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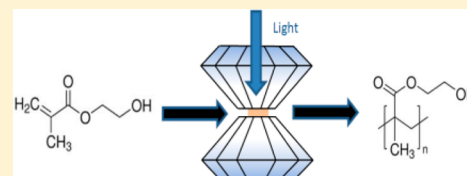
Laser-Assisted High-Pressure-Induced Polymerization of 2-(Hydroxyethyl)methacrylate

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ABSTRACT: We report on a successful room-temperature polymerization of 2-(hydroxyethyl)methacrylate (HEMA) under high pressure. The polymerization is observed in a limited range of pressures 0.1 to 1.6 GPa without the use of any initiator. When the compressed sample is irradiated at 488 or 355 nm by a laser, the polymerization reaction rate is increased by a factor of 10 or 30, respectively. Moreover, the shift of the laser wavelength to the UV improves the polymerization yield of the recovered sample to 84%. The catalysis of the polymerization process by light results from a one-photon-assisted electron transfer to π^* antibonding states of the monomer molecule. The observed polymerization is irreversible and almost complete, which makes this synthesis process suitable for applications.



1. INTRODUCTION

Organic polymerization process is commonly driven by radicals induced by the addition of initiating molecules, which usually have a negative impact on the environment or the biocompatibility of the main product. Last decade efforts were directed to develop methods of plasma-, pressure-, and laser-induced polymerization as a part of chemical processes, allowing us to reduce or even eliminate such impacts and thus leading to phase-pure materials.^{1–3} While plasma methods are restricted to interfaces and short polymer chains (oligomers), the latter two methods make feasible bulk solids and even 3D structures by using two-photon laser polymerization. Nevertheless, intense laser irradiation usually induces ions due to multiphoton absorption and efficiently only operates with the addition of molecules or clusters able to induce intermediate resonance states. As a consequence, the high-pressure (HP) chemistry approach, celebrating this year its centenary,⁴ remains today potentially the most environmental and biological friendly because it promotes polymerization from pure monomer solution.

The effects of high pressure on molecular electronic structure and chemical reactivity have been addressed by several groups in the past from both theoretical and experimental points of view.^{5–12} Basically, the rearrangement of electronic clouds induced by compression leads to substantial changes in the electronic structure of reactants and, potentially, to modifications of chemical bonds. Compared with ambient conditions, new chemical reactions pathways become available and novel reaction products may be expected. Indeed, under high pressure, the interplay between energy surfaces of ground and excited states makes the thermal excitation of excited electronic states feasible. Consequently, the electronic structure of HP reactants is quite different from that of reactants at ambient pressure, and the role of excited state in the reaction has to be considered. This is why HP chemical reactions share common

features with photochemical reactions, as reported in several experiments where an acceleration of the reaction by optical pumping of the reactants in a suitable excited state has been demonstrated to be equivalent to an increase in pressure.¹³

In general, unsaturated compounds submitted to high pressures react to be saturated by linking to each other, leading to polymerization. In accordance with the Le Chatelier principle, the replacement of weak π bonds by strong new σ bonds densifies the material. Experimentally, the permanent HP-induced polymerization has been observed in only a few simple unsaturated hydrocarbons in liquid or crystalline solid phases.^{14–18} Moreover, laser irradiation of compressed ethylene, acetylene, and butadiene molecules was found to accelerate the reaction kinetics, lower the pressure threshold, and modify properties of the final product.^{19–21} In contrast, the room-temperature HP permanent polymerization of monomers containing hydroxyl or carbonyl groups affected by intermolecular hydrogen-bond interactions has not been confirmed. The HP-induced polymerization of tetraethylene glycol dimethacrylate is partial and required heating of the sample under pressure.²² Similarly, the compression of acrylic acid up to 10 GPa leads only to the formation of short oligomer chains in the recovered product.²³ There is only one report on a permanent polymerization of 2-propyn-1-ol, where a relatively weak H-bond interaction can be expected, at relatively high pressures exceeding 8 GPa.²⁴

Among other polymers, pHEMA (poly(2-hydroxyethyl methacrylate)) is a well-known biocompatible product of high interest for medical applications in dentistry, bone cements, and biomaterials. Because of its hydroxyethyl pendant groups, pHEMA can also be prepared in the form of hydrogel

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used to manufacture soft contact lenses. Owing to this large field of bioapplications, there is a strong interest for new polymerization methods producing more pure pHEMA by avoiding the use of potentially toxic catalysts. The HEMA (2-hydroxyethyl methacrylate) monomer is known to be affected by large hydrogen-bond interactions,²⁵ which, under HP, could prevent the rearrangement of molecules required for the polymerization to take place. To the best of our knowledge, a complete HP polymerization of monomers containing hydroxyl or carbonyl groups has not been reported up to now.

We demonstrate the room-temperature HP-induced polymerization of pure 2-(hydroxyethyl) methacrylate (HEMA). We study kinetics of the polymerization process in the dark and in the presence of laser irradiation of different wavelengths and intensities to gain a deeper insight into the underlying mechanism.

2. EXPERIMENTAL SECTION

Liquid HEMA (purity >99%, Aldrich) without further purification was loaded in a hole of 250 μm in diameter drilled in a preindented metallic gasket and compressed in a symmetric diamond anvil cell (DAC). The anvils made of type IA diamonds were selected for low fluorescence in the frequency region of the Raman measurements. Pressure was monitored with a precision of ± 0.05 GPa using the ruby fluorescence scale. Raman spectra of the samples compressed in the DAC at RT were measured in the backscattering configuration using a HR800 spectrometer equipped with a Peltier-cooled CCD detector (Horiba JobinIvon) with spectral and spatial resolutions of 0.25 cm^{-1} and $5\text{ }\mu\text{m}$, respectively. Two different laser systems have been used to promote the polymerization reaction under pressure. In the first configuration, the HEMA samples in the DAC were irradiated with the blue line of an Ar⁺ laser (Coherent, $\lambda = 488\text{ nm}$) through three different microscope objectives (10 \times , 40 \times , or 100 \times), providing various power densities on the sample. In the second configuration, a frequency-tripled Nd:YAG laser (CNI MPL-F-355, $\lambda = 355\text{ nm}$, 7 ns) with high repetition rate (7.6 kHz) and maximum average power of 10 mW is focused on the sample through a biconvex lens of 750 mm focal length. In both configurations the power density on samples is measured using a CCD beam-shape analyzer (Spiricon SP620U) and a power meter (PowerMax PS10Q Coherent).

3. RESULTS AND DISCUSSION

Raman spectroscopy is a useful and widely used method for in situ observation of polymerization. Indeed, the characteristic bands of monomer and polymer change in intensity as the polymerization progresses. For example, in the polymerization of vinyl monomers, C=C double bonds are broken and C–C single bonds are formed. Consequently, the kinetics of the polymerization reaction can be monitored in situ by the decrease in intensity of vibrational bands associated with C=C double bonds in comparison with a reference band whose intensity does not change upon polymerization.^{26,27}

In the present experiments, the polymerization yield (*PY*) at the time *t*, or fraction of polymerized component, was determined from relative intensities of characteristic vibrational bands of HEMA observable between 1380 and 1800 cm^{-1} : C=C at 1407 and 1641 cm^{-1} associated, respectively, with the C=CH₂ bending and C=C aliphatic stretching vibrations, C–CH₂ at 1455 cm^{-1} associated with deformation of C–H group, and

C=O stretching at 1714 cm^{-1} . Because the C=O bond is not involved in the polymerization process, it can be used to normalize the intensities of other Raman bands. The *PY* factor was then determined according to

$$PY(t) = 1 - \frac{(I_{\text{C=C}}/I_{\text{C=O}})_t}{(I_{\text{C=C}}/I_{\text{C=O}})_{t=0}} \quad (1)$$

where $I_{\text{C=C}}$ and $I_{\text{C=O}}$ are, respectively, the area of $\nu(\text{C=C})$ and $\nu(\text{C=O})$ Raman bands.

As follows from our Raman spectroscopic measurements, polymerization of compressed HEMA occurs at pressures between 0.1 and 1.6 GPa. Figure 1 shows examples of Raman

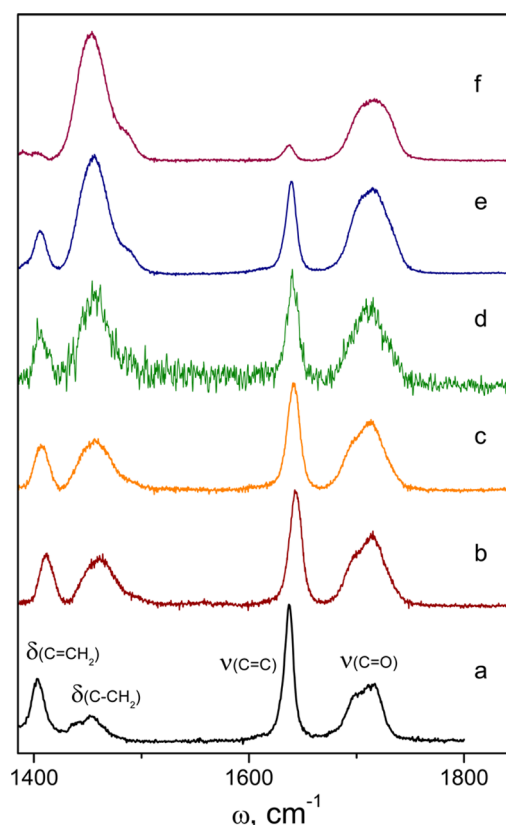


Figure 1. Raman spectra of liquid HEMA at atmospheric pressure (a) and at 0.7 GPa and RT after 5 h (b), 6 days (c), and 41 days (d). Recovered sample after just a few minutes in air (e) and after 7 days (f).

spectra of the starting HEMA, and of HEMA compressed to 0.7 GPa for different periods of time and after recovery. Compared with the atmospheric pressure spectrum (a), at HP (b–d) Raman bands are slightly broadened and blue-shifted due to a stiffening of intramolecular bonds. The main effect of pressure is a progressive decrease in the C=C bands and growing of the C–C band intensities. This behavior is characteristic of the polymerization process resulting in the double-bond opening of the methacrylate group and propagation–elongation of polymer chains. This conclusion is supported by the observed pressure drop in the sample volume from 0.7 to 0.3 GPa, which reveals the formation of a higher density product. The recovered sample in Figure 1e retains the polymerization state before decompression (d), which evidences the permanent nature of the pressure-induced modification. Moreover, apart from differences in the relative intensities of

$\text{C}=\text{C}$ (1640 cm^{-1}) and $\text{C}-\text{CH}_2$ (1455 cm^{-1}) bands, the Raman spectra of the recovered product in the spectral range 300 to 3500 cm^{-1} are identical to the Raman spectra of pHEMA obtained after thermal polymerization. It is worth remarking that after 1 week of exposure in air the recovered sample exhibits a stronger attenuation of the double bond $\text{C}=\text{C}$ bands, which was assigned to the natural sample purification owing to evaporation of the remaining HEMA monomers from the recovered sample.

Polymerization kinetics of HEMA exposed to HP of 0.7 GPa is shown by the dependence of polymerization yield, $\text{PY}(t)$, in Figure 2. The process is slow and not completed even after 41

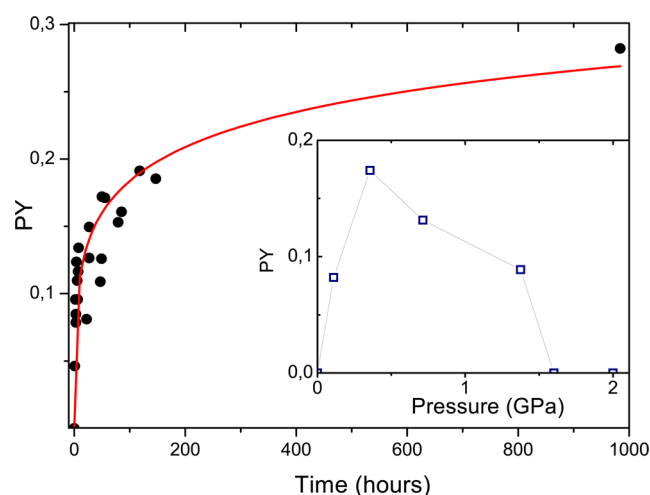


Figure 2. Polymerization kinetics of HEMA under 0.7 GPa static pressure. The solid line is a fit with the Avrami equation. (See the text.) The inset shows the PY of freshly recovered samples after 19 h under different pressures.

days, where PY remains below 0.3 . The inset in Figure 2 shows PY of the recovered samples after 19 h of compression at different pressures. The PY attains the maximum at 0.35 GPa and progressively decreases when pressure increases. Above 1.6 GPa PY becomes null even when samples are kept under pressure for several days.

The HP-induced polymerization of simple unsaturated hydrocarbon molecules has been previously reported.^{14–18} To our knowledge, in all of these reports the reactions accelerate with increase in pressure. This picture is different in the case of HEMA reported here. While the pressure threshold concerned the beginning of polymerization in previous studies, the present results evidence a pressure threshold $p^* \approx 1.6\text{ GPa}$, above which no polymerization occurs. We relate this to the influence of energetic and steric factors on the reaction activation. To check the variation of HEMA viscosity with pressure, we have loaded a copper sphere of $20\text{ }\mu\text{m}$ in diameter together with liquid HEMA into the DAC. In the range of pressure between 0.1 and 0.9 GPa , we have observed that the sphere, attracted to gravitation, could move inside the DAC. Conversely, when the pressure exceeds 1.6 GPa , no movement of the sphere is observed. Because the characteristic time of polymerization is very long (several days, Figure 2), there is no possible confusion in differentiating the viscosity change due to an increase in pressure from that due to polymerization. We assign this finding to a sudden increase in viscosity above 1.6 GPa , leading to the molecular movement restriction. The nature of this modification and possible new phase attribution remain an

open issue. In any cases, the suppressed mobility and nonfavorable arrangement of monomers in the higher-pressure state above 1.6 GPa can restrict the formation of a polymeric chain. More data about HP phases of HEMA are required to be more conclusive on this point.

Acceleration of HP-polymerization reactions upon laser irradiation has been reported in literature for samples in liquid or solid states.^{16,19–21} Accordingly, we have studied the influence of laser irradiation on HEMA samples subjected to a pressure of 0.7 GPa . Two different laser systems, described in the Section 2, have been used to irradiate freshly loaded HEMA samples at 488 (12 kW/cm^2) or 355 nm (18 W/cm^2). Raman spectra recorded on these samples, after different irradiation times, are shown in Figure 3. The obtained spectra clearly

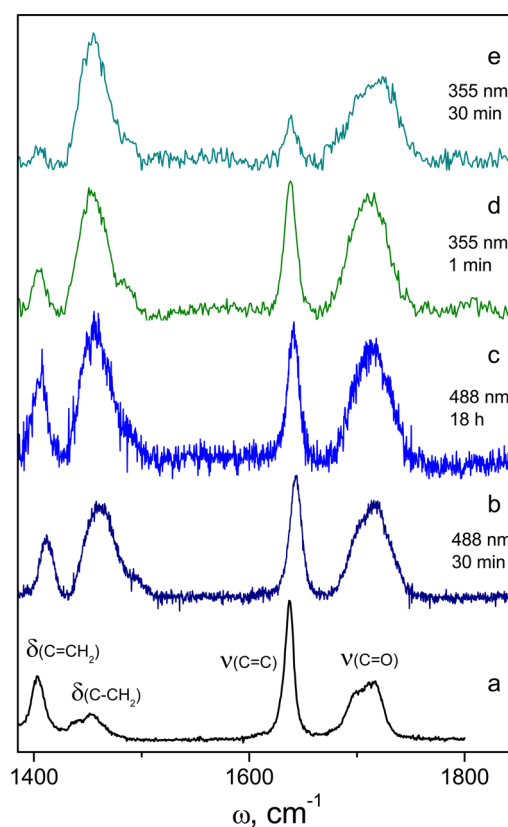


Figure 3. Raman spectra of liquid HEMA before irradiation (a) and at 0.7 GPa after irradiation at 488 nm for 30 min (b), 488 nm for 18 h (c), 355 nm for 1 min (d), and 355 nm for 30 min (e).

evidence the triggering of the polymerization reaction by light and acceleration of the reaction kinetics when the excitation wavelength is shifted to the UV. The polymerization yield $\text{PY}(t)$ as a function of the irradiation time is shown in Figure 4 for both wavelengths. In the case of the irradiation at 488 nm (12 kW/cm^2), the polymerization progress is much faster compared with the nonirradiated sample in Figure 2 and, after only 10 h , attains a plateau with $\text{PY} \approx 38\%$. Acceleration of the process is even more pronounced with an irradiation at 355 nm because a plateau with $\text{PY} \approx 84\%$ is reached after only 30 min of irradiation. The observed effects are a net synergy of the HP and light treatments because at the atmospheric pressure the same laser irradiation does not produce any polymerization of HEMA even after 1 day of irradiation.

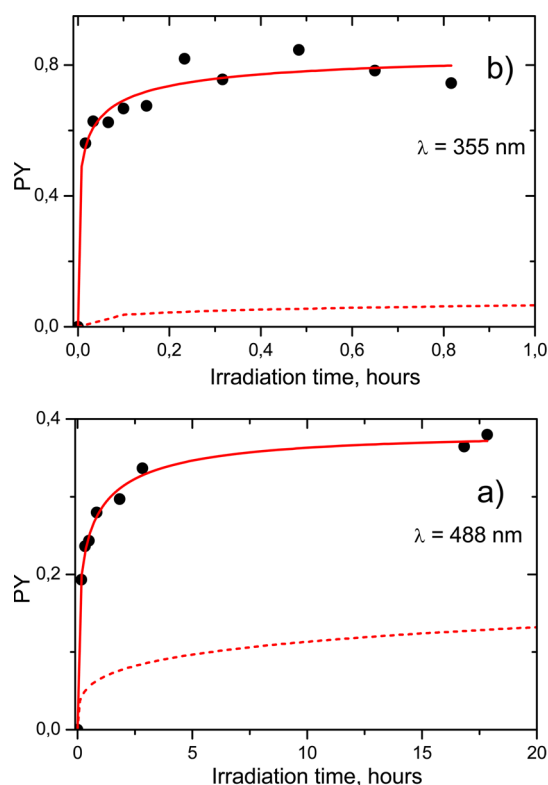


Figure 4. Polymerization kinetics of HEMA under 0.7 GPa pressure with laser irradiation at 488 nm (12 kW/cm²) (a) and 355 nm (18 W/cm²) (b). The solid lines are fits with Avrami equation. (See the text.) For a comparison with HP polymerization process without irradiation, the fit curve from Figure 2 is shown as a dashed line.

The HP compression of simple unsaturated hydrocarbons usually results in almost complete polymerization.^{14,16,18–21,28} The partial polymerization of HEMA observed in present studies, with or without irradiation, could be explained by the presence of hydroxyl and carbonyl groups of the monomer molecule involved in intermolecular hydrogen bonds. Indeed, each HEMA molecule has only one C=C double bond, and the polymer chains grow linearly without cross-linking. Consequently, the polymerization process requires a significant mobility of the monomers to fit the growing chain. Strengthening of hydrogen bonds at HP²⁹ can suppress this capacity of steric rearrangements by hindering the movement of HEMA monomers. This hypothesis is supported by recent HP experiments with monomers containing hydroxyl or carbonyl groups. Murli et al.²³ have observed nonpermanent polymerization of acrylic acid with only short oligomers found in the recovered sample. Kaminski et al.²² have reported on inefficient polymerization of tetraethylene glycol dimethacrylate at 1 GPa and room temperature.

Kinetics of the examined polymerization reactions can be analyzed in frame of the Avrami model³⁰

$$PY(t) = PY_{\infty}(1 - \exp(-kt^n)) \quad (2)$$

where $PY(t)$ and PY_{∞} are the polymer fractions at time t and at the end of the process, k is the rate constant, and n is a parameter, whose value depends on geometry of the growing polymer chains. Fits of $PY(t)$ data with eq 2 are shown in Figures 2 and 4 by solid lines. The final polymerization yield PY_{∞} is fixed at the value observed experimentally in Figures 2 and 4 to reduce the number of free parameters in the fit

procedure and improve the reliability of the fitted parameters. The obtained values of k and n are given in Table 1 together with the polymerization yield PY_{∞} values chosen for the fit.

Table 1. Avrami Model Parameters k and n Obtained from the Fit of HEMA Polymerization Kinetics Measured at Pressure of 0.7 GPa and Different Laser Power Densities and Wavelengths

wavelength	power density	k (h ⁻¹)	n	PY_{∞}
no irradiation	0	0.19 ± 0.02	0.27 ± 0.03	0.38
355 nm	18 W/cm ²	3.23 ± 0.5	0.27 ± 0.05	0.82
488 nm	12 kW/cm ²	1.37 ± 0.04	0.35 ± 0.04	0.38
488 nm	2 kW/cm ²	1.44 ± 0.08	0.34 ± 0.05	0.24
488 nm	0.12 kW/cm ²	1.41 ± 0.06	0.40 ± 0.05	0.24

The similar values of parameter n obtained in both experiments indicate that the growth geometry of the polymer chains is not strongly altered by the laser irradiation intensity and wavelength. Originally, the Avrami equation was proposed to model the crystal growth from a liquid phase^{30,31} and has been adapted later to polymerization processes.^{14,18} According to this model, the values of n are expected to increase with the dimensionality of the process, ranging from 1 to 2 in the case of linear growth. Nevertheless, in polymerization process involving a diffusion step where reactants are transported to reaction sites, values of n close to 0.5 ± 0.3 were found,^{16,18–20} in agreement with model calculations showing that n is equal to 0.5 in the case of the diffusion-controlled 1D growth process.³² The values of n reported in Table 1 suggest the diffusion-controlled linear growth of pHEMA chains. This diffusion step could be interpreted as a continuous modulation of relative orientations and intermolecular distances, leading to instantaneous configuration allowing the polymerization reaction to occur.

The obtained k values (Table 1) evidence that the polymerization reaction of HEMA under HP is more than one order of magnitude faster under laser irradiation. The optical enhancement of the HP polymerization is usually explained by excitation of π^* -antibonding states. The energy barrier hindering the system evolution toward the final state can be absent under these conditions. Even though there is no literature data about excited states of HEMA, insights regarding the photochemical processes leading to polymer formation may be proposed based on the excited-state structure of acrylic and methacrylic acid containing the same chromophore backbone C=C–C=O. In these last two compounds, the available experimental and theoretical data are nevertheless restricted to ambient pressure range. A schematic representation of acrylic and methacrylic acid energy levels is given in Figure 5; we shall adopt this scheme for HEMA. Owing to the singlet–triplet intersystem crossing, optical excitation of singlet states $S_1(^1n\pi^*)$ and $S_2(^1\pi\pi^*)$ results in the efficient energy transfer to triplet $T_1(^3\pi\pi^*)$ state.^{33,34} The excited electron of the T_1 state in the π^* orbital elongates the C=C double bond, delivering to it a single-bond character. Moreover, the rotational barrier around C–C bond is lowered in the T_1 state, and the CH₂ group can rearrange to minimize the steric repulsion with nearest molecules. Consequently, the long-lived excited T_1 monomer can initiate the polymerization reaction when it encounters an appropriate configuration with another ground-state monomer molecule. We notice that the previous observation of UV-induced polymerization of crystalline

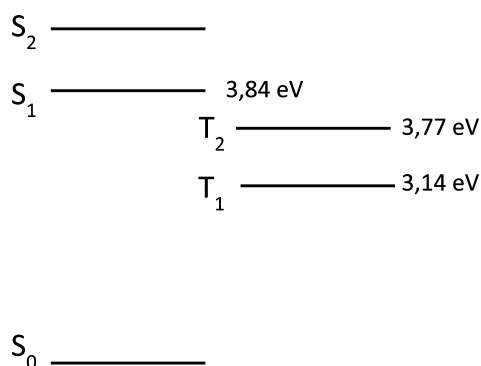


Figure 5. Schematic energy levels of acrylic and methacrylic acids. The energy values are given for acrylic acid from ref 33.

methacrylic acid³⁵ is consistent with this hypothesis. Our observed irradiation enhancement of HEMA polymerization kinetics supports the triplet-state-mediated mechanism

We now discuss the nature of the optical excitation process leading to the HEMA polymerization. In the case of the UV excitation, the photon energy (3.5 eV) seems not sufficient to excite the first singlet state. The two-photon excitation is strongly unlikely due to the low density of power used in the experiment (18 W/cm²). Three factors may explain this disagreement. (1) The increasing overlap between electronic orbitals at HP induces a decrease in the energy gap between the occupied π (HOMO) and unoccupied π^* (LUMO) orbitals.^{13,36} (2) In addition to this vertical displacement of potential surfaces, there can be also a horizontal displacement along the configuration coordinate due to different compressibility of the ground and excited states.⁶ Together, these two contributions may explain vanishing energy mismatch that allows one-photon excitation of HEMA S_1 state at 355 nm under high pressure. (3) Moreover, the low-energy forbidden $T_{1,2}$ – S_0 transitions may become at least partially allowed at HP, which can promote the direct triplet states population.

More support to our assignment of the polymerization acceleration to one-photon transitions can be obtained in measurements conducted at different laser power densities. In these experiments, the overall photon flux was conserved and the intensity varied according to the spot size by changing the microscope objective. The PY data are shown in Figure 6 for

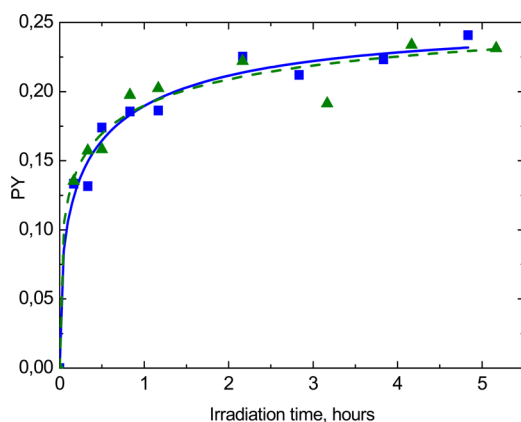


Figure 6. Polymerization kinetics of HEMA at pressure of 0.7 GPa for laser intensities 0.12 (■) and 2 (▲) kW/cm² (λ = 488 nm). Fits of PY with Avrami equation for laser power densities 0.12 (solid line) and 2 kW/cm² (dashed line).

two power densities of 2 and 0.12 kW/cm². The experimental kinetics coincide, which reflect parameters of the Avrami model reported in Table 1. This experiment shows that the rate constant, k , is independent of laser intensity, which is a strong indication of one-photon transitions.

4. CONCLUSIONS

In conclusion, we observed the HP-induced polymerization of 2-(hydroxyethyl)methacrylate at RT without the addition of any initiator. In contrast with previous observations, the polymerization process takes place at relatively low pressure (threshold pressure <0.1 GPa) and ceases above $p^* \approx 1.6$ GPa. The polymerization kinetics is diffusion-controlled and is explained by a decrease in the activation energy on compression. The HP limit p^* can be explained by a sudden increase in viscosity. The polymerization process accelerates by ~ 10 times under laser irradiation at 488 nm and by 30 times under irradiation at 355 nm. Both photoexcitation processes involve 1-photon transitions toward the low-lying excited states of HEMA molecules. The transitions at 488 nm most probably terminate on the T_1/T_2 triplet states that can be partially allowed at high pressures. At shorter wavelengths, participation of the singlet S_1/S_2 states cannot be excluded with subsequent energy conversion to the triplet states. The ability of HEMA to polymerize when compressed significantly extends its fields of applications as a biocompatible material. Compared with the usual polymerization methods (e.g., thermal activation), it reduces the environmental impact by industrial production. The relatively low pressure of the polymerization makes fabrication of large bodies and also of composites with other biocompatible materials such as diamond feasible. The reported HP treatment could allow new production methods of pHEMA thin films.

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Notes

The authors declare no competing financial interest.

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