes of the polymer molecule take place in a large scale gradually defragmentating the whole polymer molecule structure.

2. Experimental set-up

The experimental set-up consists of an excimer laser as a UV-source of different wavelengths (193 nm, 248 nm, 308 nm), an optical lens and mirror system for guiding and forming the laser beam and a vacuum chamber containing the sample holder for the PMMA sample. By this set-up a reproducible irradiation of the PMMA probe under controllable conditions in a defined gas atmosphere is guaranteed. A quadrupole mass spectrometer (QMS) was integrated into the vacuum chamber in order to examine the volatile defragmentation products ablated from the irradiated polymer surface by an in situ rest gas analysis (in situ RGA).

Additionally the irradiated PMMA samples have been examined by XPS, ATR-FTIR and NMR spectroscopy. The determination of the surface refractive index of the irradiated area was done by an Abbé refractometer and the measurement of the refractive index depth profile was performed by an optical free-space two-beam interferometer of the Mach–Zehnder type which is described in detail elsewhere [22–24].

3. Analytical measurements

3.1. Surface analytical methods

3.1.1. UV-irradiation by $\lambda = 248$ nm

During the UV-irradiation ($\lambda = 248$ nm) the in situ-QMS mass spectrum of PMMA was recorded as shown in Fig. 1. The mass spectrum clearly indicates the existence of methyl formate, a great amount of

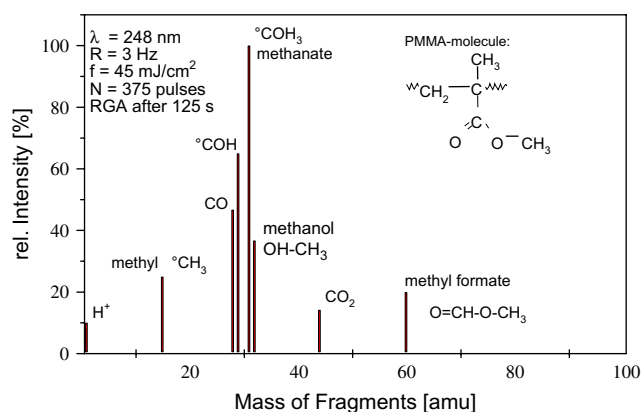


Fig. 1. Mass spectrum of irradiated PMMA (wavelength $\lambda = 248$ nm, fluence $f = 45$ mJ/cm², repetition rate $R = 3$ Hz, laser pulse number $N = 375$).

methanate, methanol and additionally the occurrence of methyl and other molecule fragments of the polymer side chain even at a low irradiation dose. It is known that a complete side chain separation generates hydrogen radicals by hydrogen abstraction from the main chain [3]. This effect was also observed in our QMS measurements.

After irradiation by 248 nm the PMMA sample has been investigated by FTIR, XPS and NMR spectroscopy. The FTIR transmission spectra shown in Fig. 2 are recorded at different pulse numbers and confirm the existence of methanol by detecting the OH-peak at 3500 cm⁻¹. The existence of water, to which the OH-peak could also be assigned, cannot be totally excluded: during the transfer of the UV-laser treated PMMA-sample from the vacuum chamber to the sample holder of the FTIR-spectrometer the UV-illuminated area of the polymer sample cannot be prevented from being contaminated by water molecules due to air humidity.

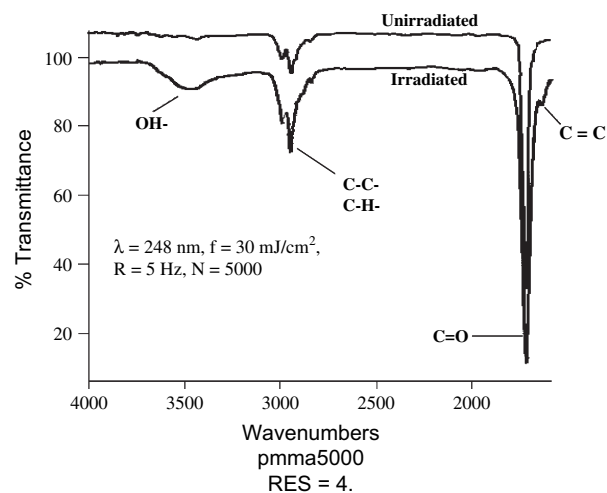


Fig. 2. FTIR spectrum of irradiated PMMA ($\lambda = 248$ nm, $f = 30$ mJ/cm², $R = 5$ Hz, $N = 5000$).

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