

# Effect of Photoinitiator on Photopolymerization of Inorganic–Organic Hybrid Polymers (ORMOCER®)

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**ABSTRACT:** Inorganic–organic hybrid polymers have been developed and tested for evaluation in optical and electrical applications. Although hybrid inorganic–organic polymers can be synthesized by sol–gel chemistry at first, the physical properties of hybrid inorganic–organic polymers are changed during thin film-making processes, that is, photocuring and thermal curing. To investigate the effect of photoinitiator on the material properties during processing, a model system containing methacrylic groups as organically polymerizable units was selected. The conversion of C=C double bond of methacrylic groups depending on some kinds of photoinitiator quantities was characterized by Fourier transform infrared spectroscopy. It was confirmed to correlate the degree of C=C double bond conversion with the refractive indices. Thermodynamically, the enthalpy of the photopolymerization of hybrid polymer was investigated by UV–DSC. UV–DSC spectra showed the exothermic nature of photopolymerization of ORMOCER® to be in dependence of photoinitiator quantities. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 42: 1979–1986, 2004

**Keywords:** photopolymerization; initiators; crosslinking; radical polymerization

## INTRODUCTION

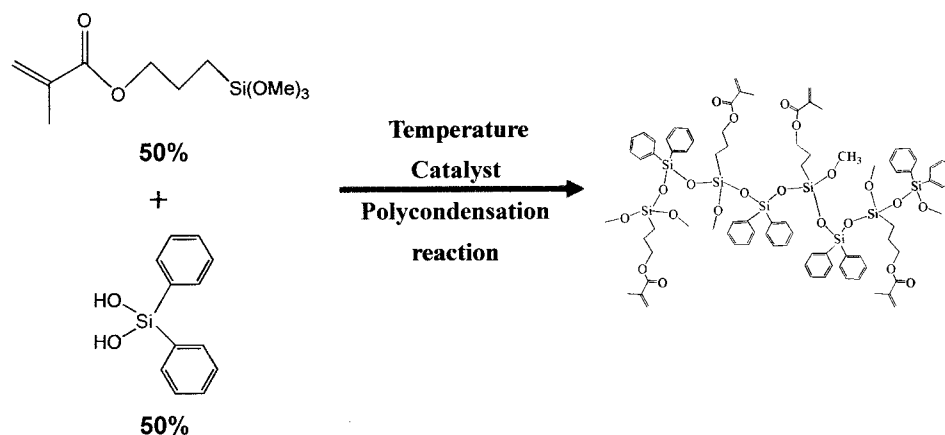
Because of the physical and chemical properties of hybrid inorganic–organic polymers (ORMOCER®), which synergistically result from their hybrid nature, they have been developed and tested for evaluation in optical and electrical interconnection technology over the last decade.<sup>1</sup> ORMOCER® materials are synthesized by sol–gel processing which yields inorganic–organic units that are organically functionalized inorganic–organic hybrid polymers.<sup>2</sup> Therefore, ORMOCER® materials represent a class of materials

that may be classified between polymers, silicones, and ceramics. A great advantage of this materials class is that the material properties can be tailored by a deliberate functionalizing of products. Among many kinds of hybrid materials, siloxane-based hybrid materials using organoalkoxysilane precursors are useful for the design of hybrid materials for photonic applications such as optical waveguide.<sup>3</sup>

Although hybrid inorganic–organic polymers can be synthesized by sol–gel chemistry at first, the physical properties of hybrid inorganic–organic polymers are changed during thin film-making processes, that is, photocuring and thermal curing. To synthesize ORMOCER® materials, inorganic-oxidic units are established by hydrolysis and polycondensation reactions, starting with hydrolyzable functionalized silanes. The reactive

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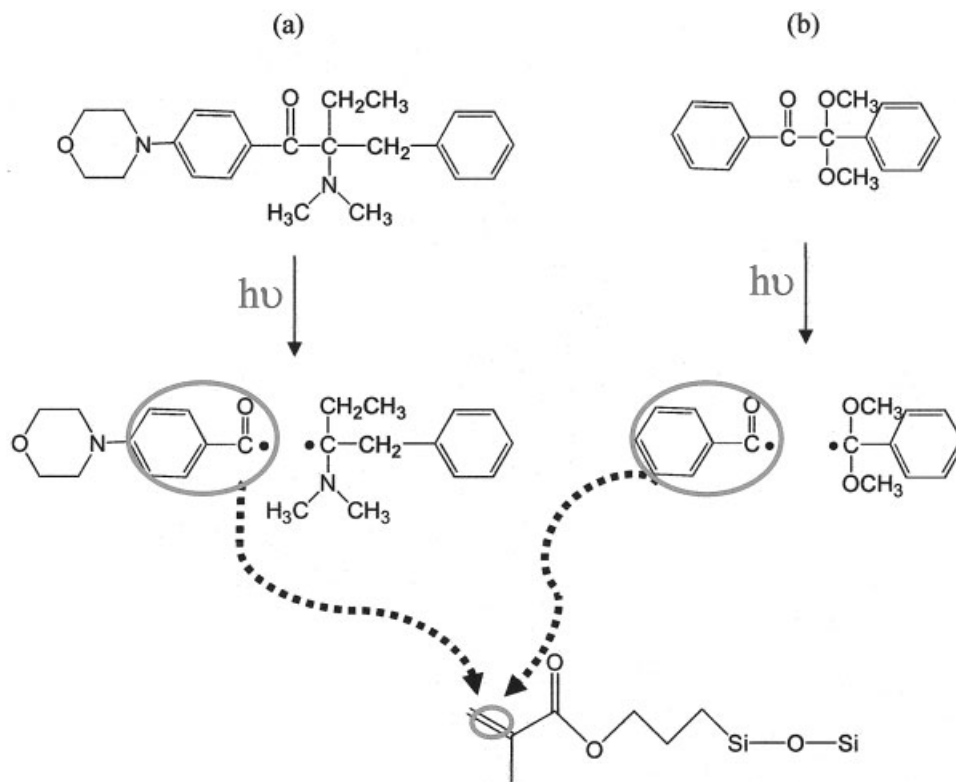
Scheme 1

organic functionalities and the inorganic-oxidic units will be connected to form the inorganic-organic network by organic crosslinking reactions, which can be UV and/or thermally initiated. Dependent on the functionality of each unit in the precursor, the material properties can be tuned. For the photolithographic process in thin film technology, there is a need for easy polymerizable groups like methacryl or styryl groups. In the present study, a model system (henceforth referred to as ORMOCER®I) consisting of the two polycondensed educts, [(methacryloxy)propyl]trimethoxysilane and diphenyl-silanediol, was used. The ORMOCER®I is shown in Scheme 1. The material has methacrylic groups as photopolymerizable functionalities that can be polymerized after adding a suitable UV initiator. The scope of this work was the investigation on the impact of photoinitiator concentration and the thermodynamic study of photopolymerization on the preparation of hybrid material. The complete processing of optical thin film preparation was followed. For the present work, the focus was on the structural analysis of the polymerization of ORMOCER®I. The methacrylic group polymerization dependent on photoinitiator quantity was performed using Fourier transform infrared (FTIR) spectroscopy. From these spectra, the polymerizable group's degree of conversion (henceforth referred to as degree of polymerization) was calculated. Besides, the influence of the UV initiator concentration on the refractive index was determined with the prism coupler method. Finally, photopolymerization during UV curing was studied by UV-DSC.

## EXPERIMENTAL

As organic polymerizable units, methacryl functionalities were used which also account for the negative resist behavior of ORMOCER®I. This allows one to pattern them by UV irradiation and makes them thus attractive for any kind of wafer-scale application. To perform the second step of the processing of the ORMOCER® resin, that is, the organic crosslinking of the material, a suitable photo and/or thermal initiator has to be introduced into the material. As photoinitiators, we used a radical photoinitiator [Ciba Geigy Irgacure 369, 2-benzyl-2-*N,N*-dimethylamino-1-(4-morpholinophenyl) butanone, and Aldrich BDK, 2,2-dimethoxy-2-phenylacetophenone]. Irgacure 369 is a common photoinitiator sensitive at about 350 nm of light and BDK is sensitive at about 220–250 nm of light typically used in a mask aligner. These two photoinitiators undergo a Norrish type 1 photocleavage to yield benzoyl radicals<sup>4</sup> which initiate the photopolymerization in the ORMOCER®I system (Scheme 2). The Norrish 1 type radical photoinitiator cleavage is a homolytic  $\alpha$  cleavage reaction between the carbonyl group and the adjacent  $\alpha$  carbon atom.<sup>5</sup> The photopolymerization of the organic component and polycondensation of the inorganic component mainly govern the property of ORMOCER®I films. However, the effect of photoinitiator has not been investigated in hybrid polymer materials in detail.

The preparation of the ORMOCER®I layers was performed using Si and glass substrates. For the FTIR measurements, transparent p-doped Si(100) wafers were used as substrates, which were cleaned by spinning with propyl acetate and



Scheme 2

characterized before the coating by FTIR spectra. ORMOCER® I was applied onto the substrates by spin-coating, followed by a thermal treatment at 80 °C on a hotplate for 1 min (prebake). The layers were then exposed to UV light, one was 250-nm wavelength light for BDK and the other was 350-nm wavelength light for Irgacure 369, in a conventional mask aligner (Suss, power density approximately 17 mW/cm<sup>2</sup>, 30 s). After the UV processing, the samples again were thermally treated on a hotplate at 80 °C for 1 min (post-exposure bake), followed by a short cool-down period. Subsequently, the layers were developed for approximately 30 s using a mixture of methylisobutylketone and 2-propanol (1:1) to remove the inhibition layer that was formed during the UV exposure in an ambient atmosphere. Finally, the samples were thermally cured at 150 °C for 3 h (Fig. 1). The FTIR measurements were performed in a Nicolet MAGNA-IR spectrometer 760, which has a resolution of 4 cm<sup>-1</sup>. Each processing step during the layer processing was characterized separately for each initiator concentration by FTIR spectroscopy. Finally, UV-DSC measurement was performed in a PerkinElmer UV-DSC with Irgacure 369 containing samples. After cal-

ibrating from the sample holder spectra, we can obtain the heat flow spectra during photopolymerization of ORMOCER® I depending on the photoinitiator concentration.

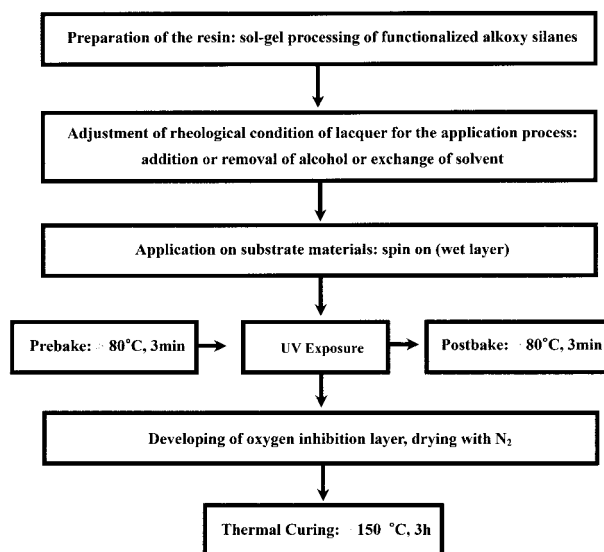
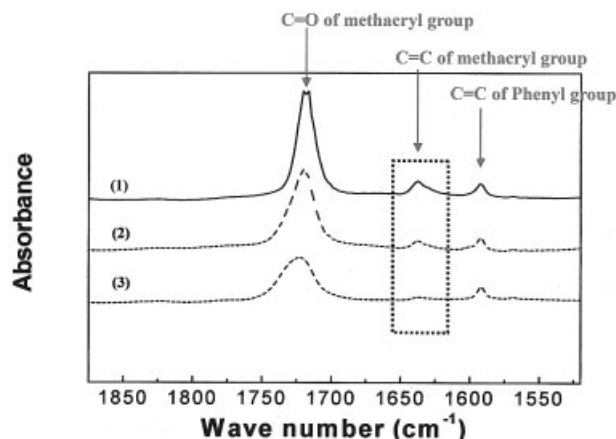


Figure 1. Processing scheme for optical thin films of ORMOCER® I.



**Figure 2.** FTIR spectra after performing the three major processing steps: particularly for the as-coated layer [wet layer, (1)], after UV exposure (2), and after the final thermal curing (3).

## RESULTS AND DISCUSSION

Figure 2 displays a zoom into an FTIR spectra of an ORMOCER®I layer for different processing steps with Irgacure 369-containing samples, particularly for the as-coated layer [wet layer, (1)], after UV exposure (2), and after the final thermal curing (3). Three individual peaks with peak positions are distinguished for each processing step. At  $1640\text{ cm}^{-1}$ , the C=C stretching vibrational mode resulting from the methacrylic groups appears. Besides, a peak at  $1720\text{ cm}^{-1}$  is observed which results from a C=O stretching vibrational mode.<sup>6</sup> The position of the C=O peak remains nearly unchanged (shift  $2.5\text{ cm}^{-1}$ ).<sup>7</sup>

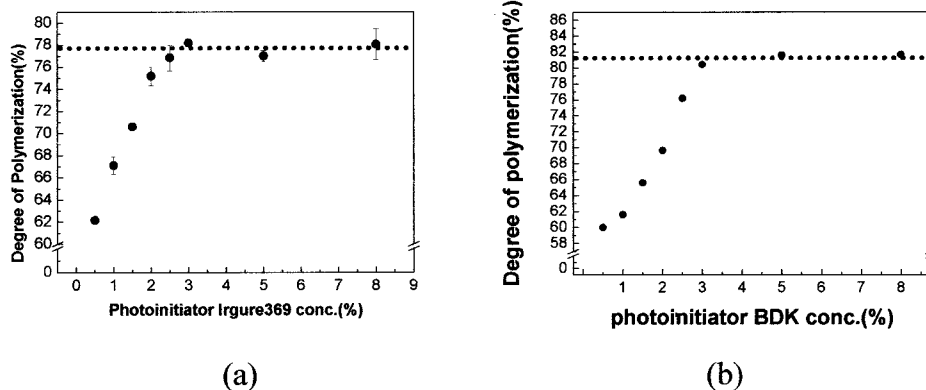
Although a tiny shift of this peak is observed and thus a change in absorption cross-section has to be considered, this peak can be used as an internal reference peak for a determination of the degree of polymerization of ORMOCER®I. The stretching vibrational mode of the C=C peak at  $1640\text{ cm}^{-1}$  resulting from the methacrylic side chains changes its intensity upon photochemical processing, which is followed by FTIR spectroscopy. The third peak which appears at  $1580\text{ cm}^{-1}$  results from the aromatic C=C double bond stretching vibrational mode of the phenyl within the coated layer.<sup>8</sup> Although these species are photochemically nonreactive, a decrease in peak intensity is observed for the thermally cured layer. The thermal curing process (i.e., the final processing step) might result in an evaporation of these species, thus accounting for the decrease in peak intensity

$$N = 100 \times \left( 1 - \frac{A_{\text{C=C}}}{A_{\text{C=O}}} \frac{A_{\text{C=O}}}{A_{\text{C=C}}} \right) \quad (1)$$

Because of accounting for film thickness changes for the different samples, the degree of polymerization  $N$  of the C=C double bond is calculated using relative peak intensities such as eq 1.  $A_{\text{C=C}}$  and  $A_{\text{C=O}}$  are the integrated peak intensities of the C=C and the C=O double bonds of the respective processed sample, whereas  $A'_{\text{C=C}}$  and  $A'_{\text{C=O}}$  are the integrated peak intensities of the wet layers, respectively. Additionally, it was assumed that each initial wet layer contains 100% of non-reacted methacrylic C=C double bonds. As obvious from Figure 2, the C=C peak intensity from the methacrylic groups decreases significantly upon processing from 100% (wet layer) down to approximately 35% (UV exposed and developed layer) and finally down to about 25% (thermally cured layer), that is, 75% of the C=C double bonds from the methacrylic groups are polymerized. Because the optical properties are determined from completely processed ORMOCER®I layers including a final thermal curing step, particular focus will now be on FTIR spectroscopy measurements of the finally processed layers.

Figure 3 presents the evaluated degrees of polymerization of the C=C double bond from the FTIR spectra using eq 1 depending on the concentration of both UV initiators, determined after the final thermal curing step. Each data point corresponds to an average value measured on three different spots of the samples. Two different slopes are observed in the viewgraph of each graph. In the range between 0.25 and 3 wt % UV initiator concentration, a continuous increase of the degree of polymerization from approximately 60–62 up to 78–81% is obvious in both of the graphs, whereas for initiator concentrations above 3 up to 8 wt %, the degree of polymerization has reached a constant value of about 78 and 81%. From the point of view of the final polymerization of the layers, a UV initiator concentration of 3 wt % is sufficient to polymerize the layers as completely as possible for the given processing parameter set.

The two slopes of the degree of polymerization of the resin in dependence of the UV initiator concentration (cf., Fig. 3) can be explained as follows, where it is assumed that the initiator is equally distributed within the resin. If the UV initiator is very diluted (low concentrations) in the ORMOCER®I resin, photochemically induced crosslinking is initiated at each point where a

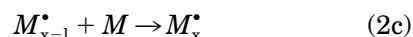


**Figure 3.** Degree of polymerization depending on the concentration of photoinitiators: (a) Irgacure 369 and (b) BDK.

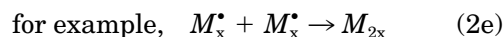
radical is formed following a Norrish type I reaction.<sup>9</sup> The reactive part is species  $I$  (cf., eq 2, starting reaction). Both parts of the UV initiator resulting from this reaction are photochemically active, initiating further polymerization until the reaction is terminated (cf., eq 2).

To understand how the UV initiator influences the degree of polymerization of the hybrid polymers, the radical chain polymerization process will be considered.<sup>10</sup> The kinetics of the photopolymerization system is hybrid polymer material consists of several steps as also observed for other conventional polymer systems: autoacceleration, autodeceleration, primary cyclization, oxygen inhibition, termination, and incomplete reaction of the double bonds. However, hybrid polymer materials mainly consist of inorganic  $\text{SiO}_2$  network and organic functional groups which are crosslinked photochemically or thermally. It is difficult to predict the kinetics or evaluate exactly how changes in the reaction conditions will impact the polymerization kinetics and, ultimately, the hybrid polymer material properties. For this purpose, quantitative FTIR spectroscopy would be necessary to completely follow the changes in the polymerization in hybrid polymer.

The hypothesis is that a small amount of initiator leads to large structural units within the finally processed layer, whereas a large amount will lead to smaller structural units.



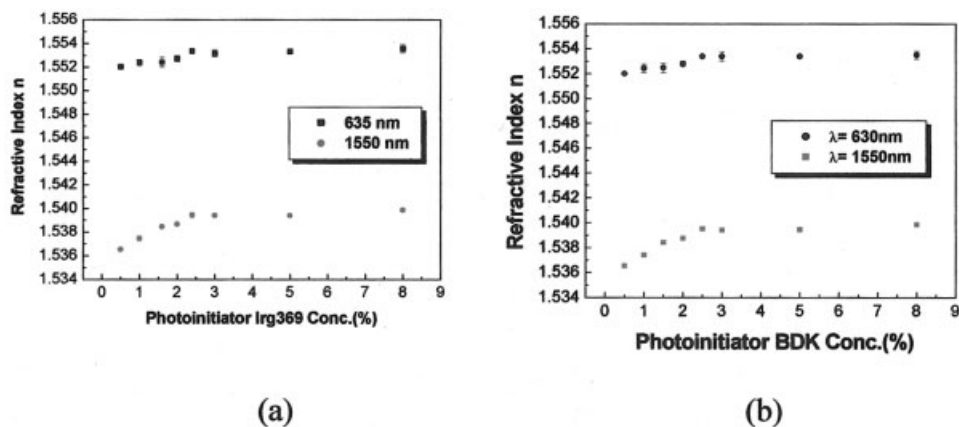
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Higher initiator concentrations would lead to denser packing of the structural units, thus resulting in a denser material. Contrary to this, small photoinitiator quantities will lead to larger units in which the degree of polymerization cannot be further increased because of sterical hindrance of the large structural units. The kinetic chain length  $\nu$  of radical chain polymerization is defined as the average number of monomer molecules consumed per each initiating radical such as eq 3.<sup>11</sup>

$$\nu = k \frac{[M]}{[I^*]^{1/2}} \quad (3)$$

Thus, the kinetic chain length  $\nu$  is inversely dependent on the square root of the initiator's radical concentration. The structural size that is initiated by a small photoinitiator quantity can become larger than the particle size that is initiated by a large amount of photoinitiator. It is certainly a key feature that an increase of the structural size changes the physical properties of the final material until a convergence limit is reached.<sup>12</sup> For example, different sizes of the structural units might cause a different density of the final material; the stacking of a small oligomer group is



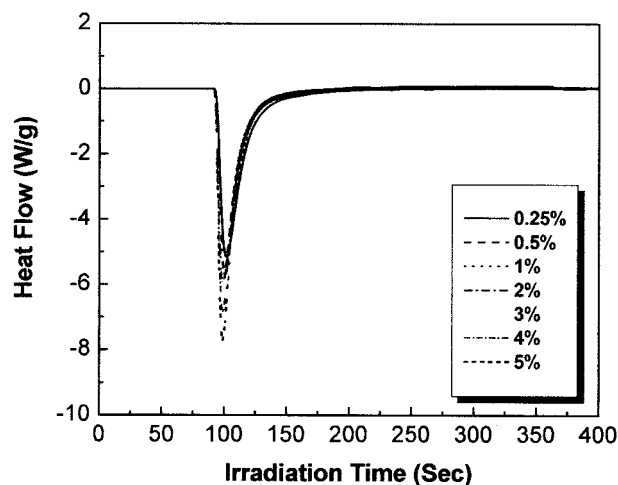
**Figure 4.** Refractive index change with variation of photoinitiators: (a) with Irgacure 369, (b) with BDK.

more densified than that of a large-size oligomer group.

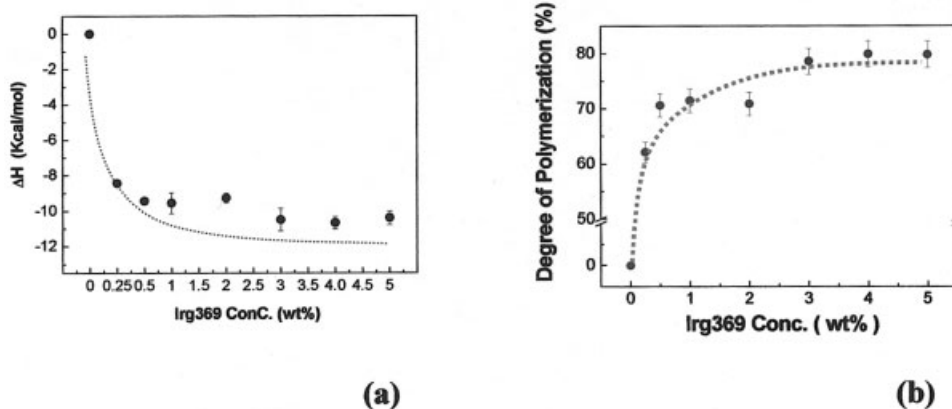
The hypothesis of different structural unit sizes can be supported by refractive index measurements on finally cured ORMOCER®I layers coated on glass substrates. Each refractive index data point is an average from three different measured spots on the sample determined by the prism coupler method. Figure 4 presents refractive index measurements depending on the UV initiator concentration at 635 and 1550 nm, respectively. Both Irgacure 369- and BDK-containing samples show that the refractive index increases from 1.536 up to 1.539 (at 1550 nm) for initiator concentrations up to around 3 wt %. For higher initiator concentrations, the refractive index has reached a constant value, which is in good agreement with the observation of a constant value for the degree of polymerization (cf., Fig. 3). The difference of the refractive index between 0.5 and 8.0 wt % Irgacure369 is large enough to account for processing waveguides and cladding from one and the same material for particular applications. These data demonstrate that ORMOCER®I becomes denser after polymerization with a large amount of UV initiator than after polymerization with a low amount of UV initiator, which results also in a higher refractive index. The more densified the material is due to polymerization, the higher the refractive index will be.<sup>13</sup>

Finally, we focused thermodynamic analysis of the photopolymerization of ORMOCER®I depending on photoinitiator concentration variations with Irgacure 369-containing samples. First, the sample holder is measured without sample. Then,

the container including the sample is exposed to UV light (300–350 nm) for about 500 s. Finally, the difference of two spectra is obtained as a calibrated result as depicted in Figure 5. UV–DSC spectra are displayed which show the photopolymerization of ORMOCER®I during UV exposure depending on the initiator concentration. The thermodynamic characteristics (enthalpy  $\Delta H$  and entropy  $\Delta S$ ) of polymerization are important to understand the effect of the photoinitiator quantity on the polymerization. The chain polymerization of C=C bonds in the methacrylic groups are exothermic (negative  $\Delta H$ ) and exoentropic (negative  $\Delta S$ ). The exothermic nature of polymerization arises because the process involves the exothermic conversion of  $\pi$ - bonds in



**Figure 5.** UV–DSC results depending on photoinitiator Irgacure 369 concentrations.



**Figure 6.** (a) Enthalpy change from the photopolymerization depending on photoinitiator concentration and degree of polymerization. (b) Degree of polymerization depending on the concentration of Irgacure 369 compared with conventional polymer poly(methyl methacrylate) ( $\Delta H \approx -13.35$  kcal/mol).

monomer molecules into  $\sigma$ -bonds in the hybrid polymer materials. The negative  $\Delta S$  for photopolymerization arises from the decreased degrees of freedom (randomness) for the final inorganic-organic hybrid polymer layer relative to the resin. Thus, polymerization is favorable from the enthalpy viewpoint but unfavorable from the entropy viewpoint.<sup>14</sup> Figure 5 shows several UV-DSC spectra depending on the photoinitiator concentration. The samples were exposed to UV light for about 60 s; the exothermic nature of polymerization ( $-\Delta H$ ) and the different depths of heat flow (W/g) for various photoinitiator quantities are shown. The enthalpy change can be calculated from the integration of the peaks [enthalpy change = heat flow (W/g)  $\times$  time(s)]. From Figure 6(a), observations suggest that the enthalpy has reached its maximum value for UV initiator concentrations around and above 3 wt %. This is in good agreement with the data presented in the previous sections, where the maximum degree of polymerization is reached for a concentration of  $\geq 3$  wt %. The higher the UV initiator concentration, the more negative is  $\Delta H$ , that is, the more exothermic is the reaction. One has to think about the amount of energy in conjunction with the UV polymerization. For comparison, the enthalpy of a conventional methyl methacryl polymer is  $\Delta H \approx -13.35$  kcal/mol.<sup>14</sup> The enthalpy of ORMOCER®I changes about  $-8$  to  $-11$  kcal/mol from the result. It means that the maximum  $-11$  kcal/mol is around 84% energy compared with a conventional methyl methacryl polymer. The degree of polymerization of the C=C double bonds

also traces about 65–78 % like this trace according to photoinitiator quantity [cf., Fig. 6(b)]. To consider the effect of photoinitiator quantity on the enthalpy change of photopolymerization, let us consider the photopolymerization steps. There are three polymerization steps (i.e., initiation, propagation, and termination). The more photoinitiator is present, the more C=C double bonds are converted by photoinitiator radicals at first, not by secondary monomer radicals. In other words, if there is a large amount of photoinitiator and it is assumed that this is equally distributed within the resin, then the crosslinking takes place just by the radicals formed upon UV exposure (cf., eq 2a). Because each radical easily finds a polymerizable group, the reaction might be terminated after this step. However, if there is a low amount of UV initiator, the polymerization of the C=C double bonds might happen as described in eq 2. According to the polymerization, each polymerizable group cannot be polymerized because they are already crosslinked parts, which sterically hinder them.

## CONCLUSIONS

This article has described the investigation of photopolymerization for inorganic-organic polymer (ORMOCER®I) used for optical thin films. The main scope of this work was the study on the dependence of two different photoinitiators' concentration on the properties of the hybrid materials. The photo- and the thermal curing have been followed in detail.

There has been little effort so far to correlate the photo- and thermal curing with ORMOCER® materials' physical properties. The degree of polymerization is strongly correlated with the optical properties of the layers. With FTIR measurements, the degree of polymerization could be followed. It increases up to approximately 75–80% and finally reaches a constant value. Refractive index data also recorded for various UV initiator concentrations showed same traces with that of degree of polymerization in both photoinitiators. From these data, the structure of polymerized ORMOCER® can be assumed to form large structural units with small amounts of initiator within the finally processed layer, whereas large amounts will lead to smaller structural units. Finally, photopolymerization has been analyzed thermodynamically by UV–DSC. UV–DSC spectra show the exothermic nature of polymerization. The depth of UV–DSC spectra differs with photoinitiator quantity. The enthalpy change of photopolymerization has been calculated by integrating of UV–DSC spectra.  $-\Delta H$  decreases and finally reaches a constant value, similar to the degree of polymerization.

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