

# Influence of a Photoinitiator on the Photochemical Stability of Poly(methyl methacrylate) Studied with Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** Fourier transform infrared (FTIR) spectroscopy was used to investigate the effect of a commercial photoinitiator [2,2-dimethoxy-2-phenylacetophenone (DMPA); Irgacure 651, Ciba, Basel, Switzerland] incorporated into poly(methyl methacrylate) (PMMA). Pure PMMA and modified PMMA (containing 5% DMPA) films were exposed to a xenon lamp in air. Qualitative and quantitative analyses of the recorded FTIR absorption spectra were done. This allowed us to determine the differences in the course of

polymer photooxidative degradation occurring in PMMA and PMMA doped with DMPA. We found that the initiator added to polymer film enhanced the efficiency of the formation of the photooxidized products containing functional groups of different types, which could be distinguished by mathematical treatment of the FTIR spectra. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1598–1607, 2010

**Key words:** degradation; FT-IR; initiators; photochemistry

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been a well-known and commonly used thermoplastic polymer for many years.<sup>1,2</sup> Because of its excellent properties, including a very high transparency, resistance to heat and light, good impact strength and surface properties, biological inactivity, easy processing, and product formation, PMMA has found applications in industry, electronics, medicine, and pharmacy,<sup>3</sup> for example, in the production of synthetic glass, laser discs (compact discs and digital video discs), bone cement, and contact and intraocular lenses. It is also a good material for cosmetic surgery and dentistry (dental fillings<sup>4</sup>), and it is a component of popular acrylic paints. Many recent scientific studies have been devoted to new applications of PMMA, for instance, in enzyme biosensors,<sup>5</sup> microchip devices,<sup>6</sup> optical elements in holography,<sup>7</sup> matrices for photochromic compounds,<sup>8</sup> and nanocomposites.<sup>9–12</sup> The synthesis and characterization of new materials based on modified PMMA have also been reported.<sup>13–16</sup>

PMMA is recognized as a photostable polymer because electromagnetic irradiation at higher wave-

lengths (>300 nm) does not cause changes in its chemical structure. However, short-wavelength ultraviolet (UV) radiation leads to its efficient depolymerization. This phenomenon is applied in high-resolution photolithography.<sup>17</sup>

PMMA is often used in modified form; thus, the effect of various additives on its polymer photostability have to be taken into consideration. Also, impurities from polymerization can influence the photochemical transformation in macromolecules, especially in the case of the presence of chromophoric groups in these compounds.

The aim of this study was to estimate the influence of a chosen, commercial photocuring agent (Irgacure 651) on the chemical stability of PMMA exposed to xenon lamp radiation.

Even when the photolysis of an applied initiator is known, it is not easy to predict the behavior of a photoinitiator incorporated into a polymer matrix, even if it is an efficient compound in the polymerization process. Our previous results indicate that some photoinitiators intentionally added to PMMA or poly(vinyl chloride) sometimes exhibit unexpected effects. They retard polymer photodegradation in some cases, but in other system and conditions, the same compounds act as sensitizers or catalysts. The inhibition is caused by the quenching of polymer excited states or by the efficient recombination of free radicals terminating chain degradation. The activity of a photoinitiator in a polymer can differ from its action in polymerization (curing) processes.

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## EXPERIMENTAL

### Materials

PMMA (Sigma–Aldrich, weight-average molecular weight = 120,000 g/mol) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA; molecular weight = 256.30 g/mol, Irgacure 651, Ciba, Basel, Switzerland) were used as supplied. The solvent tetrahydrofuran (THF) of high purity was purchased from Aldrich. Directly before use, THF was distilled under reduced pressure.

### Film preparation

PMMA and the photoinitiator (DMPA) were dissolved separately in THF at a concentration of 2% (w/v). PMMA and DMPA solutions were mixed in a proper ratio for the purpose of the incorporation of 5% (w/w) initiator with respect to the polymer mass. Polymer solutions (PMMA and PMMA–DMPA) were cast on leveled, smooth glass plates. Thin polymeric films were obtained after solvent evaporation at room temperature. Finally, the samples were dried in a vacuum oven at 40°C to remove solvent traces (the absence of THF in the polymer was controlled by ultraviolet–visible spectroscopy). The film thickness, measured by a Sylvac 229 type digital indicator (Swiss), was 20  $\mu\text{m}$ .

### UV irradiation

PMMA and PMMA + DMPA films placed on  $\text{CaF}_2$  spectrophotometric windows were UV-irradiated in an air atmosphere at 30°C for 1–24 h. The irradiation source was a high-pressure xenon lamp (XBO R 180 W/45 OFR with a ZXE 180 power supply adaptor and three detectors, Optel, Opole, Poland). The distance between the radiator and the sample was 10 cm. A constant temperature was maintained with a ventilator. The intensity of incident light, measured by an HD 9021 radiometer (Delta, Italy), was equal to 35.2  $\text{W}/\text{m}^2$  (for UVA), 9.70  $\text{W}/\text{m}^2$  (UVB), and 2.30  $\text{W}/\text{m}^2$  (UVC).

### Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the polymeric samples and photoinitiator alone were recorded by a Genesis II spectrophotometer (Mattson) immediately before and after exposure for different times. The absorbance spectrum in the 400–4000- $\text{cm}^{-1}$  range was acquired at a 4- $\text{cm}^{-1}$  resolution and signal-averaged over 100 scans.

The progress of photooxidative degradation was appointed by the calculation of integral intensities of carbonyl and hydroxyl bands in the ranges 1600–1800 and 3100–3600  $\text{cm}^{-1}$ , respectively. The baseline

correction and calculation of surface area of the analyzed peaks were done with WinFirst software. Spectra subtraction was applied for illustration of the competitive processes occurring simultaneously in the UV-irradiated samples.

A mathematical procedure of the resolution of complex carbonyl band onto components was used. Peak fitting was done with Grams/AI 8.0 spectroscopy software. The number of peaks was estimated on the basis of deconvoluted spectra and on the basis of the second derivative of the original spectrum. The correlation coefficient was at least equal to at least about 0.999, and the standard error was lower than 0.005.

## RESULTS AND DISCUSSION

### Photochemical transformations in PMMA and in PMMA containing the initiator DMPA

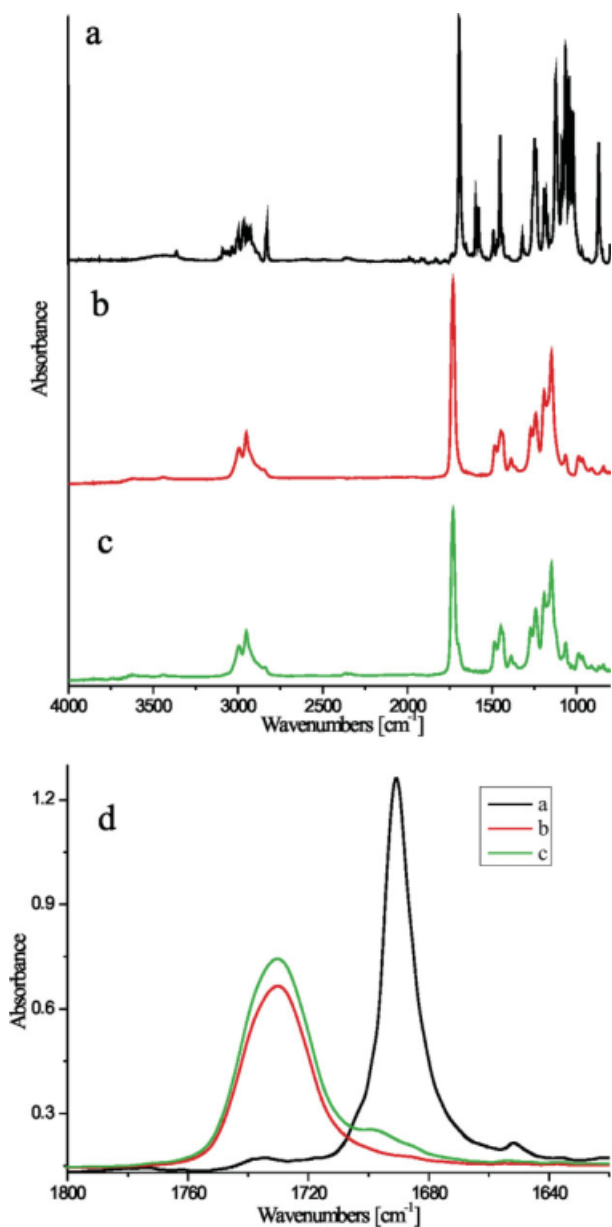
The FTIR spectra of PMMA, the initiator DMPA, and PMMA containing 5% DMPA are shown in Figure 1. The strongest absorption bands in the spectrum of virgin PMMA appeared in the stretching region [( $\text{cm}^{-1}$ ): 2995, 2950 (symmetric and asymmetric vibrations of  $\text{CH}_2/\text{CH}_3$ ); 1724 ( $\text{C}=\text{O}$ ); 1270, 1240 ( $\text{C}-\text{C}-\text{O}$ )] and the bending range [( $\text{cm}^{-1}$ ): 1481 ( $\text{CH}_2$ ); 1447, 1435, 1386 ( $\text{O}-\text{CH}_3$ ); 1190 ( $\text{C}-\text{O}-\text{C}$ ); 1145 ( $\text{CH}_2$ ); 966 ( $\text{C}-\text{CH}_3$ ); 840 ( $\text{CH}_2$ ); 750 ( $\text{CH}_3$ )].

In the spectrum of pure the photoinitiator DMPA, the most intensive bands were attributed to vibrations of methyl groups (2800–3000  $\text{cm}^{-1}$ ), aromatic rings (1594, 1450  $\text{cm}^{-1}$ ), carbonyl groups (1690  $\text{cm}^{-1}$ ), and  $\text{C}-\text{O}$  bonds (1000–1200  $\text{cm}^{-1}$ ). The spectrum obtained was almost the same as that published for Irgacure 651 in the condensed phase by the manufacturer.<sup>18</sup>

The spectrum of the modified PMMA slightly differed from the pure PMMA because the carbonyl bands from DMPA overlapped the carbonyl band from the polymer; the bands from aromatic rings were obviously characterized by a very low intensity because the amount of this additive was low (only 5 wt %).

FTIR spectroscopy was also used to monitor the changes in the polymer chemical structure caused by UV irradiation. The main changes in the spectra were observed in the hydroxyl region (Fig. 2), which was evidence of the photooxidation process of the macromolecules. Less distinct differences were found in the methyl/methylene bands (in the 2900–3050 and 1370–1470- $\text{cm}^{-1}$  ranges attributed to the stretching and deformation vibrations, respectively) and in the carbonyl range (1650–1800  $\text{cm}^{-1}$ ).

The changes in the carbonyl band had to be analyzed very carefully because, as mentioned previously, the vibrations of  $\text{C}=\text{O}$  from the initiator and



**Figure 1** FTIR spectra of the (a) DMPA photoinitiator, (b) pure PMMA, and (c) PMMA with 5% DMPA. (d) The superposition of the carbonyl band is also shown. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

polymer overlapped in the same region. They were consumed because of DMPA compound photolysis. Simultaneously, new functional groups containing oxygen atoms were formed in macromolecules as a result of photooxidation because irradiation was carried out in an air atmosphere. This was the reason the carbonyl band was very complex. The illustration of chemical changes caused by the competitive processes in PMMA and PMMA–DMPA are shown in the difference spectra (Fig. 3). In addition to the significant decrease in the absorbance at 1732 cm<sup>-1</sup>, the formation of new shoulders of the carbonyl peak

were observed at 1772, 1753, 1710, and 1654 cm<sup>-1</sup> in the PMMA difference spectrum. Similar but more intensive components were observed in the difference spectrum of doped PMMA.

The kinetics of development of the total amount of functional groups, expressed as a percentage changes in the integral intensities of the OH, C=O, and CH bands, are presented in Figure 4. As shown, a very fast increase in the OH and/or OOH group amount was observed in UV-irradiated PMMA doped with DMPA compared to the pure polymer, especially at the beginning of exposure [Fig. 4(a)]. These groups (OH and OOH) could not be distinguished on the basis of the FTIR spectra. The increase in the integral intensity of the band due to hydroxyl groups exceeded 200% in the spectrum of PMMA containing 5% DMPA after 8 h of exposure.

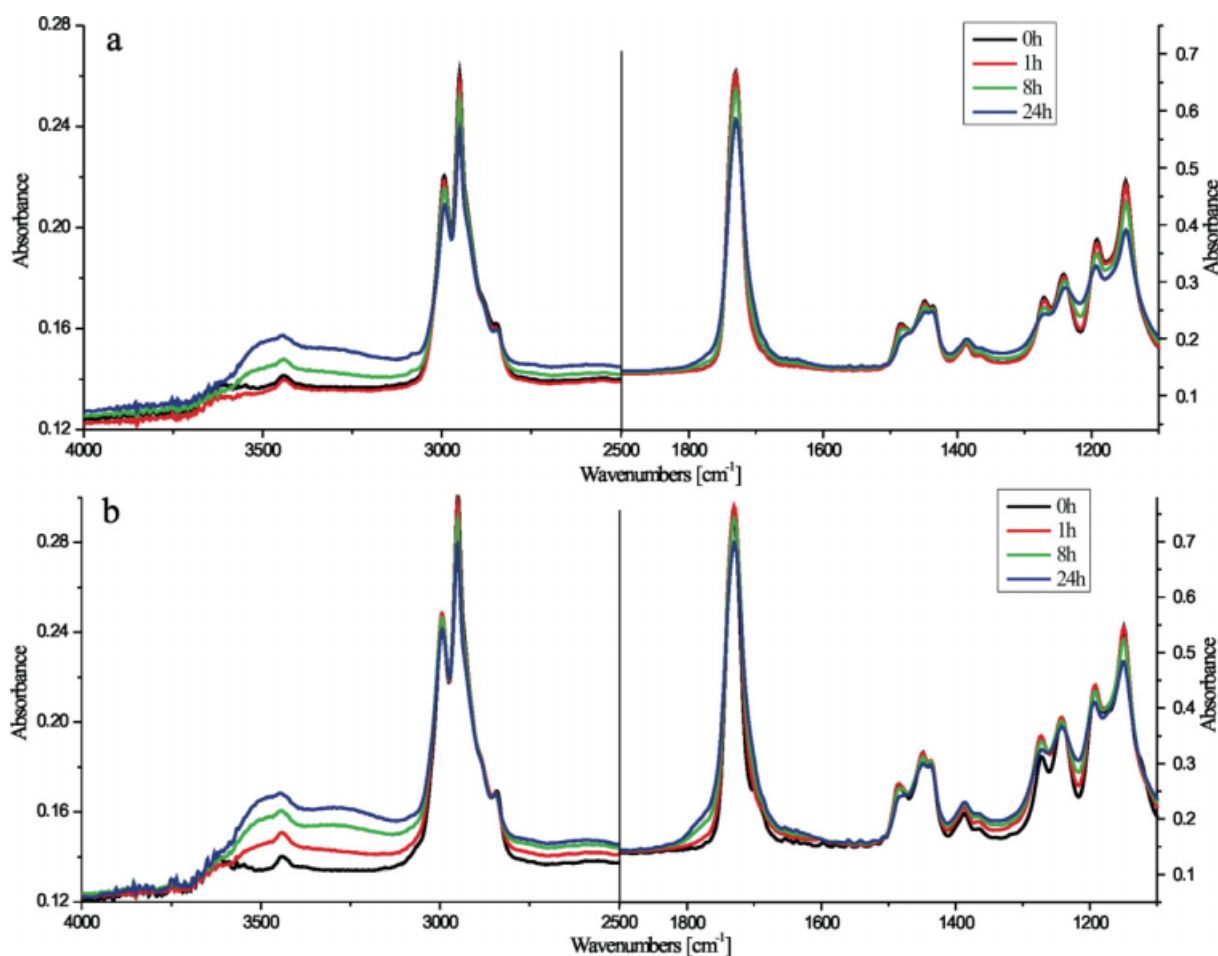
The efficiency of the formation of carbonyls was lower than that for the hydroxyl groups but the changes in the total C=O content in PMMA with 5% DMPA were still significantly higher than those for PMMA alone. This means that photooxidation of PMMA was accelerated in the presence of DPMA [mainly in the first hour of exposure; Fig. 4(b)].

Simultaneously, a drop in the methyl/methylene group amount, proven on the basis of the decrease of the band in the 2900–3050-cm<sup>-1</sup> range, took place. This indicated that polymer destruction was an accompanying process. This process was more important in the modified PMMA compared to the undoped sample [Fig. 4(b)].

The analysis of the hydroxyl band was simple (contrary to carbonyl peak) because the unexposed origin PMMA did not contain any OH groups; thus, the development of the broad band in the 3100–3600-cm<sup>-1</sup> range was obvious evidence of photooxidation.

The resolution of the complex carbonyl band in the FTIR spectra of the UV-irradiated samples allowed us to examine the detailed changes in the chemical structure of PMMA (Figs. 5 and 6). On the basis of the second derivative of the original absorption spectrum and with the best fitting possible for components having physical meaning taken into account, the decomposition of the spectra of unirradiated samples was done for four and five peaks for PMMA and PMMA–DMPA, respectively.

In the case of the photodegraded samples, the number of bands was obviously much higher in the spectra of both samples because of a variety of degradation products. The decomposition into five to six carbonyl components gave satisfying fitting parameters (correlation coefficients  $\approx 1$  and low standard errors). The number of bands was carefully chosen because this procedure was valid only if chemical interpretation was possible. It made sense, when the obtained component band could be



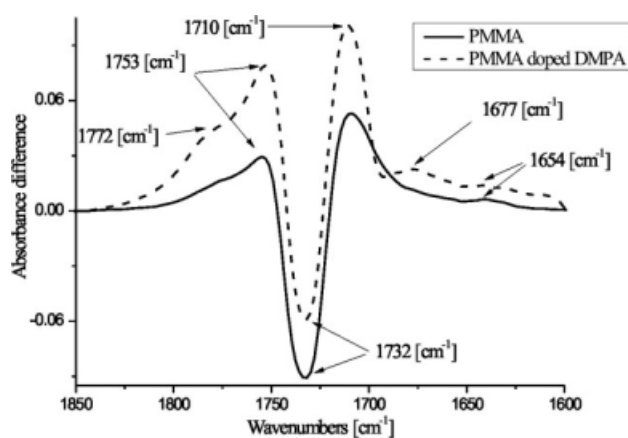
**Figure 2** Changes in the FTIR spectra of (a) PMMA and (b) PMMA with 5% DMPA after UV irradiation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

attributed to a specific group type. Before iteration, the position of peaks was fitted by hand for all of the analyzed spectra.

The main parameters characterizing the carbonyl components obtained by curve fitting are listed in Tables I and II.

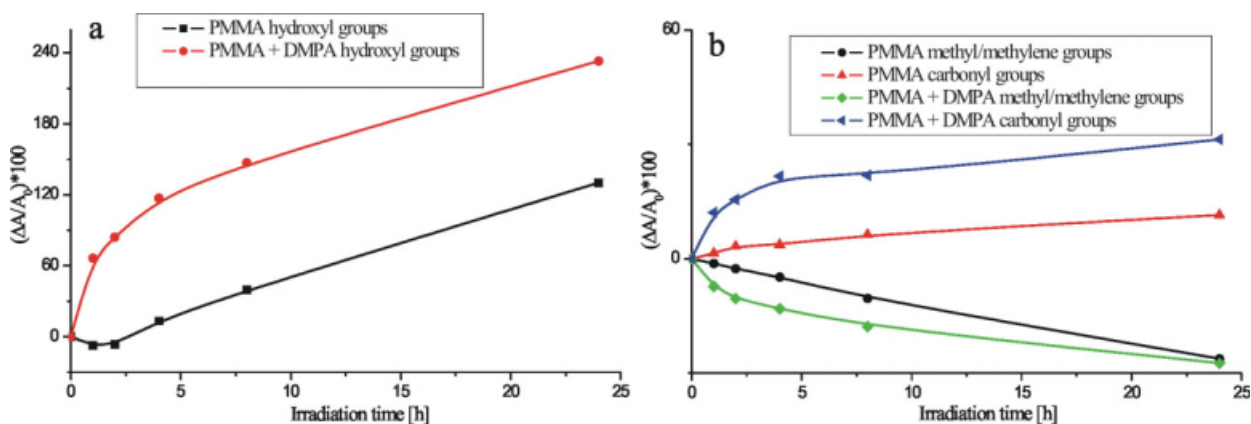
Interestingly, even in the pure unexposed PMMA, the carbonyl band was complex. The main carbonyl band was composed of two main components, which clearly arose from the differential spectra (Figs. 5 and 6). For an explanation of the differences in the microsurrroundings of the carbonyl groups in PMMA, some interactions had to be taken into account. Although typical hydrogen bonds did not exist in this polymer because of the lack of a hydrogen donor, specific interactions between the thin films of PMMA (characterized by weakly basic properties) and support usually appeared.<sup>19–22</sup> When CaF<sub>2</sub> was used as spectrophotometric windows, the forces between Ca<sup>2+</sup> ions (a hard Lewis acid) and polarized C=O bonds restrained the carbonyl vibrations and perturbed the conformations of polymeric chains. Thus, two different bands were distin-

guished: one at 1737 cm<sup>-1</sup> and a second one shifted to a lower frequency (1727 cm<sup>-1</sup>). They could be attributed to free and bonded carbonyls, respectively. A similar effect was observed in the spectra of PMMA deposited on aluminum, where highly



**Figure 3** Difference spectra in the carbonyl region for PMMA and PMMA with 5% DMPA after 24 h of UV irradiation.





**Figure 4** Relative changes in the integral intensities of (a) hydroxyl and (b) carbonyl and methyl/methylene bands calculated from the FTIR spectra of PMMA and PMMA with 5% DMPA exposed to UV irradiation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

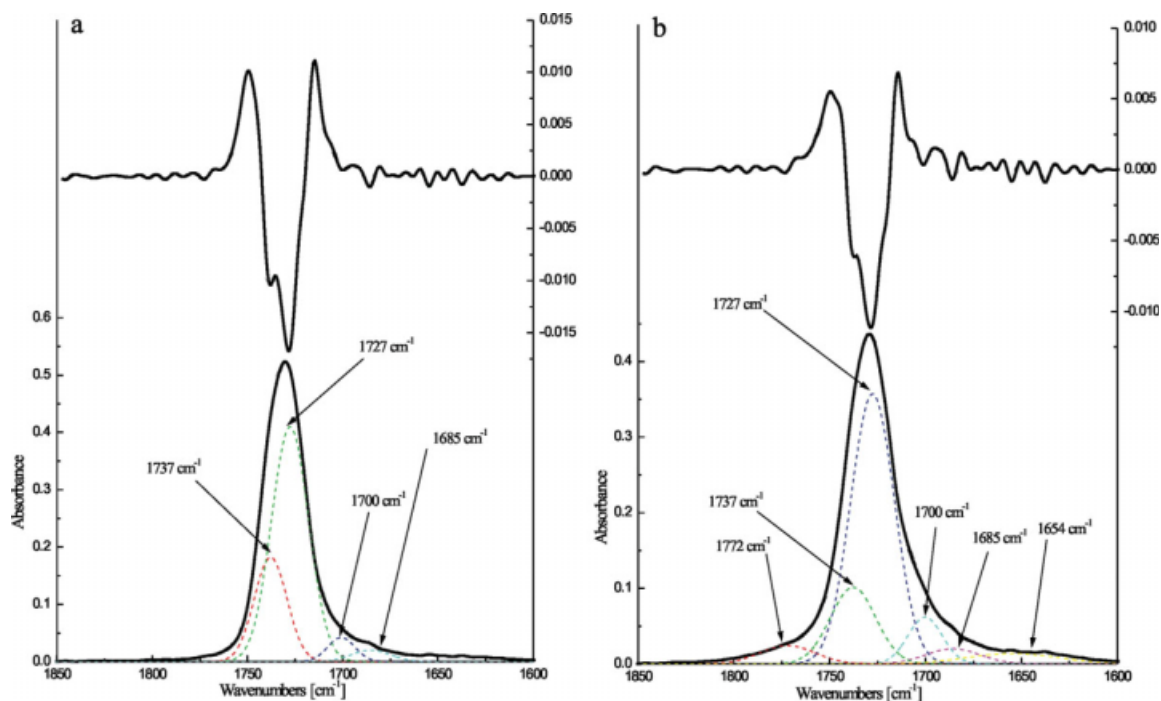
specific polymer–support interactions of an acid–base type led to chain straightening and flattening.<sup>23</sup>

The low-intensity small components (1700 and 1685  $\text{cm}^{-1}$ ) in the spectrum of the original, unexposed PMMA were assigned to some structural defects and impurities coming from the polymerization process. In the PMMA–DMPA spectrum also, the constituent originating from the initiator absorption (slightly shifted to 1696  $\text{cm}^{-1}$ ) overlapped in this region.

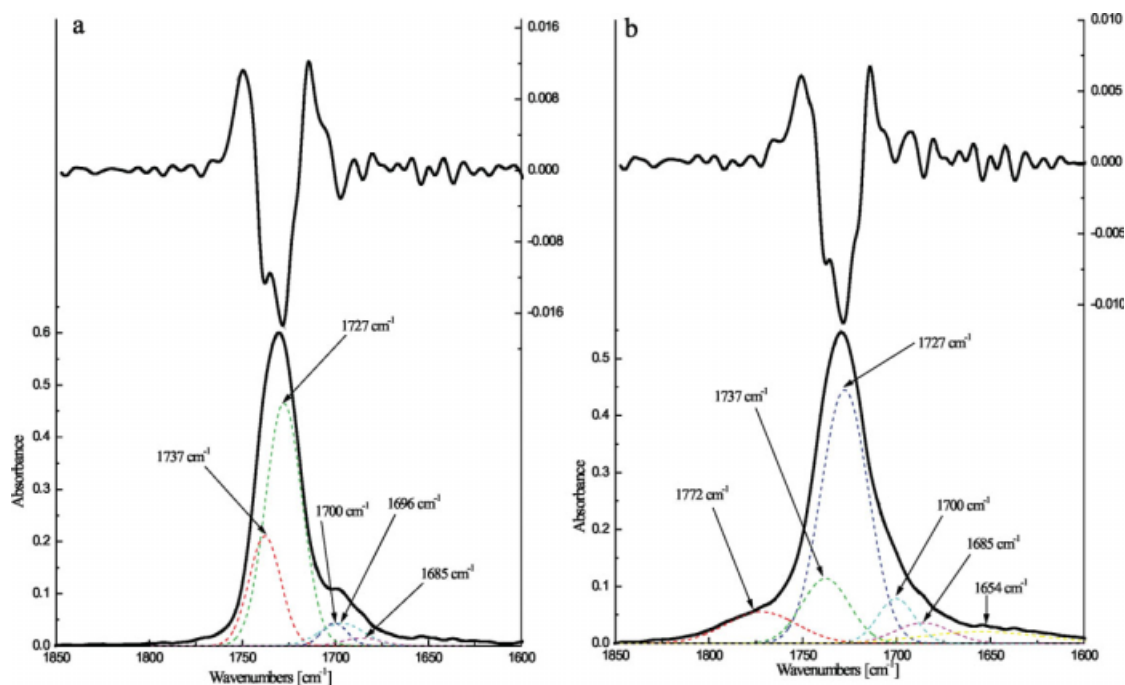
The number of components were different in the spectra of the exposed PMMA and PMMA–DMPA samples; however, we assumed that the main degra-

dation products containing C=O were the same and that only the rate and efficiency of their formation were higher in the presence of the photoinitiator. The minor peaks (1700 and 1685  $\text{cm}^{-1}$ ) existing also in the FTIR spectra of the unexposed samples were omitted in our discussion. The peak of DMPA disappeared just after the 1st h of UV irradiation, which confirmed our previous observation of the fast photolysis of this initiator in the polymer matrix.<sup>24</sup>

Later, after long-term irradiation (24 h), new bands at longer and shorter wavelengths appeared, which clearly indicated that detectable amounts of the oxidation products were formed. The band at



**Figure 5** Resolution of the carbonyl band of PMMA: spectra of (a) an unirradiated film and (b) a film UV-irradiated for 24 h (the second-derivative mode is on top). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 6** Resolution of the complex carbonyl band of PMMA with 5% DMPA: spectra of (a) an unirradiated sample and (b) a sample UV-irradiated for 24 h (the second-derivative mode is on top). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$1772\text{ cm}^{-1}$  was probably due to the mixture composed of carboxyl, peracid, and peroxyester functionalities, whereas the bands at  $1654\text{ cm}^{-1}$  were

assigned to double bonds in the main chain.<sup>25</sup> The unsaturations formed in macromolecules were responsible for the yellowing of acrylate formulations.

**TABLE I**  
Results of Carbonyl Band Decomposition by Peak Fitting from the FTIR Spectra of PMMA Before and After UV Irradiation

| Irradiation time (h) | Band range ( $\text{cm}^{-1}$ ) | C=O integral intensity (sum) | Component band maximum ( $\text{cm}^{-1}$ ) | Component band area | Component peak height | Full width at half-maximum of the component band ( $\text{cm}^{-1}$ ) | $f_{\text{C=O}}^b$ | Correlation coefficient | Standard error |
|----------------------|---------------------------------|------------------------------|---|---------------------|-----------------------|---|--------------------|-------------------------|----------------|
| 0                    | 1814–1586                       | 15.17                        | 1737  | 3.90                | 0.18                  | 20.02   | 0.72               | 0.9990                  | 0.0042         |
|                      |                                 |                              | 1727  | 10.00               | 0.41                  | 22.78   |                    |                         |                |
|                      |                                 |                              | 1700  | 0.76                | 0.04                  | 16.71   |                    |                         |                |
|                      |                                 |                              | 1685  | 0.51                | 0.02                  | 23.86   |                    |                         |                |
|                      |                                 |                              | 1685  | 0.51                | 0.02                  | 23.86   |                    |                         |                |
| 1                    | 1815–1598                       | 15.11                        | 1737  | 4.06                | 0.18                  | 20.92   | 0.71               | 0.9995                  | 0.0045         |
|                      |                                 |                              | 1727  | 9.81                | 0.40                  | 23.05   |                    |                         |                |
|                      |                                 |                              | 1700  | 0.74                | 0.04                  | 18.78   |                    |                         |                |
|                      |                                 |                              | 1685  | 0.50                | 0.01                  | 30.20   |                    |                         |                |
| 8                    | 1865–1576                       | 15.74                        | 1772  | 0.44                | 0.01                  | 30.80   | 0.75               | 0.9992                  | 0.0037         |
|                      |                                 |                              | 1737  | 3.43                | 0.15                  | 21.95   |                    |                         |                |
|                      |                                 |                              | 1727  | 10.06               | 0.39                  | 24.40   |                    |                         |                |
|                      |                                 |                              | 1700  | 1.01                | 0.05                  | 20.06   |                    |                         |                |
|                      |                                 |                              | 1685  | 0.62                | 0.02                  | 32.73   |                    |                         |                |
|                      |                                 |                              | 1654  | 0.19                | 0.01                  | 30.31   |                    |                         |                |
|                      |                                 |                              | 1654  | 0.19                | 0.01                  | 30.31   |                    |                         |                |
| 24                   | 1872–1564                       | 17.01                        | 1772  | 0.87                | 0.02                  | 33.45   | 0.77               | 0.9992                  | 0.0029         |
|                      |                                 |                              | 1737  | 3.00                | 0.10                  | 27.73   |                    |                         |                |
|                      |                                 |                              | 1727  | 10.24               | 0.36                  | 26.82   |                    |                         |                |
|                      |                                 |                              | 1700  | 1.38                | 0.06                  | 20.96   |                    |                         |                |
|                      |                                 |                              | 1685  | 0.70                | 0.02                  | 32.99   |                    |                         |                |
|                      |                                 |                              | 1654  | 0.82                | 0.01                  | 55.78   |                    |                         |                |
|                      |                                 |                              | 1654  | 0.82                | 0.01                  | 55.78   |                    |                         |                |

The least-square method and mixed Gauss/Lorentz function (number of iterations = 50) were used. The fraction of bonded carbonyl groups was determined as follows:  $f_{\text{C=O}}^b = \frac{I_{1727}}{I_{1727} + (\epsilon_1/\epsilon_2)I_{1737}}$  where  $\epsilon_1/\epsilon_2 = 1$ .

TABLE II  
Results of Carbonyl Band Decomposition from the FTIR Spectra of PMMA Containing 5 wt % DMPA

| Irradiation time (h) | Band range (cm <sup>-1</sup> ) | C=O integral intensity (sum) | Component band maximum (cm <sup>-1</sup> ) | Component band area | Component band height | Full width at half-maximum of the component band (cm <sup>-1</sup> ) | $f_{C=O}^b$ | Correlation coefficient | Standard error |
|----------------------|--------------------------------|------------------------------|--|---------------------|-----------------------|--|-------------|-------------------------|----------------|
| 0                    | 1838–1610                      | 18.34                        | 1737                                       | 4.49                | 0.21                  | 19.91  | 0.72        | 0.9998                  | 0.0045         |
|                      |                                |                              | 1727                                       | 11.43               | 0.47                  | 22.94  |             |                         |                |
|                      |                                |                              | 1700                                       | 0.74                | 0.04                  | 15.86  |             |                         |                |
|                      |                                |                              | 1696                                       | 1.29                | 0.04                  | 28.01  |             |                         |                |
|                      |                                |                              | 1685                                       | 0.38                | 0.02                  | 24.05  |             |                         |                |
| 1                    | 1871–1572                      | 21.34                        | 1772                                       | 0.73                | 0.02                  | 33.98  | 0.77        | 0.9994                  | 0.0039         |
|                      |                                |                              | 1737                                       | 4.07                | 0.17                  | 22.47  |             |                         |                |
|                      |                                |                              | 1727                                       | 13.53               | 0.50                  | 25.26  |             |                         |                |
|                      |                                |                              | 1700                                       | 1.33                | 0.06                  | 19.38  |             |                         |                |
|                      |                                |                              | 1685                                       | 1.21                | 0.04                  | 30.69  |             |                         |                |
| 8                    | 1873–1563                      | 23.72                        | 1654                                       | 0.47                | 0.01                  | 43.87  | 0.77        | 0.9999                  | 0.0042         |
|                      |                                |                              | 1772                                       | 1.70                | 0.04                  | 38.13  |             |                         |                |
|                      |                                |                              | 1737                                       | 4.14                | 0.15                  | 26.37  |             |                         |                |
|                      |                                |                              | 1727                                       | 13.88               | 0.48                  | 27.12  |             |                         |                |
|                      |                                |                              | 1700                                       | 1.77                | 0.08                  | 20.48  |             |                         |                |
| 24                   | 1877–1561                      | 25.29                        | 1685                                       | 1.22                | 0.04                  | 31.22  | 0.80        | 0.9986                  | 0.0036         |
|                      |                                |                              | 1654                                       | 1.01                | 0.02                  | 60.55  |             |                         |                |
|                      |                                |                              | 1772                                       | 2.65                | 0.06                  | 44.88  |             |                         |                |
|                      |                                |                              | 1737                                       | 3.61                | 0.11                  | 29.61  |             |                         |                |
|                      |                                |                              | 1727                                       | 14.10               | 0.45                  | 29.65  |             |                         |                |
|                      |                                |                              | 1700                                       | 1.90                | 0.08                  | 22.33  |             |                         |                |
|                      |                                |                              | 1685                                       | 1.32                | 0.04                  | 34.74  |             |                         |                |
|                      |                                |                              | 1654                                       | 1.70                | 0.02                  | 75.81  |             |                         |                |

For the calculation details, see Table I.

The efficiency of formation of the components absorbing at 1772 and 1654 cm<sup>-1</sup> in studied samples is shown in Figure 7. One can see that in the PMMA–DMPA film, both products were formed just after 1 h of UV irradiation, contrary to that in PMMA alone, where these constituents appeared only after an 8-h period of exposure. Long-term irradiation (24 h) led to the development of observed new bands, but their integral intensity was two to three times larger in the case of doped PMMA compared to that in the virgin polymer.

Moreover, the fraction of carbonyl groups engaged in interactions with the support (Tables I and II) was calculated according to a formula given by Grohens et al.<sup>23</sup> with the assumption that the ratio of the absorption coefficients ( $\epsilon_1/\epsilon_2$ ) for free and bonded C=O groups was equal to unity. Before exposure, the value of  $f_{C=O}^b$  (see Table I) was the same for both sample types, but it increased upon UV action. A considerable rise was noted after 24 h of irradiation: about 6.5 and 11.1% in PMMA and PMMA–DMPA, respectively. This means that in addition to

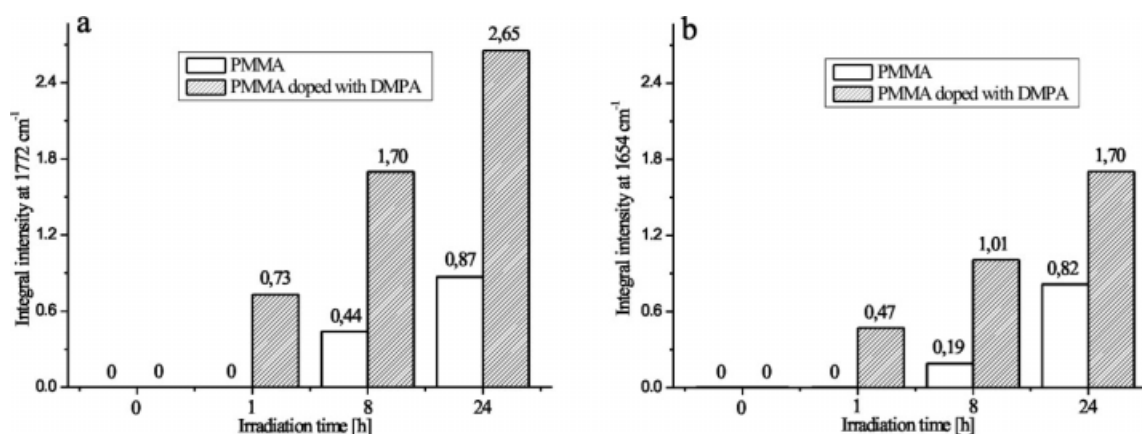
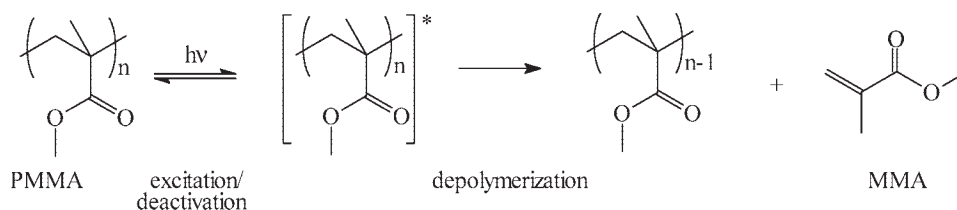


Figure 7 Efficiency of the formation of photooxidation products in PMMA and PMMA doped with DMPA on the basis of the carbonyl components absorbing at (a) 1772 and (b) 1654 cm<sup>-1</sup>.



**Scheme 1** Photodepolymerization of PMMA.

interactions between the macromolecules and support, new forces appeared. This could be explained simply by the interactions of the functional groups formed in PMMA that resulted from photooxidation, for example, hydrogen bonds between the polymeric units containing hydroxyl or carboxylic groups.

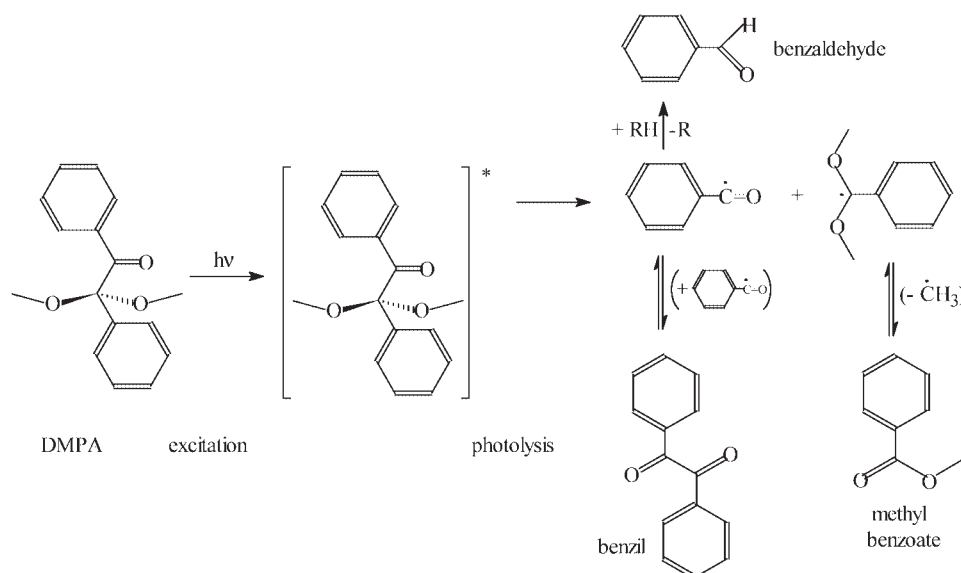
### Mechanism of the photooxidative degradation of the doped PMMA

The photodegradation of pure PMMA was a result of the excitation of carbonyl side groups present in each polymer unit followed by an abstraction of the hydrogen atom, methyl or methoxy radicals from macromolecules, and main-chain scission. Also, some external or internal impurities capable of the absorption of quantum radiation were responsible for the PMMA decomposition. This process was accompanied by the emission of volatile, low-molecular-weight products, such as the monomer, carbon monoxide and carbon dioxide, methyl formate, methanol, and formic acid. The most typical photo-reaction in PMMA was depolymerization, which had no drastic effect on its average molecular weight in early stages of exposure (Scheme 1).

The photochemical properties of initiators of various types have been studied extensively in the con-

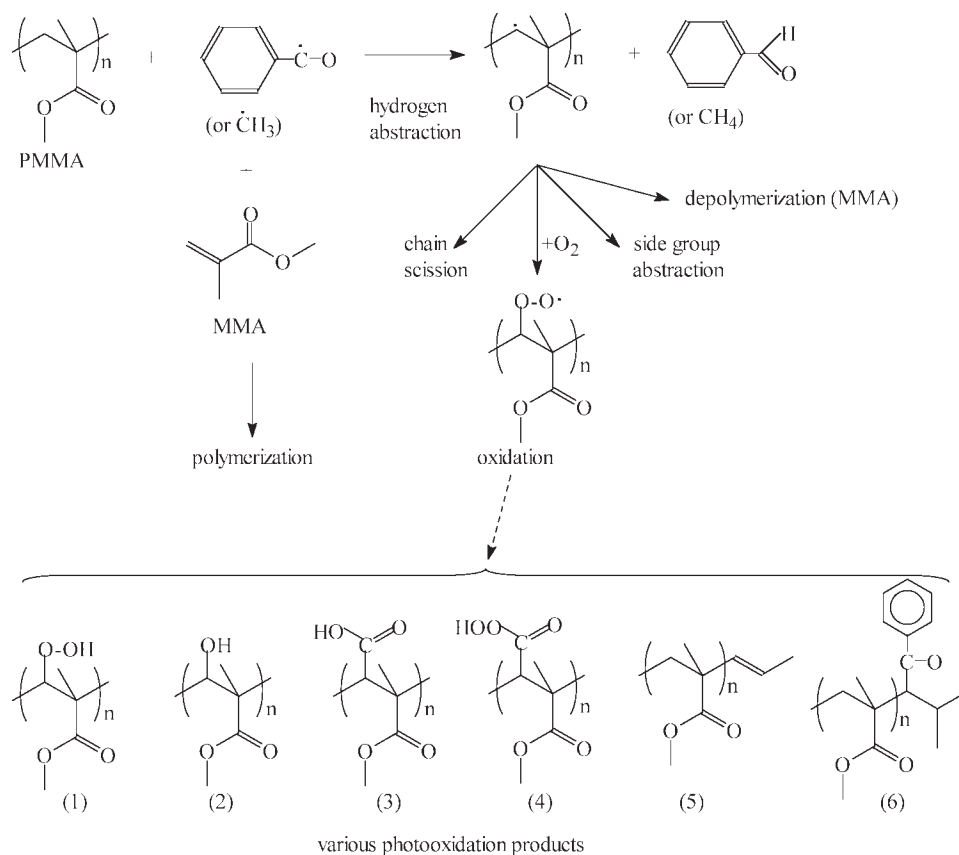
text of their activity in the polymerization of various monomers.<sup>26–29</sup>  $\alpha$ -Cleavage photoinitiators (classified as type I), such as  $\alpha,\alpha$ -dialkoxyacetophenones, are the most efficient compounds among many other initiators. Their activity and polymerization efficiency depends on many factors, for example, the lifetime of excited states and free radicals, monomer nature, presence of oxygen (or other quenchers) in reaction environment, formulation viscosity, sample thickness, and irradiation source. An important representative of these compounds is DMPA, which was examined in this study.

It is known that DMPA absorbs UV radiation below 400 nm and undergoes excitation. Its excited state is characterized by a very short lifetime.<sup>28</sup> The primary reaction is C—C scission with the formation of benzoyl and  $\alpha,\alpha$ -dimethoxybenzyl radicals (Scheme 2). The benzoyl radical reacts with double bonds (during the polymerization process), but it is also able to abstract a hydrogen atom from a molecule in close proximity. The secondary reactions lead to decomposition of  $\alpha,\alpha$ -dimethoxybenzyl radicals with the formation of small methyl radicals and methyl benzoate. Finally, recombination and hydrogen abstraction (from any other molecule) reactions occur; as a result, benzyl, acetophenone, and benzaldehyde are formed.



**Scheme 2** Photolysis of the DMPA initiator.





**Scheme 3** Main photoprocesses occurring in PMMA doped with DMPA.

In the case of a polymer matrix containing a photoinitiator, mutual reactions between both the components and products of their decomposition are possible. On the basis of our experimental results, we concluded that in the first degradation step, radicals created during DMPA photolysis could abstract hydrogen atoms from PMMA molecules and chain depolymerization started (Scheme 3).

Free radicals (R·) created in the primary reactions quickly reacted with atmospheric oxygen to give peroxy radicals (ROO·), which were able to abstract the next hydrogen atom from the same or neighboring molecule. Thus, the chains containing hydroperoxides (ROOHs) were formed. These groups were photounstable because O—O bonds easily break up upon light action. Finally, photooxidized macromolecules containing new carbonyl groups appeared.

The variety of degradation products in PMMA–DMPA was probably much higher than those in PMMA alone because the recombination of free radicals derived from both compounds was possible. For example, phenyl rings could be incorporated into macrochains resulting from the reactions shown in Scheme 3. However, the concentration of such structures in the studied samples was very low because only 5% DMPA was added to the PMMA matrix. Moreover, the quenching effect of oxygen addition-

ally decreased the concentration of excited molecules.

On the basis of the decomposed FTIR spectra, the formation of —COO— and >C=C< groups was proven among the numerous other photoproducts. The efficiency of their formation changed during the exposure time, and the initiator additive enhanced the considered photoprocesses. Simultaneously, hydroperoxides and hydroxides were created in the main chain with a relatively high efficiency.

## CONCLUSIONS

The enhancement of the photooxidation of PMMA films can be readily achieved by the incorporation of DMPA (Irgacure 651 initiator) into the polymer matrix. This finding is important from a practical point of view: a polymer characterized by accelerated photodegradation can be useful in the fabrication of degradable plastic or materials for photolithography.

The application of FTIR spectroscopy allowed for fast, easy, and reliable estimation of the additive (e.g., initiator) in the course of polymer photooxidative degradation. The various degraded products were detected and quantitatively analyzed by application of mathematical procedures such as

subtraction or differentiation of the FTIR spectra and decomposition of the complex absorption bands into components by the fitting method.

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