Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Monitoring of viscosity changes during a free radical polymerization using fluorescence lifetime measurements

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1. Experimental details

To observe the fluorescence lifetime of the polymerization, one drop of a Bodirot stock solution in MeOH adjusted for a final count rate of ~150000 cts/s was evacuated in a teflon sealable flask. The radical initiator V70 (11 mg) and MMA (2.35 g) were added, and the reaction mixture was shaken for 10 seconds and subjected to three freeze-pump-thaw cycles. Under nitrogen atmosphere, 1 mL of the reaction mixture was transferred into a glass reaction chamber with a microscopy coverslip at the bottom.

Time-correlated single photon counting (TCSPC) data were recorded on a confocal setup. A Picoquant diode laser LDH-D-C-470 (467 nm, 10 MHz, 20 µW measured at the rear aperture of the microscope) was coupled into a Zeiss Axiovert 200 microscope operating in epi mode using a z473RDC dichroic mirror (AHF Analysentechnik, Tübingen). The fluorescence signal was filtered using a BrightLine HC 488/LP filter and a ET Shortpass 680SP-2P filter (both filters from AHF Analysentechnik), detected by a Perkin Elmer SPCM-AQR-14 SPAD and processed using a HydraHarp 400. Data were acquired for 2 minutes as point measurement for low viscosity samples, and in order to avoid photobleaching as 2D area scan (80 × 80 µm²) for high viscosity samples, i.e. at conversions above 65%. Analysis of the TCSPC data was performed using the Picoquant SymPhoTime v5.3 software. The data were fitted to the biexponential fitting function 1 with n=1 or n=2 (see paper). As instrument response function (IRF) the signal of the coverslip reflex was used.

The BODIPY-C12 dye was synthesized in our lab following a procedure known from literature.[S1, S2]

2. Raman measurements to determine monomer-to-polymer conversion

All recorded spectra were measured on a Perkin Elmer Raman Station 400 using the software Perkin Elmer Spectrum v6.2 and auto-baseline correction prior to processing.
Raman spectra at different conversion are presented in Fig. S1. Conversions were determined using Raman spectroscopy as proposed by Chu *et al.*[S3] The C=C double bond stretching vibration at 1640 cm^{-1} decreases during the polymerization and was used for the determination of the conversion. The C=O stretching vibration at 1722 cm^{-1} served as a reference. A calibration curve which was recorded with monomer/polymer mixtures of known concentration was used to calculate the conversion from the ratio of both Raman signals:

$$x = 1 - \frac{\frac{I_{CC}}{I_{CO}} \cdot \frac{b_1}{a_1}}{\frac{a_2}{a_1} + \frac{I_{CC}}{I_{CO}} \cdot \left(\frac{b_1}{a_1} - 1\right)} = 1 - \frac{\frac{I_{CC}}{I_{CO}} \cdot \frac{b_1}{a_1}}{\frac{a_2}{a_1} + \frac{I_{CC}}{I_{CO}} \cdot \left(\frac{b_1}{a_1} - 1\right)}$$

The calibration parameters for MMA/PMMA, according to the nomenclature used by Chu *et al.*,[S3] were $\frac{a_2}{a_1} = 1.7763$ and $\frac{b_1}{a_1} = 0.3156$.
As it is not possible to measure the fluorescence lifetime and the Raman spectra for determining the conversion simultaneously, the corresponding conversion value for each

fluorescence lifetime measurement was interpolated from the previous and the following Raman spectra. In this time period, the rise in conversion was considered to be approximately linear.

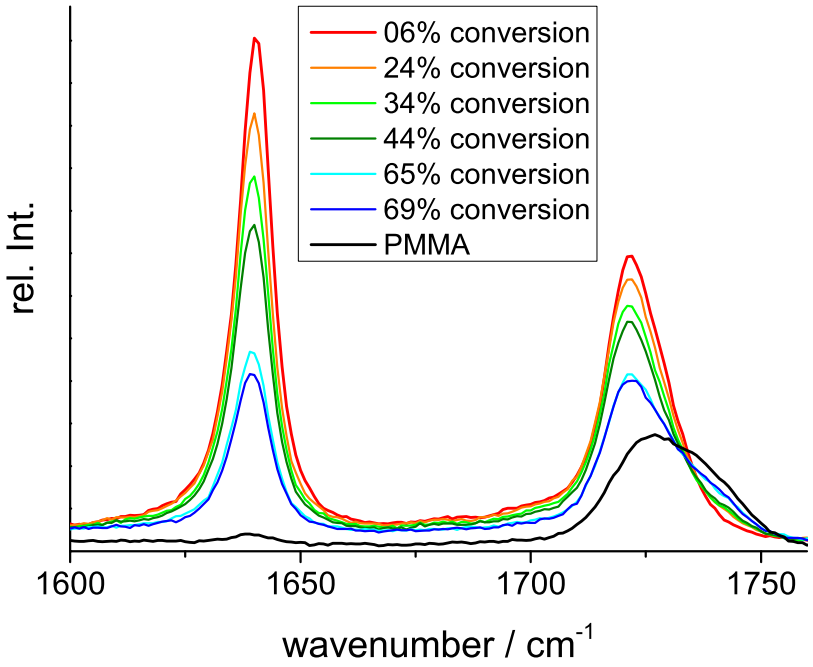


Fig. S1: Raman spectra measured at different conversions during the bulk radical polymerization of MMA and spectrum of a commercial PMMA sample.

3. Dependency of fluorescence lifetime on viscosity

We followed the evolution of fluorescence lifetimes over a broad conversion range during the bulk radical polymerization of MMA. Therefore, it is essential to investigate its dependency on viscosity in detail.

The fluorescence lifetime τ_f depends on the rates k_r and k_nr of the radiative and non-radiative deactivation processes of the excited state as follows:[S4]

$$\tau_f = \frac{1}{k_\mathrm{r} + k_\mathrm{nr}} \qquad \text{(S1)}$$

The non-radiative deactivation process depends on the free volume V_f available in the system:[S5]

$$k_\mathrm{nr} = k_\mathrm{nr}^0 \cdot \exp\left(-x \cdot \frac{V_0}{V_f}\right) \qquad \text{(S2)}$$

where k_nr^0 is the free-rotor reorientation rate, V_0 is the occupied volume, and x is a constant for the particular probe. The free volume and the viscosity can be related to each other using the Doolittle equation[S6]

$$\eta = \eta_0 \cdot \exp\left(\frac{V_0}{V_f}\right) \tag{S3}$$

where η_0 is a parameter depending on the solvent. Combining equations S1–S3, one obtains for the fluorescence lifetime

$$\tau_f = \frac{1}{k_\mathrm{r} + k_\mathrm{nr}^0 \cdot \left(\frac{\eta}{\eta_0}\right)^{-x}} \tag{S4}$$

For low viscosities (and thus small fluorescence quantum yields), the non-radiative deactivation process dominates and τ_f can be expressed as

$$\tau_f = \frac{1}{k_\mathrm{nr}^0} \cdot \left(\frac{\eta}{\eta_0}\right)^{x} \tag{S5}$$

resulting in the Förster-Hoffmann equation

$$\phi_f = C \cdot \eta^x \tag{S6}$$

For high viscosities, the non-radiative deactivation process loses weight and finally becomes negligible. Therefore,

$$\tau_f = \frac{1}{k_\mathrm{r}} \tag{S7}$$

and a quantitative fluorescence quantum yield is observed if no other deactivation process occurs. This limiting value of the fluorescence lifetime at high conversion is ca. 6 ns in our system, resulting in a value of 1.7×10^8 s^{-1} for k_r.

Using the calibration in water/glycerol of Levitt *et al.*[S2] and a fluorescence lifetime of 6 ns as the limiting value for high viscosity, we obtained the following relationship which was used as viscosity calibration (see also Fig. S2):

$$\tau_f = \left[\frac{1}{6\ \mathrm{ns}} + \frac{15}{\mathrm{ns}} \cdot \eta^{-0.7}\right]^{-1} \tag{S8}$$

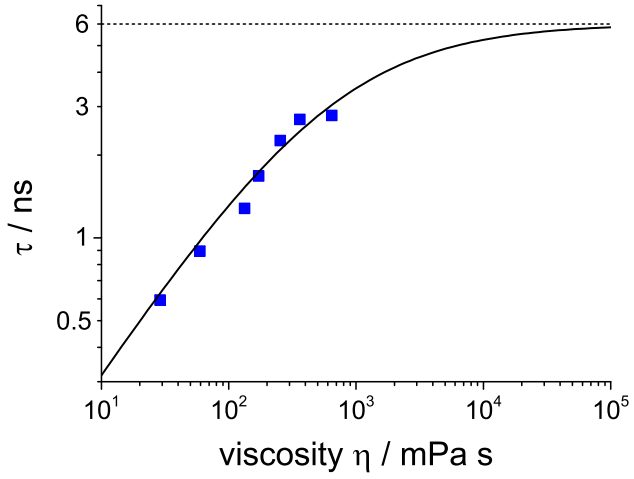
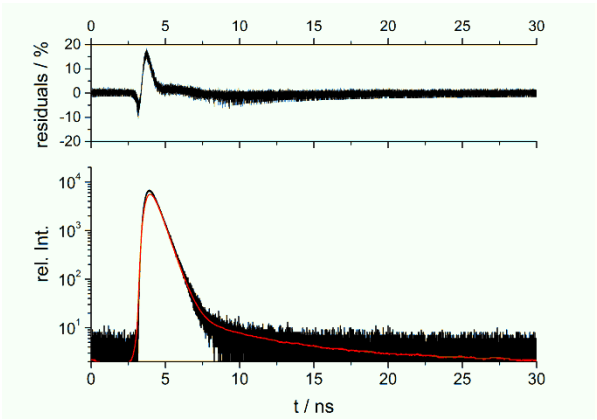


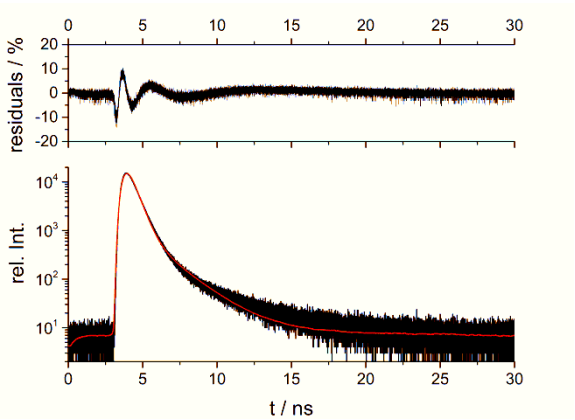
Fig. S2: Dependency of fluorescence lifetime versus viscosity as measured by Levitt *et al.*[S2] and fit according to equation S8.

4. Fluorescence decay curves and fits during polymerization

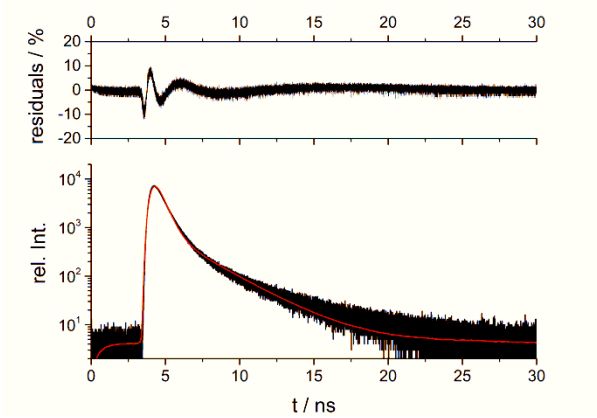
0 % conversion



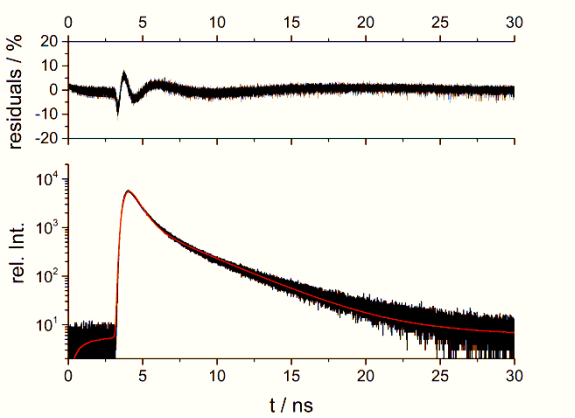
10 % conversion



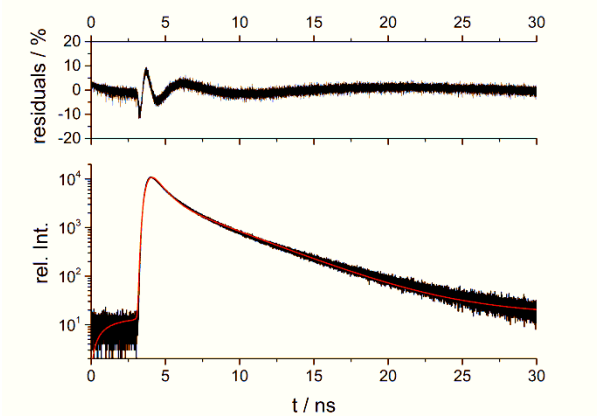
16 % conversion



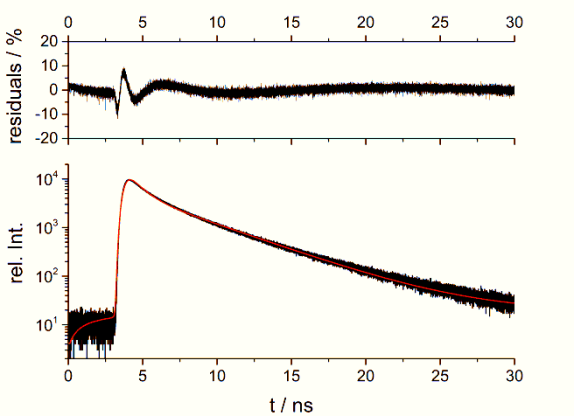
24 % conversion



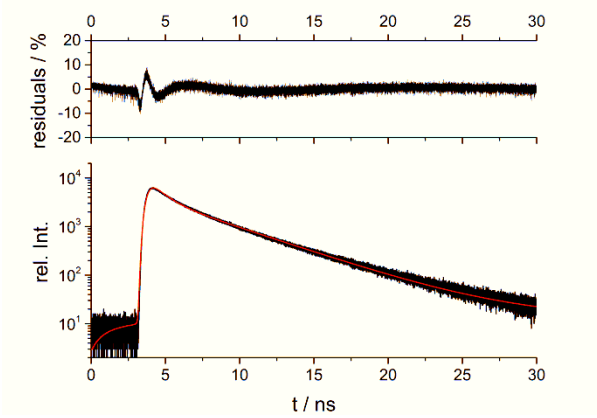
33 % conversion



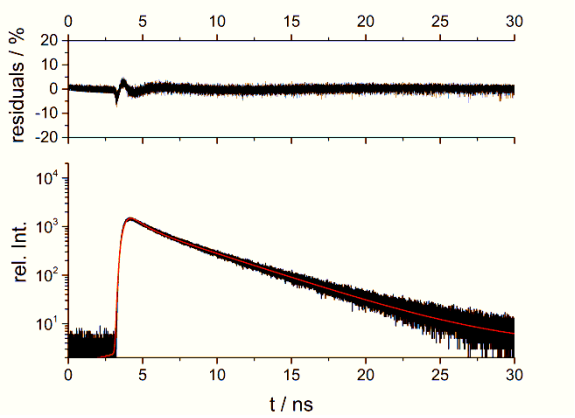
40 % conversion



47 % conversion



54 % conversion



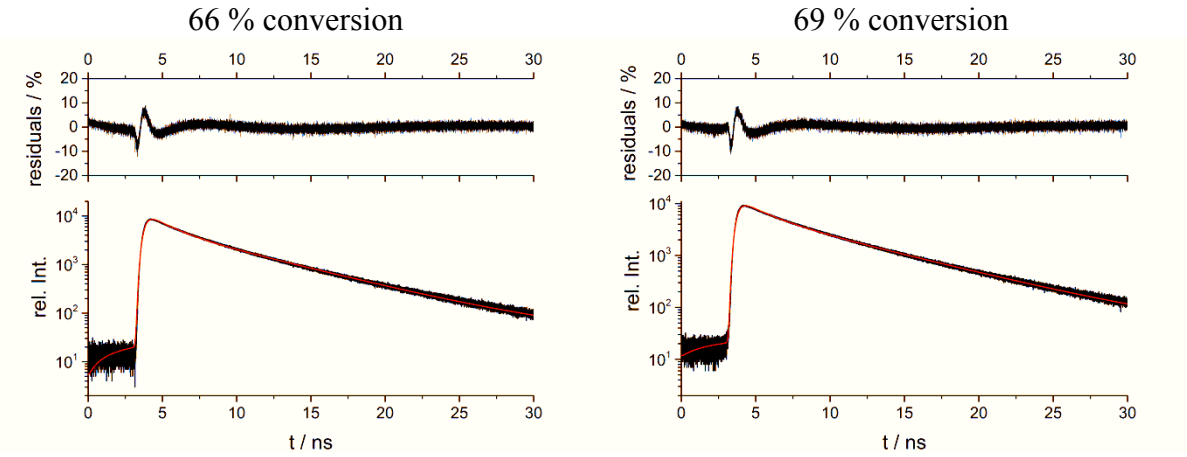


Fig. S3: Fluorescence decay curves, their fits according to equation 1 of the main paper, and the residuals of the fits for different conversions.

[S1] R. van Hameren, J. A. A. W. Elemans, D. Wyrostek, M. Tasior, D. T. Gryko, A. E. Rowan, R. J. M. Nolte, *J. Mater. Chem.*, 2009, **19**, 66-69.

[S2] J. A. Levitt, M. K. Kuimova, G. Yahioglu, P.-H. Chung, K. Suhling, D. Phillips, *J. Phys. Chem. C*, 2009, **113**, 11634-11642.

[S3] B. Chu, G. Fytas, G. Zalczer, Macromolecules 1981, 14, 395-397.

[S4] B. Valeur, Molecular Fluorescence: Principles and Applications. Wiley-VCH, Weinheim, Germany, 2002.

[S5] R. O. Loutfy and B. A. Arnold, *J. Phys. Chem.*, 1982, **86**, 4205-4211.

[S6] A. K. Doolittle, *J Appl. Phys.*, 1951, **22**, 1471-1475.