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Laser Single Pulse Initiated RAFT Polymerization for Assessing Chain-Length Dependent Radical Termination Kinetics

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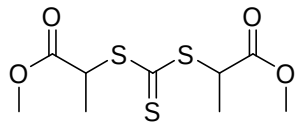
Experimental Part

Materials

The photoinitiator α-methyl-4-(methylmercapto)-α-morpholinopropiophenone (MMMP, 98%, Aldrich) was used as supplied at initial concentrations close to 1×10^{-2} mol L^{-1}. Butyl acrylate (>99%, stabilized with 0.005 wt.-% hydroquinone monomethyl ether, Fluka), was purified by distillation under reduced pressure in the presence of K_2CO_3 and treated by several freeze-pump-thaw cycles to remove dissolved oxygen. Ambersep®900 hydroxide form (Fluka) was dried in vacuum before usage. All other chemicals were purchased from Aldrich and used without further purification.

Synthesis of BMPT

The synthesis of S-S'-bis(methyl-2-propionate)-trithiocarbonate (BMPT) was performed in accordance to the procedure by Tamami and Kiasat with only minor deviations.[1] 15 g of Ambersep 900 were dispersed in 100 mL CS_2 and stirred for 5 min at ambient temperature. The anion-exchange resin turned dark red immediately. Subsequently, 1.67 g of



S-S'-bis(methyl-2-propionate) trithiocarbonate (BMPT)

[1] B. Tamami, A. R. Kiasat, *J. Chem. Res.-S.*, **1998**, 454.

methyl-2-bromopropionate as the alkylating agent were added dropwise. The reaction mixture was then refluxed for 30 h. After separation of the resin, drying with anhydrous sodium sulfate and evaporation of the solvent under reduced pressure the crude product was purified via column chromatography on silica gel (toluene). BMPT was obtained as pale yellow liquid (2.4 g, 85 %). The purity of the RAFT agent was close to 97 % as verified by ^{1}H-NMR.

^{1}H-NMR ($CDCl_3$) δ(ppm): 1.6 (d, 3H), 3.7 (s, 3H), 4.8 (q, 1H).

^{13}C-NMR ($CDCl_3$) δ(ppm): 16.9; 48.2; 52.9; 171.3; 219.5.

Single-Pulsed Pulsed-Laser Polymerizations

The BA monomer system containing of 2.1×10^{-2} mol·L^{-1} BMPT and 1×10^{-2} mol L^{-1} of MMMP as the photo-initiator, was irradiated with XeF excimer laser pulses (at 351 nm) of 2 to 3 mJ incident energy per pulse. Monomer conversion induced by a laser single pulse was monitored via online near-IR spectroscopy. For this purpose, the first overtone of the C-H stretching vibration of hydrogen atoms at the C=C double bond, close to 6170 cm^{-1}, was used. After applying a series of excimer laser pulses, each being followed by microsecond time-resolved near-IR spectroscopic measurement of pulse-induced polymerization, the reaction cell was inserted into the sample chamber of an IFS 88 Fourier transform IR/NIR spectrometer (Bruker), where overall monomer concentration was measured. The experiments were carried out at 60 °C and 1000 bar up to about 80 per cent monomer conversion.

Molecular Weight Analysis

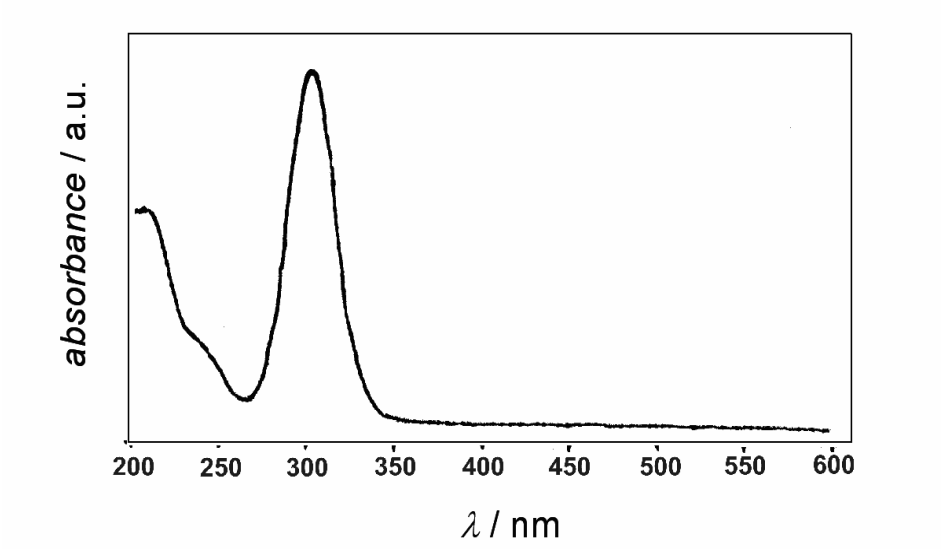
Molecular weight distributions were determined by means of size-exclusion chromatography (SEC) using a Waters 712 WISP autosampler, a Waters 515 HPLC pump, PSS-SDV columns with nominal pore sizes of 10^5, 10^3 and 10^2 Å, a Waters 2410 refractive index detector, and THF at 35 °C as the eluent. The SEC set-up was calibrated against polystyrene (PS) standards of narrow polydispersity (M_p = 410 to 2 000 000 g·mol^{-1}) from Polymer Standards Service. Mark-

Houwink parameters for poly(BA) in THF ($K = 1.22\times10^{-2}$ mL·g^{-1}, $a = 0.700$)[2] provided access to absolute molecular weights distributions according to the principle of universal calibration.

Simulations

All simulations were performed using the program package PREDICI®, version 5.4.18, on an AMD Athlon XP 1800+ computer.

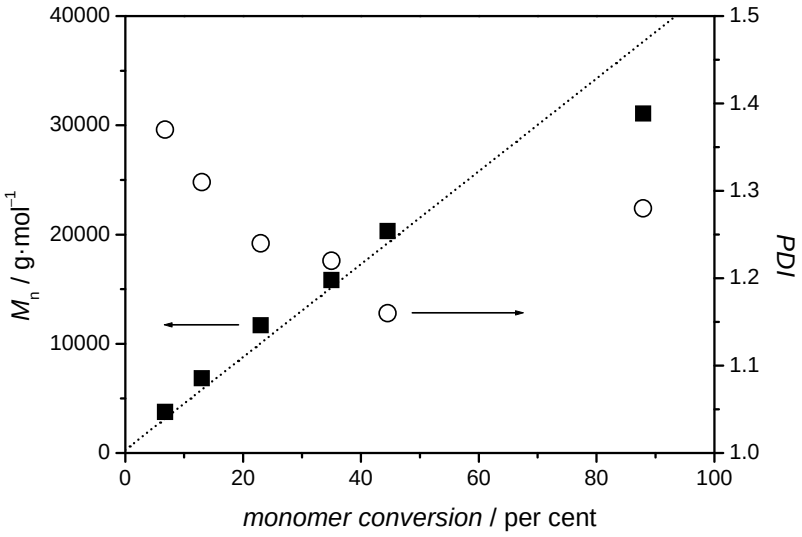
UV-Spectrum of BMPT



UV-spectrum of 1×10^{-2} mol·L^{-1} BMPT in heptane, measured with a Lambda 2 (Perkin-Elmer).

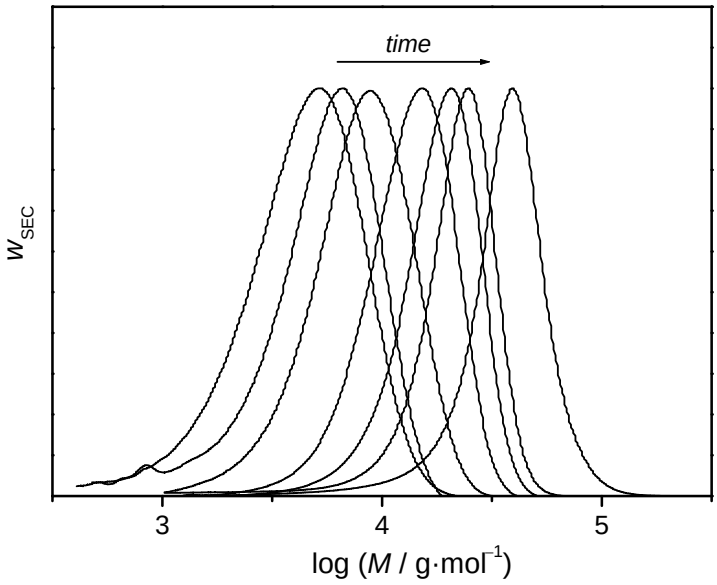
[2] E. Penzel, N. Goetz, *Angew. Makromol. Chem.* **1990**, *178*, 191.

Molecular Weight and Polydispersity vs. Monomer Conversion



Number average molecular weight, M_n, and polydispersity index, *PDI*, plotted vs. monomer conversion for pulsed-laser induced BMPT-mediated ([BMPT] = 2.1×10^{-2} mol·L^{-1}) BA polymerization at 60 °C and 1000 bar, initiated by approximately 1×10^{-2} mol·L^{-1} MMMP.

Evolution of Chain-Length Distributions with Reaction Time



Evolution of full molecular weight distributions (SEC-distributions) with reaction time of pulsed-laser induced BMPT-mediated ([BMPT] = 2.1×10^{-2} mol·L^{-1}) BA-polymerization at 60 °C and 1000 bar, initiated by approximately 1×10^{-2} mol·L^{-1} MMMP. From left to right, the curves correspond to overall monomer conversions of 7, 13, 23, 35, 44, and 88 %, respectively.