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Accessing the Activation Mechanisms of Ethylene Photo-Polymerization under Pressure by Transient Infrared Absorption Spectroscopy

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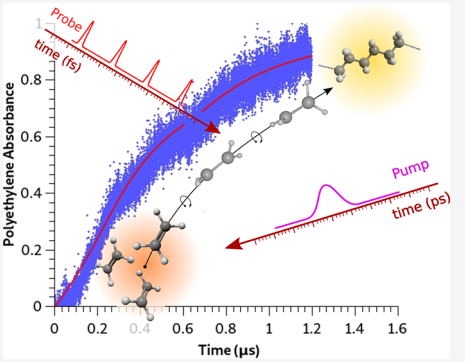
ABSTRACT: The ambient temperature photoinduced polymerization of compressed (P < 1 GPa) fluid ethylene was characterized by transient infrared absorption spectroscopy with a resolution of few nanoseconds, 3 orders of magnitude higher than previously reported. The reaction has been studied under both one- and two-photon excitation evidencing in the latter case its occurrence only in the presence of different transition metal oxides. Their photocatalytic activity is ascribed to the stabilization of the excited biradicals through electron density exchange between the d orbitals of the metal and the π antibonding orbitals of ethylene which lengthens the lifetime of the biradicals. In both one- and two-photon activation cases the polymerization is characterized by an initial step distinguished by a molecularity of 0.15 ± 0.02 identified as the activation step of the reaction lasting, in the one-photon excitation case, a few hundreds of nanoseconds. Using pulsed excitation the reaction evolves toward a free radical polymerization only under one-photon excitation whereas the critical concentration of radicals required to propagate the reaction is never achieved in the two-photon excitation case. Comparison with continuous wave excitation unambiguously identifies in the average power released to the sample the key factor to drive quantitatively and qualitatively the polymerization.



1. INTRODUCTION

Pulsed laser techniques are central in providing detailed information about the time evolution of chemical reactions in condensed phases. These studies have been so far essentially tackled in solution (see for example refs 1−3) whereas the examples regarding chemical processes in crystals are extremely limited.[4,5] Between these two extremes lie the studies of pure systems where the reaction leads to a phase change, whose most enlightening examples are the polymerization reactions. A quite large number of photopolymerizations have been treated in different reviews with particular attention to the determination of the rate constants of the different individual steps which characterize the entire process.[6,7] The principle behind free-radical photopolymerizations is rather simple: a short laser excitation pulse, generally in the ultraviolet (UV), is absorbed by the monomer creating a suitable concentration of free radicals to initiate the reaction. One of the first studies in this field regards the ethylene polymerization initiated by a 248 nm laser pulse and characterized in a ms time scale with a few μs resolution.[8] Besides the obvious importance for accessing the dynamics of the early stages of the reactive process, the relevance of this work is also related to the nature of the polymer studied. Polyethylene (PE) is indeed the most important synthetic polymer counting an incredible number of diverse applications and to the fact that the synthesis is conducted only with physical methods (light and pressure), an important issue in terms of environmental impact. In this work we succeeded in studying the first microsecond of the photoinduced reaction, a temporal range never accessed before and relevant to disclose the polymerization's initiation step where the concentration of reactive precursors necessary to propagate the reaction is built up.

The purely pressure induced polymerization of ethylene was first studied in the compressed fluid: at 0.2 GPa and 453−523 K using spectroscopic methods to characterize the kinetics of the reaction[9,10] and at 2.3 GPa and 322 K.[11,12] More recently, the polymerization was induced also at ambient temperature in the crystal phase using pressures in excess of 3 GPa by means of a diamond anvil cell (DAC)[13] and the P-T conditions of the reaction threshold in the fluid phase fully characterized.[14] The instability boundary was found to decrease remarkably under visible and near UV irradiation which induced a quantitative transformation to a high quality crystalline polymer at ambient

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temperature and pressures of a few kbar.[15] The reaction was demonstrated to occur following a two-photon excitation, a quite surprising issue due to the low cross-section of such transitions. The same approach was successfully applied to scale the reaction to mm^3 size samples.[16]

The efficiency of the photoinduced polymerization of ethylene in compressed samples and the possibility of exploring the effects of both one- and two-photon absorption by tuning the excitation wavelength (250−500 nm) make of ethylene a model system to investigate the reaction dynamics. In addition, the access to the activation mechamisms of this reaction is particularly intriguing in view of the remarkably short lifetime of the excited species[17−19] which barely agrees with the efficiency of the process. We recently developed a setup for transient infrared absorption experiments where pump pulses of 30 ps produced by a parametric generator (OPG) can be tuned from the IR to the UV, whereas the sample evolution is probed by 200 fs IR pulses with an overall time resolution better than 100 ps and the sample evolution accessible up to hundreds ms delay. This setup allowed the successful characterization of the superheating and homogeneous melting dynamics of ice crystals in a temporal interval ranging from about 100 ps up to tens of ms after the energy necessary for the melting was released to the crystal by a single pump pulse.[20,21] The characteristics of this setup are extremely appealing to extend the study of the polymerization dynamics of ethylene on a much shorter time scale than previously accessed.[8]

Here we report a detailed characterization of the first microsecond of the photopolymerization of fluid ethylene, at room temperature and pressures lower than 1 GPa, induced by both one- and two-photon electronic excitation. The reaction kinetics under irradiation has been monitored allowing the identification of the activation and propagation regimes which are characterized by a different molecularity. In addition, we demonstrated that the two-photon induced reactivity is possible only when the reaction is catalyzed by metal oxides through the stabilization of excited biradical species which act as initiators.

2. EXPERIMENTAL SECTION

Membrane anvil cells equipped with grade 1 Diacell design sapphires (from Almax-Easylab) with a culet of 950 μm have been employed to compress fluid ethylene and studying in situ the photoinduced reactivity. Cu−Be(2%) alloy gaskets were used to laterally contain the samples. They were preindented to a thickness of 30−60 μm and then drilled by spark erosion to obtain a sample chamber of 450 μm of initial diameter and eventually gilded when a non catalytic environment was required.

Ethylene (99.5% from Sapio) was loaded in the sapphire anvil cell by means of the spray-loading technique.[22] The pressure of the sample was calculated using the pressure shift of a precalibrated ethylene infrared active C−H stretching band as no gauge was used to avoid light-absorbing species within the sample.

Different sources have been employed to photoinduce the reaction depending on the experiment purpose. A cw xenon lamp (Hamamatsu L10725) was used both for one- (260−400 nm) and two-photon (400−500 nm) excitation by filtering the emission with appropriate short- and long-wavelength pass filters. In both cases the light is focused on the sample by means of a parabolic aluminum uncoated mirror with a reflective focal length of 50.8 mm to a spot of comparable dimensions of the sample diameter. The incident power was measured by means of a power meter using the empty gasket placed on the focal plane as diaphragm. For pulsed irradiations and time resoved experiments we used as a pump a mode locked Nd:YAG laser (EKSPLA PL2143A), giving a pulse duration of 30 ps and an energy per pulse up to 25 mJ at 355 nm (third harmonic), with a repetition rate up to 10 Hz. This wavelength was used for two-photon excitation, whereas in the one-photon case the third harmonic was converted by an optical parametric generator (EKSPLA PG401) into the visible at 580 nm, and then frequency doubled by a BBO crystal ($6 \times 6 \times 7$ mm^3, cut at 27°, from EKSMA) and selected by a UG11 filter to obtain a UV pulse at 290 nm. For all kind of pulsed irradiation, the beam was attenuated at the desired energy by means of reflective or absorbing neutral filters and focused on the sample with a 200 mm uncotead quartz lens. The distance between the sample and the lens is selected for every experiment to obtain an homogeneous irradiation of the sample chamber without hitting the gasket. The energy released per pulse is measured after the transmission from one sapphire by means of a calibrated Si-photodiode (Hamamatsu S1722-02) and using the drilled gasket as a diaphragm. The signal from the photodiode was read with a 2 GHz oscilloscope (Rohde & Schwarz RT2014) connected to a computer and controlled through a Python3 software.

The transient IR measurements were performed with the setup extensively described in refs 20 and 21 Briefly, a mode locked Ti:sapphire oscillator, pumped with 3.7 W at 532 nm by a doubled cw Nd:YAG laser source (OPUS 532, by Laser Quantum), produces pulses at a repetition rate of 83 MHz centered at ∼815 nm with a fwhm of ∼35 nm and a time duration of ∼28 fs. By regenerative amplification (Pulsar, by Amplitude Technology), using as a pump a Q-switched Nd:YLF laser (YLF 621D, by B.M. Industries) with repetition rate of 1 kHz, pulse duration of 120 ns and a power of ∼10 W, an amplified beam at ∼820 nm (1 kHz repetition rate, ∼0.5 mJ per pulse and time duration of 80−100 fs) is produced. This beam is used to pump an optical parametric amplifier that produces the probe and reference pulses peaked at 2880 cm^{-1} with a fwhm of about 170 cm^{-1} and a total energy of about 2 μJ per pulse. The reference pulse, produced using a ∼3% reflection from a CaF_2 window, is sent directly to the revelation system whereas the transmitted beam is used as probe. The probe beam is focused on the sample and recollected with two gold coated 90° off-axis parabolic mirrors with a focal length of 50.08 mm. The diameter of the probe beam on the sample is about the half (200 μm) of the pump pulse in order to probe the central part of it. Both probe and reference are then focused with a 30° off-axis gold coated parabolic mirror with a focal length of 108.9 mm on the slit of a monochromator (Triax 180, by Horiba) equipped with a 100 grooves/mm ruled grating blazed at 6 μm, and detected with a liquid nitrogen cooled MCT 32 × 2 array (InfraRed Associates Inc.). The resulting resolution is ∼12 cm^{-1}/pixel, and the free spectral range is about 380 cm^{-1}. One 32-element strip is reserved for the probe, the other for the reference. The signal from the detector is integrated by homemade electronics capable to work at a repetition rate of 1 kHz, therefore on the single pulse. The signal is digitized using a data acquisition board (USB-1808G, by Measurement Computing with 18 bit resolution and 0.2 MS/s sampling rate for channel) and acquired by a computer using a real-time Linux kernel and a

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Python3 homemade software. The single pulse absorbance is calculated as the base 10 logarithm of the ratio between the intensities measured for probe and reference. The neat absorbance of the product is then calculated as the mean absorbance value of the polyethylene at 2860−2880 cm^{-1}, subtracted by the background value in the region below 2750 cm^{-1}, where no absorbance of any species within the sample is present. The electronic synchronization realized between the pump/probe sources guarantees a time resolution in the order of 100 ps.[21]

Fourier transform infrared absorption spectra were measured with a Bruker-IFS 120 HR spectrometer suitably modified for experiments in diamond anvil cell, with an instrumental resolution set to 1 cm^{-1}.[23]

The stainless steel powder used as a catalyst is AISI416 steel, the same steel used as a gasket in ref 15, while the Ti-based catalyst is Ti(IV)$(MeO)_4 \cdot H_2O$ from Sigma-Aldrich with a purity of 95%.

3. RESULTS

As stated in the section 2, the region between 2860 and 2880 cm^{-1} has been chosen to quantify the amount of polymer formed from our transient spectra (Figure 1). Only the C−H stretching modes involving saturated (sp^3) carbon atoms contribute to the absorption in this frequency range thus the absorbance change in this interval represents a reliable datum to be used in the kinetic analysis of the reaction. In the top panel of Figure 2, typical single pulse transient spectra recorded after the reported number of pump pulses are shown, whereas in the lower panel we report that the time evolution of the polyethylene absorption after a single pump pulse (290 nm and 2−3 μJ) was focused onto the sample. Linear regression of these data clearly shows that we are not sensitive to the absorption changes induced by a single pump pulse. This result is not surprising if we consider that in ref 8 the polyethylene's absorbance at 2857 cm^{-1} increased by less than 0.01 in 9 ms after a single pump pulse at 248 nm (10 ns duration and an energy of 250 mJ). Here, we are using pulses at higher wavelength (290 nm); the absorption is therefore characterized by a lower cross section, and in addition our pulses have a duration of 30 ps and energies of the order of 3 μJ, resulting in a power of about 0.1 MW which is more than 2 orders of magnitude smaller than that reported in ref 8. As a matter of fact, an absorbance change of 0.04 is detected only after having accumulated 1000 pump pulses therefore in perfect quantitative agreement with the results by Buback.[8] As a result, our experimental apparatus cannot produce, with a single pump pulse, enough polyethylene to be detected independently of the delay of the probe pulse. In other words, we do not observe any change when the sample is not irradiated, i.e., the polymerization proceeds only under irradiation. The numbers of pump pulses multiplied by their duration represent therefore the temporal coordinate of our

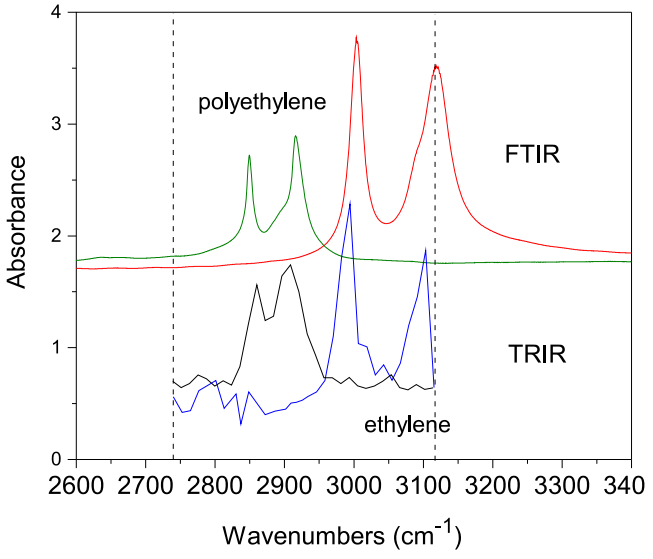

Figure 1. Comparison between the IR spectra of ethylene (blue and red traces) and polyethylene (black and green traces) measured using FTIR spectroscopy and transient infrared absorption spectroscopy (TRIR). The region included between the dashed lines (2740−3115 cm^{-1}) corresponds to the spectral width of the probe beam. In the TRIR spectra each pixel of the MCT array detector correspond to about 12 cm^{-1}. The first microsecond of the photo induced polymerization dynamics of ethylene has been characterized by using both one- and two-photon excitation and different metal catalysts in contact with the sample. For the sake of clarity we will present separately the results obtained with and without the catalysts. The polymerization has been followed by measuring the transient IR absorption spectrum in the region of the C−H stretching modes which undergo a remarkable change going from the monomer to the polymer because of the different hybridization of the carbon atoms. To quantify this issue and demonstrate the capability of our TRIR setup, we compare the spectra measured in pure ethylene and polyethylene samples contained in the sapphire anvil cell (SAC) by conventional FTIR spectroscopy and by averaging hundreds of single pulse transient spectra.

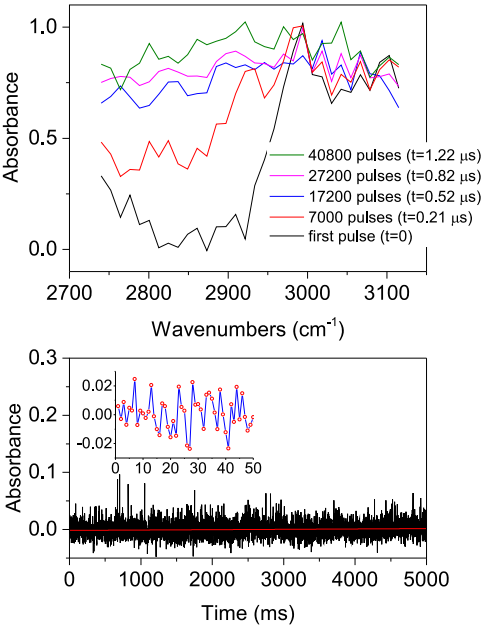

Figure 2. Upper panel: representative transient IR absorption spectra measured after the number of pump pulses reported in the legend were sent onto the sample. The conversion in irradiation time is also reported. The polymer formation is revealed by the progressive absorbance increase detectable between 2800 and 2900 cm^{-1}. Lower panel: evolution of the absorbance changes measured in the transient spectra between 2860 and 2880 cm^{-1} as a function of the probe delay after a single pump pulse was focused on the sample. The red line is the linear regression of these data characterized by a zero slope.

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process, and it will be used in the following to interpret the kinetic data.

3.1. Reaction in the Absence of Metal Catalysts. With the absence of metal catalysts, we mean that in all of these experiments we avoided the contact of fluid ethylene with the metal gasket employed for confining the sample and with the possible derived compounds, as for example oxides. This was achieved by protecting the Cu−Be gaskets with gold that, as it will be shown in the following, does not exhibit any catalytic activity in these conditions. An excitation wavelength ranging from 286 to 290 nm was employed to one-photon excite the monomer to the symmetry allowed $1B_{1u}$ state ($\pi\pi^*$) which is extremely broad and centered at ambient conditions at 7.66 eV (~162 nm).[24] This absorption overlaps sharper absorption bands relative to the transition to the $1B_{3u}$ state which has Rydberg character (π,3s). After each pump pulse, with an energy of 2.6 μJ, we acquired and averaged from 300 to 500 transient spectra each one measured with a single probe pulse, in order to improve the signal-to-noise ratio. The absorbance variation detected in the averaged spectra between 2860 and 2880 cm^{-1} is reported as a function of the irradiation time in Figure 3. The time scale is obtained by multiplying the number

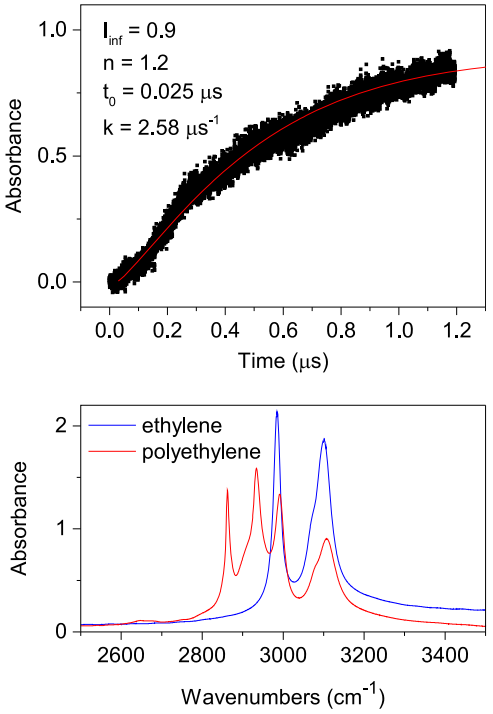

Figure 3. Reactivity induced by one-photon excitation with pulsed laser radiation (30 ps; 2.6 μJ) at 290 nm. Upper panel: absorption of the polymer bands as a function of irradiation time as obtained by the transient spectra. The red line is the fit of these data according to the Avrami's model (eq 1), the parameters used in the fit are reported as an inset. Lower panel: comparison of the FTIR spectra measured before starting the irradiation (blue trace) and after its completion (red trace).

of pump pulses by their duration (30 ps) that it is possible, as mentioned before, in view of the missing reaction's evolution with time after a single pump pulse. This graph is therefore the kinetic curve of the photoreaction measured in the first 1.2 μs. In the same figure we also report the comparison of the IR spectra measured by FTIR spectroscopy before and at the end of the irradiation, showing that a conversion of about 53% of the monomer took place in this time interval. The kinetics, exhibiting a sigmoidal shape as expected for an activated process, presents an inflection point after about 0.15 μs and a clear slope decrease after about 0.3 μs. The curve has been reproduced using the Avrami model formerly developed to describe the crystal growth from the melt[25−27] and then extended to the study of solid-state reactions controlled by diffusion.[28] The amount of PE formed as a function of time is described by the relation:

$$I(t) = I_\infty(1 - e^{[-k(t-t_0)^n]}) \quad (1)$$

where I_∞ is the intensity of the PE absorption at the end of the reaction ($t = \infty$), t_0 is the reaction starting time, $k^{1/n}$ is the rate constant, and n is a parameter related to the dimensionality of the growth process. The fit parameters are reported as an inset in Figure 3. The t_0 value of 25 ns is mainly related to our sensitivity in detecting a minimum amount of polymer, whereas the n value of 1.2 indicates that an overall linear growth of the polymer, the absence of branching, takes place.

When gold rings were used to prevent the contact with the gasket metal, and its possible catalytic effect, we did not detect any reactivity once the sample was irradiated with laser pulses at 355 nm and power up to 25 μJ which, accordingly to our previous experiments,[15] should be extremely efficient in triggering the reaction between 0.2 and 0.8 GPa through two-photon absorption processes. A further confirmation of the sample stability to irradiation with wavelengths out of one-photon resonance was gained by the missed observation of reactivity when the sample was irradiated by a Xe lamp (400−500 nm) which guaranteed a much higher power (45−160 mW and a duration 1−2 h) released to the sample. The difference with the results obtained in ref 15 is ascribed to the catalytic effect of the stainless-steel gasket which was, in that case, in contact with the sample, making it mandatory to explore the reactivity in the presence of catalytic materials.

3.2. Reaction in the Presence of Metal Catalysts. Two-photon induced polymerization was instead observed when the sample was in contact with different metallic compounds sharply demonstrating its occurrence only in the presence of catalysts. In one case we just avoided the gasket gilding leaving the copper−beryllium alloy (2% in Be) gasket in contact with the sample. In other two experiments we used gilded gaskets adding to the sample a very small amount of fine powdered titanium(IV) methoxide $Ti(OCH_3)_4$ in one case, and stainless steel in another. With two of the three catalysts we irradiated fluid ethylene compressed at 0.2 GPa, Cu−Be, and 0.7 GPa, $Ti(OCH_3)_4$, with 25 μJ per pulse of the third harmonic (355 nm) of the Nd:YAG laser source, a wavelength that can only be absorbed by ethylene through a two-photon process.[15,29,30] In these cases, we did not measure the transient spectra but we just checked the occurrence of the reaction by measuring FTIR absorption spectra. In the two experiments where stainless steel powder was added to the sample we measured two kinetics using the transient absorption technique with the same pump wavelength and 20 and 40 μJ per pulse, respectively. In Figure 4 we report some of the IR absorption spectra measured in the first two experiments and those obtained after the completion of the kinetic studies performed in the presence of stainless steel. Contrary to the observation made in the absence of catalysts, we observe, as a consequence of irradiation, the appearance of the characteristic C−H stretching bands of the polymer below 3000 cm^{-1}. The reaction is also rather efficient in agreement with previous

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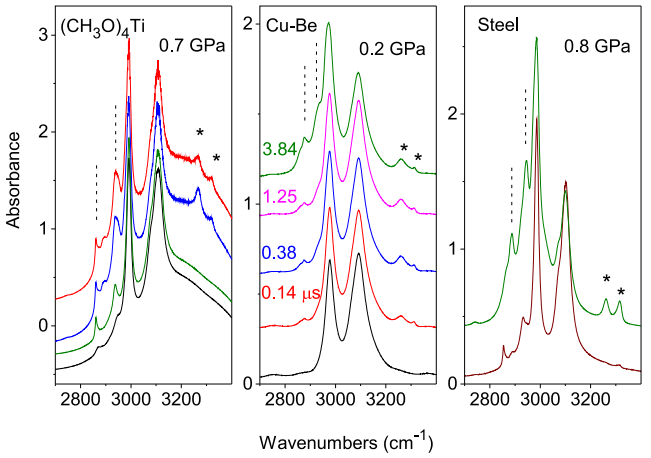

Figure 4. FTIR spectra measured in the C−H stretching region during and after the two-photon induced reaction using 355 nm laser pulses in the presence of different metal catalysts. Dashed lines mark the position of the polymer C−H stretching bands, and asterisks mark the bands assigned to C−H stretching involving carbon atoms with sp hybridization. Left: evolution of the spectrum in the presence of titanium methoxide. The green trace is obtained after 20 min of irradiation with cw light (400−500 nm and 160 mW) from a Xe lamp; the blue trace after 1 μs of irradiation with pulses having an energy of 20 μJ (36 000 pulses) and the red one after 24 h without irradiation. Center: evolution of the spectrum with the irradiation time with uncoated Cu−Be gasket, pulses of 25 μJ at 355 nm have been employed, and the times reported in the figure correspond to the number of pulses multiplied by their duration (30 ps). Right: final spectra obtained after the end of the kinetic studies performed using pulses of 20 μJ (red trace) and 40 μJ (green trace) in the presence of stainless steel powder.

report,[15] leading to a conversion of about 20% of the monomer for supplied energies of about 3 and 1 J when the reaction is catalyzed by Cu−Be and $Ti(OCH_3)_4$, respectively. The comparison of these results are extremely qualitative because of the different pressures where the two experiments have been performed.

The infrared spectra of the polymer obtained by two-photon irradiation are worth investigating further. The asymmetric and symmetric $-CH_2$ stretching give rise to two bands, at about 2925 and 2855 cm^{-1}, respectively, which characterize the spectra of PE. A third band of weaker intensity forms between these two bands at about 2895 cm^{-1}, and this band can be assigned to the symmetric stretching of the $-CH_3$ group, whereas the band corresponding to the asymmetric stretching of this group appears as a shoulder on the high frequency side of the corresponding band relative to the $-CH_2$ groups. The spectral signatures of $-CH_3$ groups suggests the presence of a large number of terminations. Another peculiar feature present in all of the spectra of the polymers obtained in these catalyzed two-photon reactions is the presence of two bands at 3263(3) and 3315(3) cm^{-1}. These are unambiguously assigned to C−H stretching modes of sp hybridized carbon atoms representing therefore or chain terminations or byproducts of the polymerization reaction. As can be seen in the case of the reaction catalyzed by titanium methoxide the intensity of these two bands decreases with time (53% in 24 h) when the sample is not irradiated (see Figure 4), thus suggesting their metastable character. Another interesting observation is that these bands appear only when ethylene is irradiated with pulsed laser light but are not present in samples irradiated by cw light (see Figure 4), both from a laser source or a lamp, in agreement with the findings reported in ref 15.

The two-photon induced polymerization kinetics was studied by transient IR absorption spectroscopy in samples containing stainless steel powder at a pressure of 0.8 GPa. Two different experiments were performed irradiating the sample with laser pulses at 355 nm and energies of 20 and 40 μJ per pulse, respectively. As already reported for the one-photon experiments, we averaged 300−500 transient spectra for every pump pulse obtaining the reaction evolution reported in Figure 5. Also in this case we report the data using a time scale

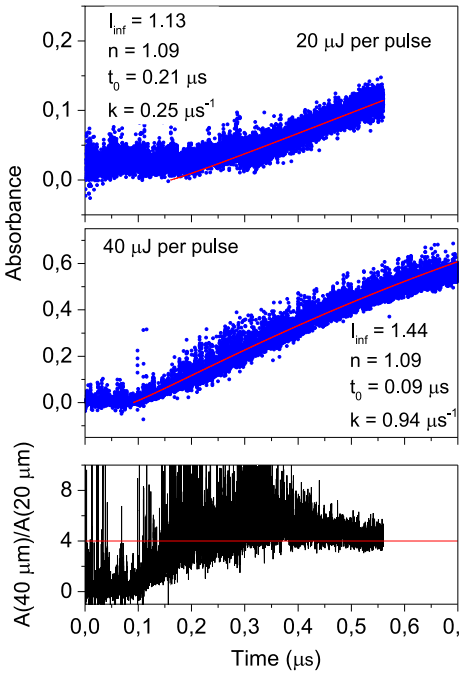

Figure 5. Upper panels: kinetics of the two-photon induced reaction with 20 (top) and 40 (middle) μJ per pulse at 355 nm. In both panels the fit parameters according to the Avrami eq (eq 1) are also reported. Lower panel: evolution of the ratio between polymer absorbances measured in the two kinetics: as the energy per pulse ratio is 2, an absorbance ratio equal to 2 is expected for a linear dependence on the incident power (one-photon absorption), whereas a ratio equal to 4 indicates a quadratic dependence and thus a two-photon absorption process.

obtained by multiplying the number of pump pulses for their duration (30 ps) because the reaction proceeds only under irradiation.

The two sets of data were reproduced by using the Avrami model (eq 1) fixing the I_∞ parameter to the expected PE absorbance assuming the complete ethylene transformation, with the datum obtained by using the FTIR spectra measured at the end of the experiments (these spectra are reported in the right panel of Figure 4). In reproducing the two kinetics, we used in both cases the same n value of 1.09, which indicates a linear growth of the polymer. An almost double induction time t_0 is measured in the experiment performed with the lower pulse energy, in which also the rate constant is about four time smaller than in the 40 μJ experiment. This ratio between the rate constant values is that expected for a two-photon activation process since the amount of excited ethylene molecules, which is in first approximation equal to the number of active species, shall scale with the square of the incident

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power. This is clearly shown in the lower panel of Figure 5 where we report the ratio between the polymer absorbance in the two experiments as a function of time. As it can be seen the quadratic dependence on the incident power is perfectly satisfied in the time range where both reactions proceed. Finally, as already observed in the other two-photon induced catalyzed reactions, absorption bands that can be assigned to C−H modes involving sp carbon atoms also form in this case. Interestingly, the intensity ratio between these bands measured in the two experiments, 20 and 40 μJ, is much higher (~10 times) than expected for a two-photon process (~4 times) suggesting their possible origin by a higher order absorption process.

3.3. Reactions Molecularity. We can gain further information about the mechanisms characterizing the very first instants of the photoinduced reaction by studying the molecularity of the process and its possible evolution with time. This information is crucial for the identification of the number of species characterizing the different reaction steps. To this purpose we used the simple kinetic relation[9,14]

$$v = k[\mathrm{Csp}^2]^m \quad (2)$$

where the reaction rate v is related to the ethylene concentration through the rate constant k and the process' molecularity m. Since our detection window was centered on the frequency of the C−H stretching of the polymer we could not reliably detect the ethylene absorption bands. For this reason instead of the monomer concentration we follow that of sp^3 carbon atoms whose increase in time is proportional (K_p), because of the different absorption cross-section, to the ethylene concentration decrease. The above kinetic law is usually analyzed through the log−log relation which taking into account the use of the polymer concentration becomes

$$\log(v) = m\log[\mathrm{Csp}^3] + \log(k) + \log(K_p) \quad (3)$$

We fitted the time evolution of the polymer concentration using a stretched exponential to have an analytical function for calculating at any time the corresponding reaction rate value. In Figure 6 we report the log−log plot for the reaction induced by one-photon absorption of 2 μJ pulses at 290 nm. As it is evident from the figure, at least two different regimes are identified with a remarkably different value of the molecularity. The early reaction stage is characterized by a molecularity of 0.15 which becomes 2.4 after about 0.3 μs from the reaction beginning, a time corresponding to the slope change detected in the kinetic curve (see Figure 3).

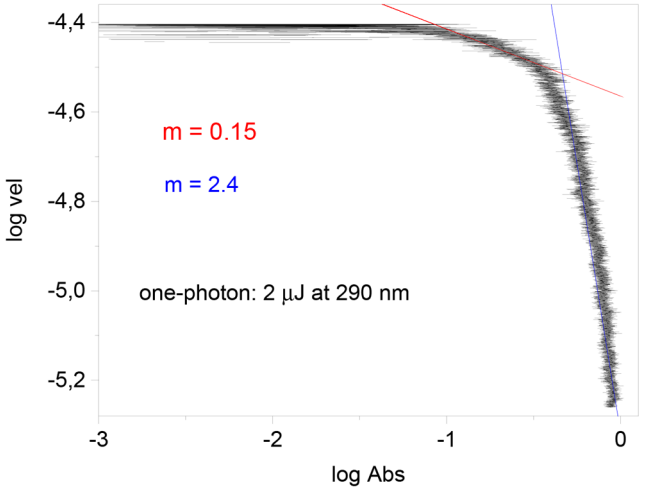

Figure 6. log−log plot of the reaction rate vs the absorbance (concentration) of polyethylene for the one-photon induced reaction. The two linear fit indicate the reaction steps characterized by a consistent change of the molecularity value.

The same analysis has also been performed for the two-photon induced reaction using stainless steel in contact with the sample and laser pulses of 20 and 40 μJ. The corresponding log−log plots are reported in Figure 7. Contrary to what we observe in the one-photon excitation case, the two-step regime is observed only in the reaction performed with higher energy pulses. The molecularity of the initial reaction step is nearly identical in both experiments, also nicely agreeing with that characterizing the analogous step in the one-photon reaction. This step is likely the only probed in the reaction performed with 20 μJ per pulse because of the very limited amount of polymerized monomer. Where the higher energy pulse experiment is concerned, a slope (molecularity) change is observed after about 0.45 μs but the extent of the molecularity change is not as large as observed in the one-photon experiments changing only from 0.14 to 0.6.

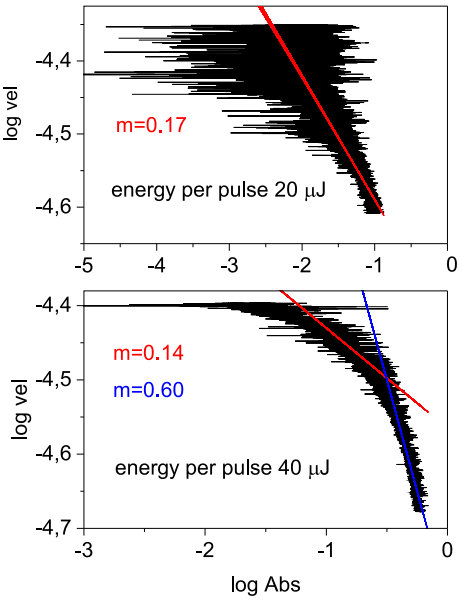

Figure 7. log−log plot of the reaction rate vs the absorbance (concentration) of polyethylene for the two-photon induced reaction. Upper panel: reaction induced by 20 μJ laser pulses (355 nm) exhibiting a single molecularity regime. Lower panel: reaction induced by 40 μJ laser pulses (355 nm) where two regimes characterized by different molecularity values can be identified.

4. DISCUSSION

The free radical polymerization of ethylene can be triggered by absorption of light resonant with the transition to the valence $\pi\pi^*$ excited state ($1B_{1u}$). This transition, one-photon symmetry allowed and characterized by an oscillator strength of 0.34, appears as a broad band peaked at 7.66 eV (~162 nm) and extending to the red up to 215 nm at ambient conditions in low pressure gas phase.[31] Superimposed to this broad absorption are observed sharper bands related to the transition to the Rydberg (π,3s) state with origin at 7.11 eV (~175

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nm).[24,31] Ethylene undergoes an enormous structural change upon excitation to the $\pi\pi^*$ excited state consisting in a 90° relative twisting of the CH_2 groups and the consequent formation of a biradical[32] with the carbon atoms described by a sp^3-like hybridization and a C−C bond length which is estimated in the 1.38−1.47 Å range.[33,34] The same effect, i.e., the formation of biradicals able to trigger the polymerization reaction, is also achieved by using two-photon excitation.[15] The excited state reached by absorption of two photons at 350 nm is presumably the same $\pi\pi^*$ state reached by one-photon absorption. This transition is two-photon forbidden, but it could be activated by vibronic coupling or by virtue of the molecular symmetry change which relaxes the selection rules. It should be mentioned that an alternative assignment, proposing the final state as the π,3s Rydberg state,[29,30] is barely compatible with the changes observed upon compression.[15] According to the low cross-section of the two-photon transition, the polymerization reaction initiation is therefore related to the interaction of the excited biradical with a ground state ethylene molecule. However, the excited molecule relaxes to the ground state through conical intersections thus reducing the lifetime of the valence state to a few (20 ± 10) femtoseconds.[17−19] The extremely fast relaxation, 1−2 orders of magnitude shorter than the collision frequency calculated at the density conditions of the reaction, raised doubts about the effective primary role of the excited biradical in the reaction activation.[15]

The first remarkable result of this study is to shed light on this issue. In fact, we demonstrated that the polymerization can be two-photon induced only in the presence of a metal catalyst or better of a metallic ion. When the sample is contained by gilded gaskets, we do not observe any two-photon induced reactivity both with cw and pulsed laser light. On the contrary, the reaction is observed when metal gaskets (Cu−Be and stainless steel) are employed or when a few amount of titanium(IV) methoxide or stainless steel powder is put into the sample. The catalytic activity is ascribable to the presence of the oxides of these transition metals which are always present on their surface. As a matter of fact, the missed observation of the reaction with gold is an indirect proof of the oxides activity, since gold is extremely inert to oxidation at the sample loading conditions. On the contrary the reaction is observed in any condition, including with the sample in contact only with gold, when it is induced by one-photon absorption. This is not surprising since the two processes, one- and two-photon absorption, are characterized by cross sections that differ by several orders of magnitude. This means that the number, i.e., the concentration, of excited molecules is sufficiently large in the reaction triggered by one-photon absorption to guarantee the propagation of the reaction likely also by means of the direct reaction between two biradical species. The initiation and propagation steps of the one-photon induced reaction are perfectly identified and quantified by the log−log plot reported in Figure 6. The early stage of the reaction presents a molecularity lower than 1 (0.15), a value indicating that most of the reactive species prepared through the excitation "relax" to the ground state molecular structure without reacting. This stage can be identified as a kind of activation step. After about 0.3 μs the concentration of reactive species is such to guarantee a molecularity $\geq$2 which is the minimum value expected for the polymerization reaction. The value found here, 2.4, is in excellent agreement with those found by Buback at comparable reaction pressures both in the photoinduced[8] (2.0) and in the thermal[9] (2.5) polymerization reactions. The time window where the regime change occurs obviously depends on the incident power, i.e., the concentration of reactive initiators, but for the first time this initiation step is identified and quantified in a few hundreds of ns. One aspect worth highlighting regards the time (0.3 μs) where we observe the sudden molecularity change, in fact although a clear slope decrease is detected at the same delay in the kinetic curve (see Figure 3), no interpretation of this feature can be provided by the Avrami's model.

It is interesting at this stage to compare these findings with the molecularity data obtained in the two-photon induced reaction (see Figure 7). A clear difference is noted for the two incident powers used: a single regime characterized by a molecularity of 0.17 is observed in the entire time window (0.55 μs) investigated when energy laser pulses of 20 μJ were used, whereas when a double energy per pulse is employed we observe, as in the one-photon case, two regimes: the first characterized by a molecularity of 0.14 increasing also in this case after about 0.3 μs to 0.6. The comparison with the one-photon findings unambiguously confirms a preliminary activation step common to all the kinetics characterized by a molecularity ranging between 0.14 and 0.17 and exhibiting a different duration depending on the concentration of initiators (excited biradicals). This step is the only detected in the two-photon induced reaction with pulses of 20 μJ where the critical concentration of reactive species requested to propagate the reaction is likely never reached, at least in the time window investigated. By doubling the power we have indications of a change in the mechanism but without reaching molecularity values characteristic of the reaction propagation.

As we clearly demonstrated the two-photon induced reaction is catalyzed by transition metals ions. Recently Cr^{VI}, in the form of monochromate supported on silica, has been used as photocatalysts to trigger the ethylene polymerization at room temperature in the gas phase.[35] The suggested two-step mechanism envisages the Cr^{VI} reduction by presumably excited ethylene molecules and the successive polymerization. The formation of ethylene-metal complexes is rather well established to occur through the donation and possible back-donation of electron density between the d orbitals of the metal ion and the π and π^* molecular orbitals of ethylene.[36] The interaction between ground state ethylene and different metal cations was studied by DFT calculations showing that the main contribution to the covalent term stems from the σ donor part, whereas the back-donation (π) acceptor bonding is less important.[37] However, in the present case, the stabilization of the biradical is of interest, i.e., of the excited molecule whose lifetime is normally too short for trigger efficiently the reactivity. The formation of biradical states through electronic charge transfer in complexes between excited S_1 ethylene and metals has been studied by ab initio calculations in the case of Ca atoms.[38] The formation of a rather stable complex having the biradical geometry where the Ca atom anchors to the two carbons through the bond formed from the d_{xy} orbital of Ca and π^* orbital of ethylene was demonstrated. Assuming an analogous stabilization of the biradical species, a concentration large enough to make possible reactive collisions with ground state ethylene molecules or already formed oligomers can be envisaged. As a matter of fact, the almost linear growth of the polymer is fully supported by the kinetic analysis with the Avrami's model, which always supports through the dimen-

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sional n parameter a linear growth of the product in a diffusion controlled reaction.

The last comment regards the differences observed between the reaction induced by two-photon absorption with cw or pulsed sources. In the first case, cw lasers or lamps, we fully confirm the results of ref 15 obtaining a complete transformation of the monomer to a high quality crystalline polyethylene, notwithstanding that the reaction occurs through the catalytic action of the metal gasket as extensively discussed above. When pulsed laser sources (30 ps) are used the reaction is remarkably slower, partial and moreover the formation of acetylenic moieties and methyl groups is observed especially in the two-photon experiments (20−40 μJ per pulse) suggesting the presence of a larger amount of terminations (shorter oligomers). In addition, the amount of sp carbon atoms spontaneously decreases with time when the sample is not irradiated thus indicating that the triple bonds belong to metastable byproducts. Due to the remarkable reproducibility of these findings, we ascribe this diversity to the nature of the light field employed. The laser pulses used in this work are characterized by peak powers of the order of 1 MW but average power of the order of 10^{-1} mW and, therefore, 3 orders of magnitude smaller than the one characterizing cw experiments. The average power appears therefore as the key parameter in preparing and maintaining a concentration of initiators sufficient for propagating the polymerization reaction. On the other side, a high peak power is the prerequisite for inducing non linear optical phenomena, as in this case can be multiphoton absorption to the diffuse Rydberg states,[31] which can lead to the deprotonation of the monomer and the consequent formation of an acetylenic species. The latter statement is also supported by the strongly nonlinear dependence on the incident power of the formation of sp species in the stainless steel catalyzed reaction.

5. CONCLUSIONS

The photopolymerization of ethylene induced by one- and two-photon excitation has been characterized in the fluid phase for pressures below 1 GPa. The outcome of this study is 2-fold contributing to considerably deepen our fundamental knowledge of this reaction. The most important and innovative result concerns the characterization of the reaction's first microsecond by time-resolved transient infrared absorption experiments with a few ns resolution. Thanks to this careful sampling of the photopolymerization dynamics we identified the activation step of the reaction, characterized by a molecularity of 0.15 ± 0.02, and a temporal extension dependent on the concentration of excited ethylene biradicals that on turn results from the incident power and the transition cross-section. In one-photon induced reactions after 300 ns, the activation step is replaced by a molecularity increase to more than 2, as expected for the free radical propagation reaction. This is instead never observed in the two-photon induced reactions where the critical concentration for triggering the propagation step is evidently never reached because of the much lower cross-section. The second important result of this study is the recognition of the catalytic role played by the metal gaskets in triggering the two-photon induced polymerization, a general and critical issue in many studies conducted at high pressure in the presence of laser light. The reduced concentration of excited molecules and their ultrafast relaxation to the ground state prevent the reactivity unless the excited biradicals are stabilized by the interaction with different metallic ions (Ti, Fe, and Cu). This stabilization, corresponding to a lengthening of the biradical lifetime, likely occurs through the electronic interaction between the d orbitals of the metal ion and the π^* molecular orbitals of ethylene. Finally, as the quality of the polymer resulting from the photoinduced reaction is concerned it appears that cw irradiation allows the attainment of a reduced amount of defects and chain terminations, and then a much better crystallinity, with respect to pulsed irradiation. The latter, characterized by high peak power, can favor the molecule photodissociation through the transition to Rydbergh states by means of multiphoton absorption processes with the consequent formation of methylic and acetylenic groups.

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Notes

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