

Viscoelastic-Conversion Scaling of the Free Radical Photopolymerization of Isobornyl Acrylate

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Cite This: *Macromolecules* 2026, 59, 4497–4509



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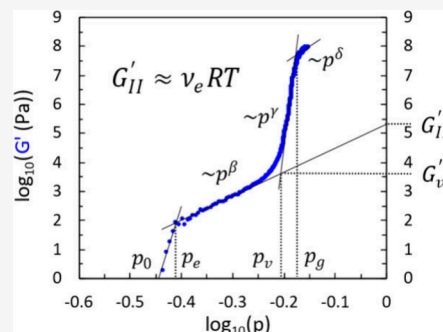


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ABSTRACT: To clarify the structural changes behind the viscoelastic build-up during fast free-radical polymerization, the photopolymerization of isobornyl acrylate (IBoA) was studied in detail from a synchronized viscoelastic-conversion perspective using time-resolved FT-MIR photorheology. Before effective elasticity development, polymerization proceeds in a viscous fluid state where the polymerization rate reaches a steady value after a steep ramp within the first 10% of conversion irrespective of the initiation conditions. For soft to moderate initiation the (semi)dilute entangled polymer regime before vitrification covers the second major conversion range after elasticity sets in. Interestingly, extrapolation to full conversion of the latter regime provides an alternative means to estimate the equilibrium plateau modulus and molar mass between entanglement for the bulk IBoA polymer. Further up the conversion path vitrification takes over as characterized by a steep modulus increase of at least 3 orders of magnitude over a small conversion window. Additionally, the acceleration and deceleration processes of the polymerization are discussed along the viscoelastic-conversion path.



INTRODUCTION

Radical photopolymerization (or UV-curing) is a wide ranging technology used in applications such as inks, coatings, adhesives, additively manufactured parts, composites etc.^{1–11} Starting from a liquid precursor, a polymerized or cross-linked material is rapidly formed upon exposure to light, typically with the aid of photosensitive initiators.^{1–4} While the chemical processes underlying the transformation have received large attention, the link with material properties has been much less addressed.^{12–24} Here we report a detailed study combining FTIR spectroscopy and rheology to simultaneously monitor the evolution of the conversion rate and the viscoelasticity during polymerization of vitrifying acrylate monomers.

Established techniques in photopolymerization such as time-resolved (mid/near) FTIR spectroscopy or photorheology are widely used to follow the fast radical polymerization kinetics from a chemical or a viscoelastic perspective, respectively.^{25–34} Still, the coupling of the two methods has rarely been called forth to explore the relation between polymerization kinetics and structural development.^{35,36} Hence, detailed or systematic correlation of the viscoelastic changes upon monomer conversion during polymerization has never been reported in the literature, in spite of its meaningful technological value. Many applied photopolymerization processes require careful control to achieve specific material or coating properties which are traditionally optimized following practical or empirical rules, showing limited value when it comes to predict an intermediate or final mechanical state of the polymerized material.

In the field of photopolymerization, few reactive monomers are available with a single double bond that can generate quickly thermoplastic polymers with a high glass transition temperature (T_g) i.e. beyond 80 °C. A notable example is the hydrophobic monomer isobornyl acrylate (IBoA) which combines low volatility, low viscosity, fast reactivity and T_g values reported in the range 80–100 °C.^{37–40} While IBoA is in use since more than three decades now, interest in research and industry has reactivated owing to its (partly) renewable status when camphene is used as reagent in synthesis.^{41,42} The monomer is used in numerous liquid coating applications, mostly with UV-curing, ranging from adhesives to elastomers in electronics or medical devices, but also in hard protective coatings where it is appreciated as toughness and adhesion enhancer when properly formulated.^{4,5} Its methacrylate counterpart however benefits from much less industrial interest due to the significantly lower photoreactivity.

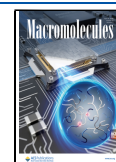
The free-radical polymerization of IBoA is assumed to follow a kinetic behavior similar to other vitrifying unsaturated monomers such as methyl methacrylate (MMA) or styrene.^{43–45} The radical polymerization of these monomers has been thoroughly studied over decades and revealed the

Received: January 5, 2026

Revised: March 9, 2026

Accepted: March 10, 2026

Published: March 23, 2026



complex interaction between structural development and polymerization rate, as famously embodied by the well-known Trommsdorff-Norrish or gel effect. Many papers were devoted to the understanding and modeling of the latter autoaccelerating effect in terms of the diffusion aspects behind the radical termination process.^{46–56} At the end of the polymerization, the rate decelerates owing to overall diffusion limitations for the initiation, propagation and termination mechanisms. Earning less attention so far, deceleration has been most successfully accounted for using free-volume concepts.^{12,20}

With a propagation rate coefficient about 2 orders of magnitude higher than MMA and styrene, substantial changes are expected in the overall kinetic behavior of IBoA which can only be investigated experimentally using rapid analytical tools.^{38,57} Beyond pulsed laser method which are highly successful to quantify kinetic parameters at very low conversions, the kinetic details for the free-radical polymerization of acrylates are still hard to unravel experimentally over the entire course.^{56,57} Hence, with the growing computational power a lot of research efforts went to numerical simulations and modeling as a complementary approach over the last decades.^{58–64}

In this work, we used time-resolved Fourier-transform mid-infrared spectroscopy and photorheology in a coupled setup (here referred to as TR-MIR photorheology³⁷) to follow simultaneously the polymerization of IBoA induced by exposure to UV-LED light. Carrying on along the same run without interruption, the glass transition properties of the polymerized sample could immediately be recorded using shear rheology. Furthermore, some polymerized samples were also characterized independently after the TR-MIR photorheology experiment for e.g. molar mass distribution or glass transition temperature (T_g) using gel permeation chromatography (GPC) and differential scanning calorimetry (DSC), respectively.

The rich body of data resulting from single TR-MIR photorheology experiments is here examined in various ways. In the first part, the data are presented in the time domain as common practice to demonstrate and quantify photoreactivity in the literature. The influence of factors affecting the kinetics such as light intensity and photoinitiator content are highlighted and related to the T_g of the resulting polymer.

In this work, proper time alignment of the viscoelastic and conversion data sets resulting from a TR-MIR photorheology experiment with unidirectional UV-exposure is an important prerequisite. Hence, to control our experimental setup in sufficient detail, a computational analysis of the depth dependence of the photopolymerization kinetics of IBoA along the illumination path is here conducted from a simulation perspective, taking into account the presence of dissolved oxygen. From this, time shifts are recommended to align properly the spectroscopic and viscoelastic data sets. Next, the synchronized TR-MIR photorheology data are examined in detail from a fresh perspective by mapping the viscoelastic properties against the extent of polymerization or monomer conversion.

■ EXPERIMENTAL SECTION

Materials

Commercial grade isobornyl acrylate (IBoA, $M_w = 208.3 \text{ g mol}^{-1}$) was supplied by allnex (Belgium) and used as received. An acrylate double

bond content of 5.1 mmol g^{-1} was determined by proton NMR spectroscopy. The monomer contains $\approx 100 \text{ ppm}$ 4-methoxyphenol (MEHQ) as inhibitor. A density value of 0.986 g mL^{-1} was determined by pycnometry at 23°C . The viscosity is 7.8 mPa s at 23°C .

For the photopolymerization experiments, TPO-L (ethyl phenyl-(2,4,6-trimethylbenzoyl)phosphinate, $M_w = 316.3 \text{ g mol}^{-1}$) was added as photoinitiator at levels of 0.2 and 0.5 w/w% (i.e., $[\text{TPO-L}] \approx 6.2$ and 15.6 mmol L^{-1} respectively) which amounts to ≈ 0.12 and $0.31 \text{ mol \%}$ with respect to the double bond content. The molar extinction coefficient ϵ of TPO-L was determined by UV-vis spectroscopy at a concentration of 0.1 w/w% in IBoA. At a wavelength of 405 nm , $\epsilon_{405} = 105 \text{ L mol}^{-1} \text{ cm}^{-1}$ was found.

Experimental Monitoring of the Polymerization Process

Photorheology coupled to time-resolved FTIR-MIR spectroscopy was used to monitor the polymerization of the IBoA monomer upon photoactivation. The small-strain viscoelastic properties were measured in oscillatory shear mode in parallel with the spectral changes in the MIR range. For this purpose, a MCR302 rheometer (Anton Paar) was equipped with a UV-transparent quartz-cylinder (diameter 7.9 mm) mounted in a steel shaft as upper body of a parallel plate configuration (Supporting Information SI-1).³⁷ Light emitted from a UV-LED at a wavelength of 405 nm (Thorlabs) was guided optically onto a mirror at the top of the shaft and redirected through the quartz cylinder toward the sample filling a gap of $300 \mu\text{m}$ between the plates. The bottom plate of the rheometer was fixed in a Peltier heating element for temperature control (limited to a maximum temperature of 100°C). An attenuated total reflectance mid-infrared (ATR-MIR) monitoring probe was fitted within a circular opening machined in the center of the bottom plate. The IR probe was connected to an MCT detector of a Tensor 27 FTIR spectrometer (Bruker). IR spectra were acquired at the highest rate ($\approx 2.3 \text{ s}^{-1}$) for the wavenumber range with the best instrumental signal-to-noise (S/N) ratio, i.e., the fingerprint zone between 650 and 1800 cm^{-1} at a resolution of 2 cm^{-1} .

Instead of using a single specific absorption band to quantify the double bond consumption over time, the recorded spectra were correlated to time following the partial least-squares correlation method (PLS provided in the JMP16 statistical software package) which increases sensitivity.³⁵ PLS-C extracts two new variables (scores) as linear combinations of the original ones which maximize the covariance between two data tables, i.e. a matrix of the recorded spectra over time (the absorbance values at each wavenumber are considered as individual variables) on one hand and the time vector on the other hand.⁷² Hence, the resulting scores are respectively assigned to the reaction time and the acrylate double bond consumption, in the assumption that all spectral changes primarily result from the conversion of double bonds into single bonds by free-radical polymerization. The area of the absorption peak at 810 cm^{-1} , specific for the acrylate unsaturation ($\tau(=\text{CH}_2)$), was used as a gauge for the double bond content at the onset and end of the photopolymerization for proper scaling. The polymerization rate R_p was calculated numerically from the derivative of the time-conversion profile after preliminary smoothing with a cubic spline.

The photopolymerization step was conducted at 20°C . The viscoelastic properties were measured with time intervals of 0.1 or 0.5 s using an oscillatory strain with an amplitude of 10% and a frequency of 10 Hz . Viscoelastic data recorded at a strain of 10% were not significantly different compared to data from experiments conducted at much lower strain amplitudes (e.g., 0.2 and 0.5%), suggesting that linearity conditions were fundamentally obeyed. Strains exceeding 10% often led to sample detachment from the plates following the rapid and intense stress growth when vitrification occurred. The sample was exposed for a maximum duration of 10 min to UV-light with intensities ranging from 0.7 to 30 mW cm^{-2} at sample location (measured using a high-resolution thermal power sensor of Thorlabs). The orifice in the bottom plate did not significantly alter the values of shear modulus as compared to the absolute values obtained with a flat plate without IR probe.

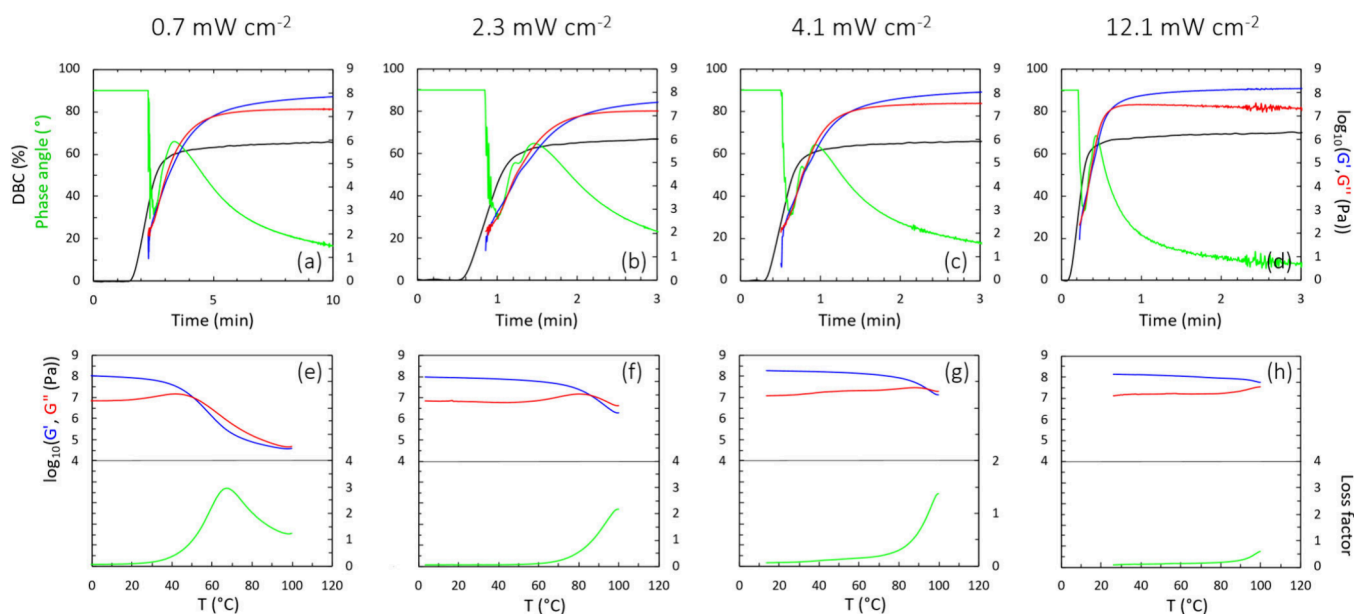


Figure 1. Top row (a–d): Time domain plots showing the photopolymerization kinetics of IBOA as measured by TR-MIR photorheology at four light intensities, i.e., 0.7 (a), 2.3 (b), 4.1 (c), and 12.1 mW cm^{-2} (d). Light exposure was triggered at time zero and data were recorded continuously over 10 min for all experiments (plots are zoomed-in over first 3 min for clarity when required). The black line represents the double bond conversion (DBC, left ordinate axis) determined from the acquired FTIR spectra over time. The blue and red lines show the elastic (G') and loss (G'') modulus, respectively (right log scale) whereas the green line stands for the viscoelastic phase angle (left axis). Bottom row (e–h): DMA (dynamic mechanical analysis) curves recorded just after the respective photopolymerizations shown on top. Samples were quickly heated to 100 $^{\circ}\text{C}$ and data were recorded in cooling. Again, blue and red curves represent G' and G'' , respectively, while green stands for the loss factor (i.e., the tangent of the phase angle). Within the experimental temperature limits, the glass transition could not be captured entirely for all polymerization conditions. Hence, after measurement, the glass transition temperature of the recovered polymer sample was verified independently by DSC.

For a reliable correlation of the viscoelastic and the spectral data in a TR-MIR photorheology experiment, it is a prerequisite to achieve maximum uniformity of the absorbed light intensity and, hence, the initiation rate across the sample volume during polymerization. Whereas the lateral homogeneity of the incident beam is easily verified experimentally, the light absorption along the incident path depends on the molar concentration and the molar extinction coefficient of the photoinitiator at 405 nm. The latter aspect is elaborated more quantitatively in the Results section.

Glass Transition

After a 10 min period of light exposure in isothermal conditions, the temperature of the polymerized sample was raised rapidly to 100 $^{\circ}\text{C}$. The glass transition was next recorded in small-strain oscillatory shear (0.5%, 10 Hz) upon cooling at a rate of -3 K min^{-1} . $T_{g,G'}$ and $T_{g,LF}$ are defined as the temperatures at maximum loss modulus and maximum loss factor, respectively. After the rheology experiment, the sample was collected for an independent T_g determination using conventional differential scanning calorimetry (Mettler DSC853) in a heat–cool–heat sequence with a heating rate of 10 K min^{-1} . $T_{g,DSC}$ is evaluated at the inflection point of the heat capacity step of the glass transition.

RESULTS

Time-Domain Analysis of TR-IR Photorheology Data

Photoreactivity and kinetic data of photopolymers are commonly examined in the time-domain. Likewise, Figure 1 shows a set of plots where the time evolution of the double bond conversion, the elastic and viscous shear moduli G' and G'' and the respective phase angle all demonstrate the photopolymerization of IBOA for increasing light intensities at 20 $^{\circ}\text{C}$. Note that the initial oscillatory stress response of the light-exposed monomer in the shear gap is below the torque limits until the moduli magnitudes reach $\sim 100 \text{ Pa}$ in the

present experiments. Several elements stand out in this representation as further highlighted in Figure 2. As long as

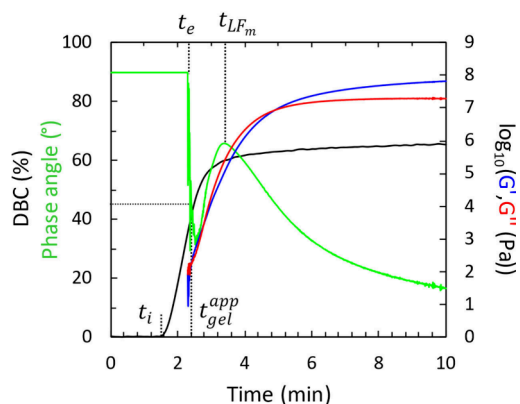


Figure 2. Enlarged plot showing the double bond conversion, the phase angle, the elastic and viscous shear modulus as a function of time for the free-radical photopolymerization of isobornyl acrylate. t_i indicates the induction period before effective polymerization, t_e stands for the time where the viscoelastic properties start to change significantly, t_{gel}^{app} is the apparent gel time at the crossover point between G' and G'' , and t_{LFm} is the time where the phase angle reaches a maximum (equal to the loss factor maximum).

the phase angle ticks 90° , the reacting medium behaves as a low-viscous liquid with no real information about the actual progress of the polymerization, as the torque is immeasurably small in the present experimental configuration.

At time t_e , however, the phase angle drops abruptly corresponding to the onset of fast viscoelastic build-up. The

time needed to reach a phase angle of 45° (equivalent to the crossover point between G' and G'') is commonly reported as (apparent) gel point t_{gel}^{app} . Noteworthy, following a minimum the phase angle transits through a maximum value upon vitrification at time t_{LF_m} before gradually fading out toward zero, consistent with a predominant elastic behavior.

On the other hand at the level of the IR probe below the shear gap, no spectral changes are evidenced over a time t_i referred to as the “induction period”.^{65–67} In this period, there is no detectable double bond consumption as the photoinitiator radicals are primarily scavenged by dissolved molecular oxygen, a strong radical inhibitor. As shown in Figure 3 for IBoA (log–log plot), the measured induction time

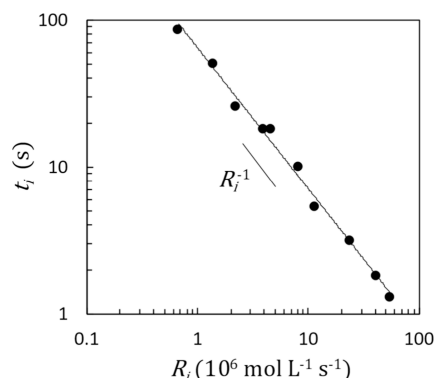


Figure 3. Experimental induction times vs average initiation rate for the photopolymerization of IBoA at 0.2 and 0.5 w/w% of TPO-L and five light intensities.

behaves inverse proportional to the initiation rate for different photoinitiator contents and light intensities. The average initiation rate R_i of the photopolymerization process is well-approximated by the average decomposition rate of the photoinitiator, i.e., $R_i \approx R_d = \int_{d_1}^{d_2} r_d dz$ with $r_d = \varphi_i \epsilon_i [PI] I_{0,i} e^{-\epsilon_i [PI] z}$, which follows an exponential decay according to the law of Beer–Lambert. Here, φ_i is the quantum yield and z is the depth along the light path. In the shear gap ($d_1 = 0 \mu m, d_2 = 300 \mu m$), the initiation rate is fairly approximated by the “thin-film approximation” $R_i = 2.303 \varphi_i \epsilon_i [PI] I_{0,i}$. However, along the ATR crystal below the shear gap ($d_1 = 300 \mu m, d_2 = 1500 \mu m$), an average reduction by 11 and 24% is predicted for R_i at 0.2 and 0.5 w/w% TPO-L, respectively, assuming $\varphi_i \approx 0.5$ for initiators of the phosphine oxide class. The latter values of R_i were used in Figure 3. At this point, it is recalled that initiation conditions, as defined by the spectral characteristics and the intensity of the light source, along with the type and content of the photoinitiator package (including co-initiators) and inhibition mechanisms, can vary significantly among applications. While any variation in initiation will *de facto* influence the induction period it will also affect the polymer mass distribution and, as a consequence, the viscoelastic build-up. The cleavable initiator TPO-L was selected in combination with a LED light source of 405 nm to align with modern applications such as additive manufacturing and lightweight constructions, but also to keep the initiation mechanism simple enough for prediction purposes. After depletion of the dissolved oxygen pool, the polymerization starts quickly and completes roughly in less than 1 min, even at the lowest light intensity. With increasing

intensity, the induction period reduces significantly, and the polymerization accelerates as expected. In this short time frame, the liquid IBoA monomer converts into a solid polymer along various structural transformations, ending in a vitrified state as concluded from the final shear modulus level ($G' \approx 10^8$ Pa after 10 min).

For any dynamic experiment driven by a periodic excitation, the linearity and coherence of the acquired data points can be tested by comparing the mutation time of the process to the relevant experimental observation time.⁷³ For oscillatory shear, the mutation time has been defined from the complex modulus as $\tau_{Mu}^{[G^*]} = |G^*| / \frac{d|G^*|}{dt}$ which should be longer than the time required to measure the viscoelastic response of the material i.e. 0.1 s, the period of one shear oscillation in this study. From the $|G^*|$ data of the fastest polymerizations, it is found that $\tau_{Mu}^{[G^*]} \geq 0.83 \text{ s} \gg 0.1 \text{ s}$, satisfying the coherence condition. Similarly, the mutation time of the FTIR spectrum τ_{Mu}^{IR} could be determined from the corresponding PLS score. The mutation time was always shortest in the early seconds of the polymerization. In general $\tau_{Mu}^{IR} \gg 0.4 \text{ s}$, i.e. the acquisition time of the spectrum, with an exception at the highest light intensities where the condition was not satisfied during the first five to six seconds of the polymerization.

The glass transition characteristics of the samples just after photopolymerization are illustrated in the second row of Figure 1 where DMA (dynamic mechanical analysis) profiles recorded with the rheometer just after photopolymerization are shown. Unfortunately, the temperature window is limited by the heat-sensitive shaft optics to 100°C which cuts some profiles in the transition. T_g values are often reported as the temperature at maximum loss factor which is not available for all curves here. The temperature at maximum loss modulus reflects a resonant behavior at the mechanical excitation frequency of the test and falls close the onset of the elastic dispersion step. Hence, we also report this value here. To complete, T_g of the *in situ* prepared polymers was additionally determined by conventional DSC for some experiments. All the T_g values for the photopolymerization experiments conducted at 20°C in this work are gathered in Table 1, along with the initiator content, light intensity and final double bond conversion, p_f .

Synchronization of the Viscoelastic and Conversion Data

In order to correlate the viscoelastic changes recorded in the shear gap with the spectral evolution monitored underneath, the respective time of the data sets should be in due

Table 1. Overview of the Various T_g Values Measured after Photopolymerization of IBoA at 20°C^a

TPO-L (w/w%)	$I_{0,i}$ (mW cm ⁻²)	p_f	$T_{g,G''}$ ($^\circ \text{C}$)	$T_{g,LF}$ ($^\circ \text{C}$)	$T_{g,DSC}$ ($^\circ \text{C}$)
0.2	0.7	0.656	42	68	46
0.2	2.3	0.694	80	100	71
0.2	4.1	0.68	88		79
0.2	12	0.72	100		83
0.5	0.7	0.73	71		
0.5	2.3	0.78	100		
0.5	4.1	0.81	100		
0.5	12	0.81	>100		

^a $T_{g,G''}$ and $T_{g,LF}$ are the temperatures at maximum loss modulus and maximum loss factor, respectively. $T_{g,DSC}$ is the inflection point of the glass transition as determined by DSC. p_f is the final double bond conversion.

synchronization. While triggering of the light source and data acquisition are precisely controlled from an instrumental point of view, unidirectional light exposure creates gradients in initiation rate along the light path owing to absorption. As discussed in the previous section, departures for R_i are acceptable at TPO-L contents of 0.2 w/w% and below, but more questionable at 0.5 w/w%. However, an even more important time inconsistency might result from a difference in induction time which introduces a lag of the spectral data relative to the viscoelastic measurements. To predict this latent induction discrepancy, inhibition mechanisms, and more specifically related to dissolved O_2 in the present case, should be taken into account in the free radical polymerization process.^{66–69} Dendukuri et al. described a convenient approach to estimate the induction time changes along the light path.⁶⁷ As outlined in Supporting Information SI-2, a set of coupled partial differential equations involving the diffusion and reaction of molecular oxygen in the radical polymerization kinetics need to be solved numerically to simulate monomer and oxygen consumption along the illumination path. Based on this model, we adapted the boundary conditions to mimic the confinement of a sample in the closed environment of the shear gap (neglecting the narrow free surface on the side) during measurement on the rheometer, i.e. without external oxygen supplied to the sample. Inhibition results then merely from the equilibrium amount of oxygen initially dissolved in the IBoA sample. The kinetic profiles were systematically computed at six positions in steps of 300 μm downward from the top where the light impinges. Simulations were conducted at TPO-L concentrations of 0.2 and 0.5 w/w% and light intensities in line with the experimental ones (cf. Table 1). The molar extinction coefficient is $\epsilon_{405} = 105 \text{ L mol}^{-1} \text{ cm}^{-1}$ for TPO-L and the quantum yield is assumed in the range between 0.5 and 2 primary radicals per absorbed photon. Further input parameters required to solve the equations were taken from the literature, i.e. the equilibrium O_2 concentration in the range $[O_{2,eq}] \approx 1$ and 2 mM for typical acrylates,^{70–72} the propagation rate coefficient for IBoA at 20 °C, i.e. $k_p = k_p^0 = 1.049 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$,³⁸ the translational radical termination coefficient $k_t = k_{t,d}^0 \approx 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$,³⁹ the diffusivity of O_2 in IBoA, i.e. $D_O \approx 7.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and finally the oxygen inhibition coefficient $k_O \approx 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$.⁶⁶ With the latter set of parameters, simulations predict induction times which are of the same order of magnitude than the experimental ones. An example of computed kinetics for the double bond conversion is plotted in Figure S2 and illustrates the depth profile at six positions between the 0 and 1.5 mm from the incoming light flux. Overall, a time lag of 4 and 11% was respectively found for TPO-L contents of 0.2 and 0.5 w/w% between the average kinetic profile under the shear gap (at the level of the ATR crystal) and within the rheological shear gap. Accordingly, a corrective time shift was systematically applied to the conversion series to align closely with the viscoelastic data set.

Viscoelastic-Conversion Mapping of Polymerization Kinetics

Figure 4a shows the kinetic data for the radical photopolymerization of IBoA (0.2 w/w% TPO-L, 12.1 mW cm^{-2}) transformed into a viscoelastic-conversion map. In the early stage of the polymerization the stresses are predominantly viscous and immeasurably small with the used experimental setup. The growing polymer starts to build macroscopic

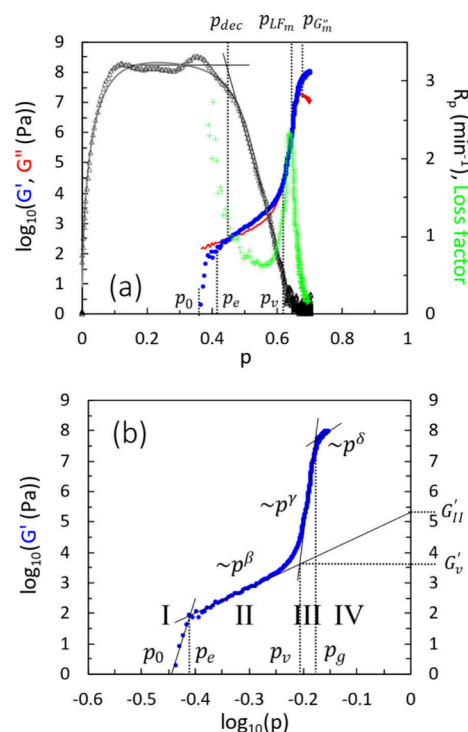


Figure 4. (a) Representation of the viscoelastic moduli G' (blue), G'' (red) and loss factor (green) in the conversion domain. p_0 , p_e , p_v , p_{LF_m} and p_{G_m} indicate the DBC at the onset of elasticity, at the onset of the dilute entangled polymer regime (DEPR), at the onset of vitrification, at the loss factor maximum and at the maximum of G'' , respectively. Also mapped is the experimental polymerization rate (triangles) along with a nonlinear least-squares comparison of the nonsteady kinetic scaling model for radical polymerization (gray continuous line). p_{dec} indicates the conversion at which the radical polymerization starts to decelerate. (b) Double-logarithmic plot of the elastic shear modulus versus DBC highlighting four distinct power-law regimes delimited by p_0 , p_e , p_v and p_g , the DBC at the onset of the glassy zone. The four stages of the profile are conveniently approximated using a piecewise power-law model. Regime II between p_e and p_v (referred to as (semi) dilute entangled polymer regime, DEPR) extrapolates to the modulus value G'_{II} at full conversion which provides an estimate of the plateau modulus of the bulk polymer. G'_v denotes the shear modulus value at the conversion where vitrification sets in.

elasticity at the double bond conversion, p_0 , which quickly transition to a new regime at p_e before vitrification kicks in at p_v . The elastic build-up proceeds up to the glassy zone crossing the maximum loss factor at a conversion p_{LF_m} first, before reaching the maximum in loss modulus at p_{G_m} where the polymerization virtually halts. While the viscoelastic properties reflect the macroscopic state of the material, the chemical polymerization is primarily driven by mechanisms at a molecular level. With the polymerization rate added to the map in Figure 4a, one notices an acceleration step within the first 10% of DBC. This step, commonly referred to as the Trommsdorff-Norrish effect, is preceded by the initial jump toward steady-state in the very beginning. Obviously, the acceleration is not linked to any elastic effect and agrees with diffusion-controlled kinetics for the biradical termination reaction of chain radicals growing in a dilute polymer solution.

Over the next 30% in conversion, the polymerization rate remains fairly flat while the polymer solution turns into an entangled viscoelastic fluid. The polymerization rate starts to

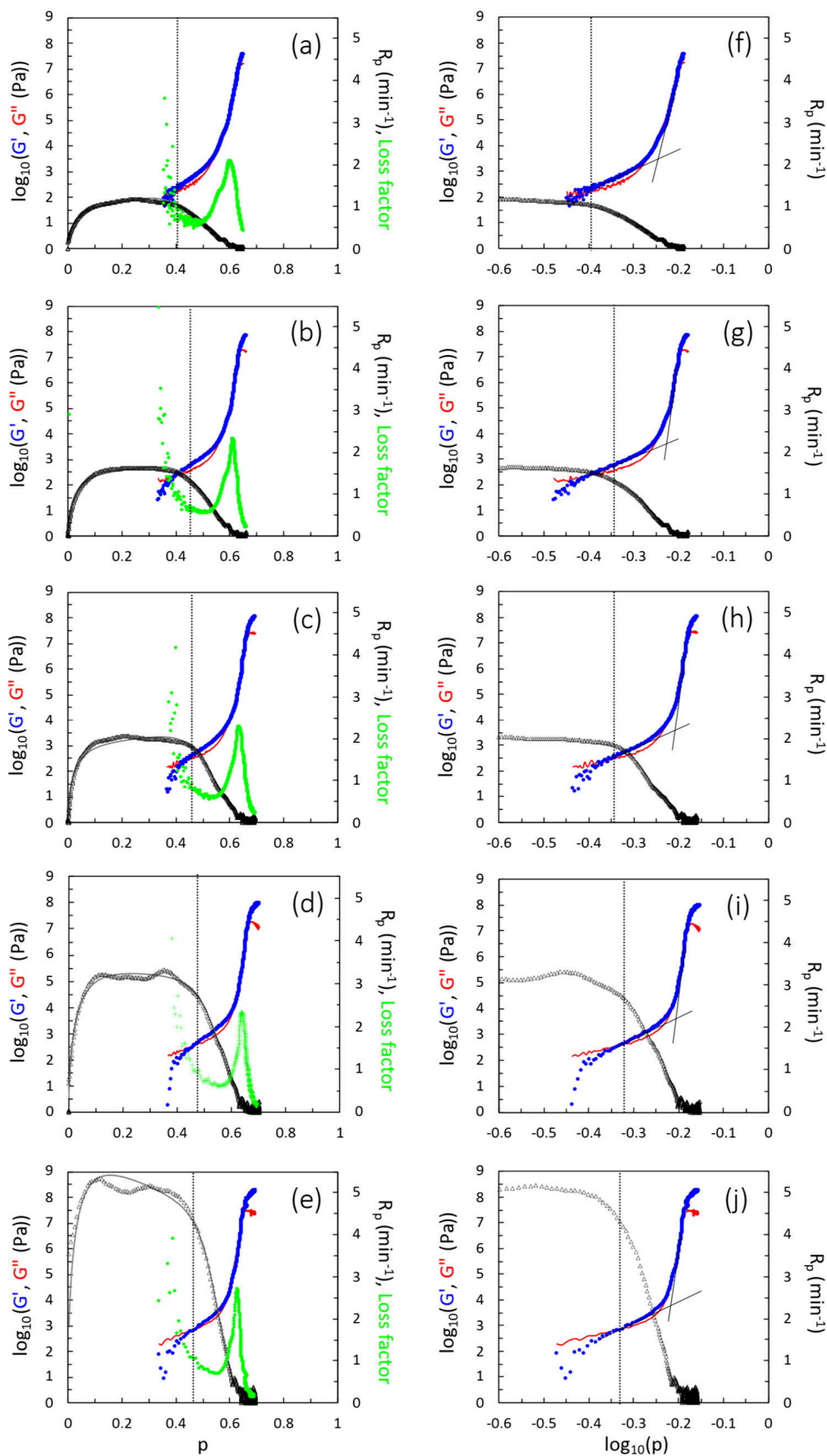


Figure 5. Left-hand side (a–e): Viscoelastic-conversion maps for the photopolymerization of IBoA at five light intensities, i.e., 2.3 (a), 4.1 (b), 5.2 (c), 12.1 (d), and 29.5 mW cm^{-2} (e). The amount of TPO-L was 0.2 w/w% and the rheological data were acquired every 0.1 s for 3 min. G' and

Figure 5. continued

G'' are represented by the blue and red curves, respectively, whereas the green symbols refer to the loss factor. The polymerization rate is shown with black triangles while the continuous gray line is a NLLS fit of the semiempirical kinetics scaling model to the R_p data. Right-hand side (f–j): Double logarithmic representation of the respective viscoelastic-conversion maps on the left side. The lines show linear approximations of regimes II and III according to eqs 1b and 1c. The intersection of the two lines corresponds to the vitrification point (p_v , G'_v). At this point, R_p is close to zero. The vertical line indicates the double bond conversion, p_{dec} where the polymerization rate R_p starts to drop significantly according to the definition in Figure 4a.

decelerate at p_{dec} well before the onset of vitrification (p_v) in the (semi)dilute entangled polymer regime (DEPR). When the conversion p_{LF_m} at maximum loss factor is reached, the polymerization rate drops close to zero. The nonsteady kinetic scaling model for radical polymerization, introduced by Roose et al.,^{35,74} provides a good approximation of the rate data as illustrated by the continuous line (nonlinear least-squares comparison). The best agreement indicates that biradical termination is controlled predominantly by transitional diffusion and weak reaction diffusion over the entire conversion domain. Figure 4b highlights the elasticity-conversion relationship in a double-logarithmic plot. Four regimes are identified which are approximated by a continuous piecewise linear model,^{75,76} reflecting different power-law behaviors expressed as,

(I)

$$G' = G'_v \left(\frac{p_e}{p_v} \right)^\beta \left(\frac{p - p_0}{p_e - p_0} \right)^\alpha \quad p_0 \leq p \leq p_e \quad (1a)$$

(II)

$$G' = G'_v \left(\frac{p}{p_v} \right)^\beta \quad p_e \leq p \leq p_v \quad (1b)$$

(III)

$$G' = G'_v \left(\frac{p}{p_v} \right)^\gamma \quad p_v \leq p \leq p_g \quad (1c)$$

(IV)

$$G' = G'_v \left(\frac{p_g}{p_v} \right)^\gamma \left(\frac{p}{p_g} \right)^\delta \quad p_g \leq p \quad (1d)$$

The set of expressions 1a to 1d articulates mathematically around the onset of the vitrification regime, p_v , and G'_v which denote the conversion and shear modulus at this point, respectively. The four regimes are characterized by distinct scaling behaviors. The first regime spans a small conversion range where the polymer solution starts to develop quickly soft elastic behavior. Here, the polymer solution is assumed unentangled. This clearly changes at the critical conversion p_e where the formation of entanglements becomes the driving mechanism behind the elastic build-up in regime II. In this zone, the polymer system compares to a temporary network of polymerized IBoA swollen by its own monomer. As the monomer conversion is tantamount of the polymer concentration, $\phi_p \sim p$, Figure 4a (and 5) indicates that the DEPR typically covers the range $\phi_p \approx 0.4$ to 0.6. In this concentration

range, the longest relaxation times are expected in the order $o(10^{-2}-10^{-1} \text{ s})$ (cf. estimation of longest relaxation time in Supporting Information SI-3), i.e. close or larger than the experimental angular frequency ($\omega\tau_{max} \geq 1$), pointing toward plateau values for the respective elastic moduli of the polymer solution.⁷⁷ Hence, extrapolation of this regime to full conversion provides an estimate for the elastic modulus of the polymer melt in the rubbery plateau, designated as G'_{II} in Figure 4b. It is emphasized that owing to the inherent polydispersity of free-radical polymerization and the resulting broad relaxation spectrum, only entanglements of unrelaxed chains at the time scale of deformation will effectively contribute to G'_{II} . The power β in regime II quantifies the scale of entanglement formation against monomer conversion in semidilute polymer conditions. Likewise, γ provides the scaling exponent for the vitrification regime III where the shear modulus raises by more than 3 orders of magnitudes over a DBC interval less than 10%. Conversion p_g stands for the onset of regime IV where the polymer system reaches the glass state. This point matches closely with p_{C_m} . Beyond this point, the modulus grows further in the glassy state at a very slow pace with minor conversion changes. It is recalled that modulus growth in the vitrified state often goes along with performance-reducing mechanical changes such as enhanced brittleness.

Effect of Initiation Rate

Figure 5 gives an overview of the viscoelastic conversion maps for the photoinduced polymerization of IBoA at light intensities between 2 and 30 mW cm^{-2} using 0.2 w/w% TPO-L. In the rate plateau, the maximum polymerization rate scales as $R_p \approx R_i^{0.59}$ with an exponent higher than 0.5 expected from classical radical kinetics in quasi steady state.

Correspondingly, O'Brien and Bowman predicted higher exponent values ranging from 0.5 to 1 from numerical simulations when dissolved oxygen is present during photopolymerization.⁶⁶ At the lowest intensities, vitrification, as detected by a maximum in loss modulus, was not reached within the three minutes run-time. Overall, the moduli curves exhibit closely similar trends regardless of the intensity and initiation rate. This is further substantiated in Figure 6a with an overlay of the different curves. The double logarithmic representation emphasizes regimes II and III, central in the viscoelastic development during polymerization. The sloping lines result from a linear regression to the data in the respective regimes and demonstrate a close overlap in the DEPR, regime II. The vitrification behavior reveals some larger spread, likely from local nonisothermal deviations related to the generated polymerization heat. According to the set of power-law expressions eqs 1a–1d, the slopes and intercepts evaluated in log–log space provide estimates for the exponents β and γ , and the modulus values G'_{II} and G'_v at the conversion p_v . The vertical lines in Figure 5 indicate the conversion, p_{dec} where the polymerization starts to slow down. This point comes close to the onset of the DEPR, well before vitrification, in this series of

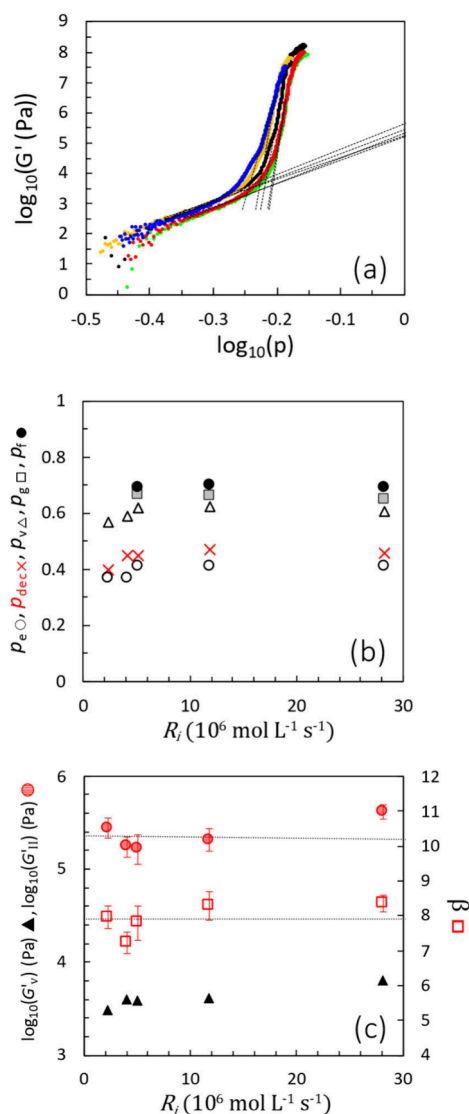


Figure 6. (a) Overlay of the elastic-conversion curves at the five light intensities in log–log scale with linear approximations in regimes II and III. (b) Plot of the characteristic conversions p_e (○), p_{dec} (×), p_v (Δ), p_g (□) and p_f (●) versus initiation rate R_i for the photopolymerization of IBoA with 0.2 w/w% TPO-L. The values were determined from the curves in Figure 5. (c) Plot of the elastic modulus values G'_{II} (●), G'_v (▲) and the scaling exponent β (□) of regime II (DEPR) versus initiation rate R_i . Error bars correspond to 95% confidence intervals.

experiments which is even more obvious from Figure 6b where the characteristic conversions are plotted as a function of initiation rate.

The close match between p_{dec} and p_e around 0.4, as well as the relative invariance toward the initiation rate R_i , are striking. While these results suggest a correlation between the rate of deceleration and the entanglement formation, free volume changes have been raised since long to account for the diffusion limitations of radical termination and propagation, driving respectively the acceleration and deceleration processes. According to classical free volume theory, kinetic reaction constants can be cast in a decaying form $k \sim \exp[-B(f^{-1} - C)]$ to account for the structural effect on the rate coefficients for propagation and termination in isothermal conditions (B and C are constants).^{78,79} The fractional free

volume f is further expanded as $f = 0.025 + \phi_m \alpha_m (T - T_{gm}) + \phi_p \alpha_p (T - T_{gp})$, which involves the volume fractions (ϕ_m , ϕ_p), the coefficients of thermal expansion (α_m , α_p) and the glass transition temperatures (T_{gm} , T_{gp}) of both monomer and polymer (note that $\phi_m + \phi_p = 1$ and $\phi_p \approx p$). As the thermal properties of the full-converted polymer are not expected to vary much with initiation rate in the explored range, the free volume changes and the kinetic constant decay should behave similarly, and so the acceleration and deceleration behavior as observed. The initiation invariance also holds for $p_g \approx p_{G_m} \approx 0.65$ and $p_v \approx 0.62$ which seems to decrease slightly below 0.6 at the low intensity end. The vitrification step involves a little 3% in double bond conversion to freeze all segmental and chain mobility. Panel c in Figure 6 shows the elastic modulus values G'_{II} , G'_v and the scaling exponent β of regime II (DEPR) against the initiation rate R_i . Within experimental error, the scaling exponent β appears largely independent of initiation kinetics with an average value $\beta \approx 7.9$ (dotted line in Figure 6c). This result shows that once the entanglement threshold is crossed, the entanglement density develops extremely fast per conversion unit. Using a straightforward dilution argument for an entangled polymer solution one would expect a much lower power according to the established scaling $G' \approx \phi_p^x$ with x between 1 and 2.3.^{76,77} For comparison with gelation and network development theories, it is more appropriate to examine the data in terms of the reduced bond probability or equivalently, the relative extent of reaction $\epsilon = (p - p_0)/p_0$. This analysis is treated in a sequel paper dedicated to networks of IBoA involving entanglements and permanent cross-links.

At a first glance, the intercept modulus G'_{II} in Figure 6c seems to cross a minimum which would relate to a minimum in the density of entanglement strands ν_e according to the premise that $G'_{II} \approx G_e \approx \nu_e RT$, i.e., the equilibrium modulus of the fully converted polymer melt (T is the absolute temperature and R is the gas constant as usual).^{77,80} As pointed out before, the latter correspondence assumes that the polymer chains are basically unrelaxed at the characteristic time scale of deformation. An estimate of the mass spacing between entanglements then follows from $M_e = \rho/\nu_e$ with $\rho = 1.077 \text{ g cm}^{-3}$ for the density of *poly*(IBoA) at room temperature, and ranges from 6 to 16 kg mol⁻¹. A variance comparison of G'_{II} at a 95% confidence level learns that there are no significant differences between these values, except at the highest initiation rate. Excluding the latter value, the variance-weighted mean value $\bar{M}_e = 11.9 \pm 0.8 \text{ kg mol}^{-1}$ is determined for the molar mass between entanglements of *poly*(IBoA), consistent with the typical order of magnitude for other (meth)acrylates.⁸¹ In Supporting Information SI-4, gel permeation chromatography data reveal broad molar mass distributions at the end of the photopolymerization with number averages $M_n \sim 10^5 - 10^6 \text{ Da}$, many times larger than the estimated molar mass between entanglements. According to the classical radical polymerization theory, the actual radical concentration, and hence the initiation rate, controls the average molar mass of the polymer chains. The kinetic chain length is defined as the average double bonds consumed per initiated radical and scales roughly as $\nu = R_p/R_i \sim R_i^{1/2}$.⁸² From the initiation and plateau polymerization rates in Figure 5, ν is estimated in the range 1.5×10^4 to 7.5×10^4 corresponding to molar mass values of the order $10^6 - 10^7 \text{ Da}$, 1 order of magnitude higher than the GPC results. The kinetic chain length does not return any distribution average as provided by

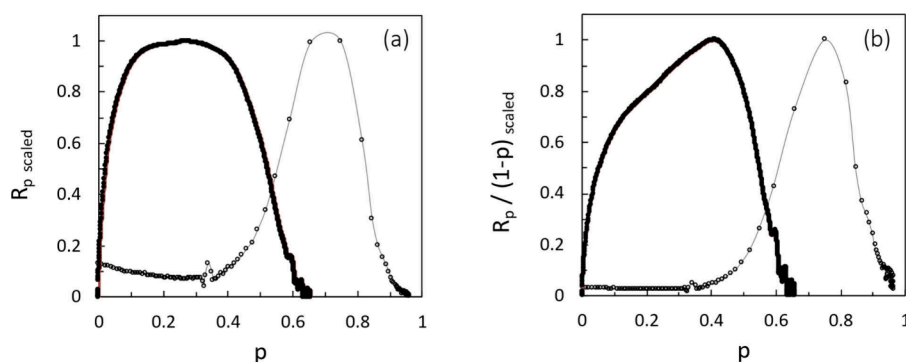


Figure 7. (a) Polymerization rate scaled to its maximum value plotted against conversion for IBoA at 20 °C (photoactivation, 0.2 w/w% TPO-L, 0.7 mW cm⁻²) (solid symbols) and MMA at 25 °C (thermal initiation, 2.9 w/w% BPO and 2.7 w/w% DPpT) (open symbols). (b) Same data as (a) expressed in reduced form, $R_p/(1-p)$, plotted against conversion.

GPC and, hence, is merely indicative. But also GPC data do not truly quantify the polymer mass and might contain some bias, for example, from the calibration source. Figure S3 shows that the molar mass distributions of *poly*(IBoA) after photopolymerization using different initiation conditions are relatively comparable, showing some nuances in terms of average, width and shape but overall similar in magnitude. In the assumption that the build-up in elasticity mirrors the development in molar mass distribution, it is not unexpected to find a parallel in the weak dependence with respect to initiation conditions for the final polymer distribution.

DISCUSSION

The projection of the polymerization rate in the viscoelastic-conversion maps offers an elegant perspective to rationalize the kinetic behavior in terms of entanglements, cross-linking and vitrification. It is also helpful to delimit clearly where rate acceleration and deceleration take place in terms of elastic build-up.

Various kind of chemical models have been reported in the literature to account for the radical polymerization kinetics over the full conversion range. The viscoelastic kinetics however have seldom been addressed in depth, and never beyond phenomenological considerations to explain experimental data. Most generally, it is recalled that the elastic build-up rate can be decomposed as

$$R_{G'} = \frac{dG'}{dt} = \frac{\partial G'}{\partial p} \frac{\partial p}{\partial t} = \frac{\partial G'}{\partial p} R_p \quad (2)$$

The factorization in eq 2 provides the link between the development of the macroscopic elasticity and the microscopic rate of polymerization. By establishing explicitly the relationship between elasticity and conversion, as reported in this work, kinetic models developed for the chemical polymerization rate R_p can be extended to $R_{G'}$ by means of eq 2.

The free-radical photopolymerization kinetics of IBoA looks quite different from the familiar polymerization profile of MMA. While MMA photopolymerization is hard to achieve in practice, its kinetic characteristics are fundamentally similar to the thermo-initiated polymerization.^{43–47,55,56,83} The distinct kinetic behaviors of the two vitrifying monomers are compared in Figure 7a where the polymerization rate, scaled to its maximum value, is plotted against the double bond conversion. In this specific example, the polymerization of MMA was recorded at 25 °C using 2.9 w/w% benzoyl peroxide (BPO) as initiator paired with 2.7 w/w% dipropyl *p*-toluidine (DPpT) as

accelerator. The profile displays the characteristic features of the MMA radical chain polymerization.^{45,53}

Note that the maximum polymerization rate used to normalize the MMA data is 1 order of magnitude lower when compared to IBoA with 0.2 w/w% of TPO-L at the lowest intensity of the study, i.e., 0.7 mW cm². Hence, the polymerization is much slower and achieves its ultimate conversion in approximately one hour. When scaled to its maximum value, the rate–conversion profile of IBoA is rather independent from the initiation conditions, an observation which could not be confirmed for MMA. In the literature, estimates have been reported for the initial rate coefficients of propagation and termination of both monomers, i.e. $k_{p,IBoA}^0 = 1.05 \times 10^4$ L mol⁻¹ s⁻¹, $k_{td,IBoA}^0 \approx 10^7$ L mol⁻¹ s⁻¹ (20 °C), $k_{p,MMA}^0 = 3.2 \times 10^2$ L mol⁻¹ s⁻¹ and $k_{td,MMA}^0 \approx 6 \times 10^7$ L mol⁻¹ s⁻¹ (25 °C) at the beginning of the polymerization.^{38,39,57,84} An approximation of the radical content is provided by the reduced polymerization rate $R_p/(1-p)$ in the assumption of constant propagation kinetics which is reasonable before deceleration.⁴⁵ For IBoA, Figure 7b shows that the radical content builds up significantly at low conversions until $p \approx 0.1$, and grows more softly afterward up to the deceleration onset. The strong initial increase in radical concentration is consistent with the transition to steady-state which is determined by the ratio $\rho = k_t/k_p = k_{td,IBoA}^0/k_{p,IBoA}^0 \approx 10^3$, as discussed by Roose et al.^{35,74} While it is expected that ρ reduces to some extent, the acceleration in the nonsteady transient step is often confused with the gel effect. Once steady state is achieved at $p \approx 0.1$, the polymerization rate scales as $R_p \approx k_p/\sqrt{k_t}$ with k_t decreasing according to the diffusive slowdown of the polymer radicals in the concentrating polymer solution. Whatever initiation, the fast polymer growth for IBoA induces effective diffusion limitations which impact termination early in the polymerization. The magnitude of k_p relative to k_t explains the high molar mass range of the formed polymers which in turn leads to vitrification at relatively low conversions. The latter affects T_g adversely owing to the plasticizing action of the residual monomer. This is in stark contrast with MMA where the polymerization rate is low and the radical content stays constant over a significant conversion range up to 40%. Beyond this conversion, diffusion limitations become rate controlling for radical termination, leading to autoacceleration. It is emphasized that steady-state is achieved instantly for MMA as $k_{t,MMA}^0/k_{p,MMA}^0 \gg 10^4$.⁷⁴ In addition, the ultimate conversion is close to 1 with a final T_g value ≈ 90 °C.

Few kinetic models have been suggested for direct comparison of the polymerization rate to experimental data over the entire course of conversion. Most are merely phenomenological. As an exception, the nonsteady scaling model introduced recently is the single semiempirical model resulting from mass-action kinetics which captures properly nonsteady effects.⁷⁴ Derivation of the model results in the general form $R_p = \phi R_p^{ss}$ where $\phi = \sqrt{1 - e^{-4\theta}}$ represents the growth factor toward steady-state and R_p^{ss} is the classical stationary approximation, i.e. $R_p^{ss} = (1 - p)\sqrt{R_i k_p / 2\rho}$. The radical growth factor is characterized by the exponent $\theta = \int_0^p \frac{\rho(p')}{(1-p')} dp'$. The rate coefficient for radical termination incorporates contributions for center-of-mass/segmental diffusion and reaction diffusion, conveniently approximated by power law functions. Likewise, loss of initiation and propagation efficiency are handled using appropriate power law expressions which eventually enable to return analytical approximations for ρ , θ , R_p^{ss} , ϕ and finally R_p in terms of the conversion p . Finally, R_p is further rearranged to a closed-form expression with five adjustable parameters.⁷⁴ As illustrated in Figures 4 and 5, the model captures well the overall qualitative behavior of the experimental data after nonlinear least-squares fitting. The estimated parameters provide valuable information about the conversion dependence of the various rate coefficients. Beyond the scope of this report, the parameter values will be discussed once data for other well-defined acrylates and methacrylates are available.

The piecewise power-law model described by the set of eqs 1a–1d provides a simple approximation to the viscoelastic build-up upon double bond conversion. Regimes II and III account for the bulk of the elastic-build-up with respective scaling exponents β and γ . The ultimate regime IV beyond vitrification, ($p > p_g \approx p_{G_m}$) develops very slowly owing to severe motional constraints and involves the scaling exponent δ .

For any step with exponent m , the derivative of G' has the simple form $\frac{\partial G'}{\partial p} \approx mp^{m-1}$ but step discontinuities do not provide a smooth mathematical form for straight use to estimate the elastic build-up rate according to eq 2. Still, the piecewise representation provides a basis for further modeling.

CONCLUSION

We have shown that viscoelastic-conversion relations of rapid photoinduced free-radical polymerization can be established from carefully controlled TR-FTIR-photorheology experiments. This was demonstrated for isobornyl acrylate, a vitrifying acrylate monomer, over a range of initiation conditions at various light intensities and photoinitiator content. The type of photoinitiator (TPO-L, Norrish type I) and light source (405 nm LED) were primarily chosen to limit initiation complexity in the experiments, while still aligning with popular conditions in modern applications such as additive manufacturing and lightweight constructions.

Beyond the familiar time domain picture, mapping of the viscoelastic data against double bond conversion offers a new perspective which highlights at least four different regimes in the elastic build-up. The viscoelastic-conversion map uncovers the overall visco-elastic transformation from low-viscous polymer solution to solid vitrified bulk polymer. A one-to-one comparison of the polymerization rate and the elastic

shear modulus in a linear conversion map provides insights on the structural features impacting the polymerization kinetics. The initial acceleration process is understood from transient radical build-up toward steady-state and diffusion limitations in the polymer solution. Deceleration starts clearly at a conversion well before vitrification, nearly independent of initiation rate.

It was shown that the elastic-conversion behavior can be conveniently approximated by a continuous piecewise power-law model, providing critical conversions and power-law exponents for the different regimes which were discussed in terms of initiation rate. Furthermore, we have demonstrated that extrapolation of the elastic shear modulus toward full conversion in the dilute entangled polymer regime (DEPR) provides an alternative way to estimate the molar mass between entanglements of a linear polymer. For poly(IBoA) we report an average value $\bar{M}_e = 11.9 \pm 0.8$ kg mol⁻¹. Finally, as a corollary of this study, we also provide a comprehensive set of glass transition temperature values for poly(IBoA) in well-characterized conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.6c00028>.

SI-1, MIR photorheology coupling; SI-2, numerical prediction of the induction period during photopolymerization of IBoA along the illumination path for the MIR-photorheology coupling; SI-3, estimation of longest relaxation time; SI-4, molar mass distribution of poly(IBoA) after TR-MIR photorheology experiment; SI-5, conversion scaling exponent for the vitrification regime; SI-6, reduced polymerization rate (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Patrick De Doncker and Dr. Laurence Bouteau (Allnex) are acknowledged for their kind help in TR-IR photorheology and GPC experiments, respectively. We thank Prof. Dirk Burth (Hochschule für angewandte Wissenschaften München) for providing the diffusion data of oxygen in IBoA. Also a word of thank to Prof. Guy Van Assche (Vrije Universiteit Brussel) for highlighting discussions about free-radical kinetics and vitrification.

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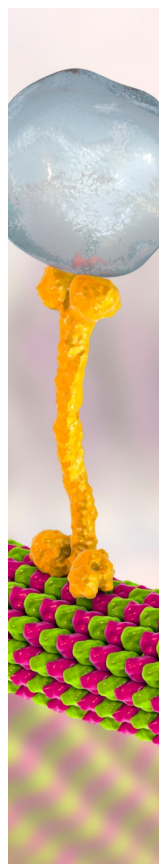
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