Light-Induced Thermal Decomposition of Alkoxyamines upon Infrared CO2 Laser: Toward Spatially Controlled Polymerization of Methacrylates in Laser Write Experiments

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ABSTRACT: Systems combining photopolymerization and thermal polymerization have already been reported in the literature. Upon near-infrared (NIR) light exposure, this principle of polymerization is called photoinduced thermal polymerization or photothermal polymerization. Thanks to an NIR dye used as the light-to-heat convertor (called hereafter a heater), an alkoxyamine (e.g., BlocBuilder-MA) is dissociated upon NIR light irradiation, initiating the free-radical polymerization of methacrylates. In the present paper, a novel approach is presented for the first time to decompose the alkoxyamine through a direct heat generation upon mid-infrared irradiation by a CO2 laser at 10.6 μm. Compared with previous approaches, there is no additional heater used in this work, as the heat is directly generated by laser irradiation on the alkoxyamine/monomer system. The polymerization can be initiated for benchmark methacrylate monomers with spatial controllability, that is, only in the laser-irradiated area, opening the way for laser write or three-dimensional printing applications in the presence of fillers.

INTRODUCTION

Photopolymerization of (meth)acrylates is reported widespread in the literature. In general, the polymerization process is possible with a photoinitiator, that is, a generator of active species (e.g., cations or free radicals) after light absorption. Traditionally, UV light is used for such polymerizations, but now, the use of visible light has been democratized.1,2 Thanks to the use of these longer wavelength light, curing of filled samples and more particularly composites is more and more promising. More particularly, the use of near-infrared (NIR) light for photopolymerization of (meth)acrylates is a good answer to such an issue.3–6 The closer the wavelength is to the infrared region, the deeper the penetration of light inside the media, especially in the presence of fillers, can be. In the present communication, we propose to use long-wavelength light (mid-IR CO2 laser), rather than visible or even NIR light, for the polymerization process. Carbon dioxide lasers can deliver light with the wavelength in the mid-infrared region, as presented in Scheme 1.

Actually, the use of carbon dioxide lasers for polymer applications is not new. Indeed, carbon dioxide lasers are already extensively used in selective laser sintering.7–9 In such processes, blends of polymer powders are typically employed, and the carbon dioxide laser is used to melt the powders to construct the shape of the desired object in three dimensions (3D).

Herein, the principle is different: the heat delivered by the laser will be used for the first time to decompose a thermosensitive initiator, namely an alkoxyamine, dispersed in a liquid resin. To the best of our knowledge, very few studies have been devoted to this principle of polymerization, and all of these works are based on thermal initiators other than alkoxyamines.10–12 In particular, methyl methacrylate was successfully polymerized with a continuous-wave CO2 laser.10 Examples of frontal polymerization ignited by CO2 laser are given in refs 13 and 14. Therefore, we propose to polymerize a benchmark methacrylate monomer blend (Mix-MA, depicted in Scheme 2) containing an alkoxyamine as the thermal initiator (BlocBuilder-MA).

RESULTS AND DISCUSSION

As specificity, in classical photopolymerization processes, the transitions involved during the excitation of the photoinitiator are between well-defined electronic levels (i.e., between its ground state and its excited state). To get this result, the energy of the photons must be compatible with the energy gap between the ground state and the excited state to allow the occurrence of electronic transition. Therefore, a high energy is usually necessary to induce such an electronic transition. As the energy delivered by the light is inversely proportional to the wavelength, the
photon energy is extremely low while using infrared light and not sufficient to enable the electrons to reach the higher electronic excited state. With such low-energy wavelengths, transitions are only observed between vibrational levels. Therefore, the loss of energy from the vibrationally excited levels is in the form of heat. Therefore, upon CO2 laser irradiation, the sample is locally heated, leading to a potential homolysis of the alkoxyamine (BlocBuilder-MA), enabling the initiation of free-radical polymerization. The mechanism is presented in Scheme 3. Such a behavior can be demonstrated through electron spin resonance (ESR) experiments. Indeed, using a solution of BlocBuilder-MA in tert-butylbenzene (10⁻⁴ M), almost no radical species were observed (Figure 1, curve a) before irradiation. Conversely, upon exposure to carbon dioxide laser, an important increase of the radical signal was detected (Figure 1, curve b). The ESR spectrum obtained clearly corresponded to the nitroxide radicals generated by the cleavage of BlocBuilder-MA, that is, the acyclic β-phosphorylated nitroxide SG1 (N-tert-butyl-N-[1-(diethoxyphosphoryl)-

2,2-dimethylpropyl-N-oxyl nitroxide) radical characterized by the hyperfine coupling constants: aN = 13.7 G; aP = 45.7 G.² Considering that initiating carbon-centered radicals were also generated upon irradiation with carbon dioxide laser, polymerization experiments were carried out. A 2 wt % of BlocBuilder-MA was dissolved into the benchmark monomer blend and irradiated by the carbon dioxide laser. Remarkably, the polymerization of Mix-MA could be induced only in the simultaneous presence of BlocBuilder-MA and IR light (Figure 2, curve 3), that is, no polymerization occurs at the investigated timescale without IR irradiation (Figure 2, curve 1) or without BlocBuilder-MA (Figure 2, curve 2).
and the polymerized parts can be easily removed. Without BlocBuilder-MA, no polymerization occurs, showing the crucial role of this compound to generate initiating radicals upon CO2 laser exposure.

**CONCLUSIONS**

In conclusion, alkoxyamines can be decomposed upon cheap and easily accessible CO2 lasers. A benchmark methacrylate resin has been successfully polymerized upon CO2 laser irradiation in the presence of an alkoxyamine. The patterns obtained in the CO2 laser write experiments for clear resins are not yet well defined. However, remarkably, the polymerization of filled samples is highly satisfying: a well-resolved polymerization is observed. Therefore, polymerization of composites and in particular highly filled samples is possible using this approach. Further applications in 3D printing experiments will be examined in the forthcoming works. The wavelength of excitation must be selected to ensure the light penetration in the filled samples.

**EXPERIMENTAL SECTION OR COMPUTATIONAL METHODS**

**Materials.** The blend “Mix-MA”, used as a benchmark monomer, has been prepared with 33.3 wt % of (hydroxypropyl)methacrylate, 33.3 wt % of 1,4-butanediol dimethacrylate, and 33.3 wt % of a urethane dimethacrylate monomer, obtained from Sigma Aldrich and represented in Scheme 2. Mix-MA was already used in previous works. 

More particularly, its viscosity is well adapted for the preparation of formulations. In addition, interestingly, Mix-MA is not too viscous. Therefore, oxygen inhibition occurs, and only good-performance systems can polymerize it. BlocBuilder-MA was obtained from Arkema. tert-Butylbenzene was obtained from Sigma-Aldrich.

**CO2 Laser and Laser Write Experiments.** A 10 W CO2 laser derived from an engraving machine was used as the irradiation source. In laser write experiments, the engraving machine has been modified to work with an organic liquid and filled resins using a home-made resin tank.

**ESR Experiments.** A Magnettech MS400 ESR spectrometer was used.

**Polymerization Experiments.** The photosensitive formulations were deposited on a BaF2 pellet under air (thickness ≈ 1.4 mm for thick samples) and irradiated with a light source. The evolution of the C==C peak relative to the methacrylate function was continuously followed by Fourier transform infrared spectroscopy (JASCO FTIR 6600), as previously described, at about 6165 cm⁻¹ for thick samples.

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**Printed pattern 3D**

**Figure 2.** Polymerization profiles of mix-MA (methacrylate function conversion vs irradiation time): (1) without irradiation; (2) upon CO2 laser irradiation but without BlocBuilder-MA; (3) upon CO2 laser irradiation with 2 wt % BlocBuilder-MA.

**Figure 3.** Laser write polymerization experiments upon CO2 laser using different powers of irradiation (shape expected: a star).

**Figure 4.** Polymerization upon CO2 laser of filled resin in laser write experiment.
The authors declare no competing financial interest.

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