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Measurement of chain transfer to monomer constants in ketene acetal homo- and copolymerization

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Experimental Section

Reagents. Styrene (Aldrich) was distilled under reduced pressure prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Vinyl acetate (Reakhim) was dried with $CaCl_2$ and fractionally distilled at atmospheric pressure under argon. 1,4-Butanediol (Reakhim) was purified by repeated fractional freezing, dried over anhydrous Na_2SO_4, doubly distilled *in vacuo* in the presence of Na_2SO_4 and stored over 4Å molecular sieves. *p*-Toluenesulphonic acid was dried at 100 ºC for 4 h under water-pump vacuum with P_2O_5 as desiccant to absorb water vapor. Methanol was boiled and distilled over magnesium methylate. Di-*tert*-butyl peroxide (DTBP) (Trigonox B grade, Nouryon), bromine (Reakhim), Bu_4NBr (Kemstor), and benzene (HPLC grade, Reakhim) were used as received.

Synthesis of 2-methylene-1,3-dioxepane (MDO). The monomer was synthesized in 3 steps according to the literature procedures. First, bromoacetaldehyde dimethyl acetal was obtained in 54% yield by bromination of vinyl acetate in methanol similar to the procedure in ref.[S1] Further the ring closure reaction of $BrCH_2CH(OMe)_2$ with 1,4-butanediol in the presence of a catalytic amount of *p*-toluenesulfonic acid at 80–125 °C for 30 h led to the formation 2-bromomethyl-1,3-dioxepane in 81% yield.[S2] Finally, the elimination reaction of 2-bromomethyl-1,3-dioxepane with KOH and Bu_4NBr at 80 °C for 19 h afforded MDO in 42% yield.[S3]

Polymerization. (Co)Polymerization mixtures were prepared as described previously:[S4,S5] initiator and MDO (and styrene) were weighted into 0.3-1.0 mL vial. The reaction mixtures were degassed by several freeze-thaw cycles in a vacuum to 1,3 Pa and sealed off. The (co)polymerization was carried out at 70 or 125 °C.

The molecular weight characteristics of the polymers were determined by gel permeation chromatography (GPC) using the Agilent 1260 Infinity Multi-Detector GPC/SEC System equipped with two PLgel 5 μm MIXED B columns ($M = 5 \times 10^2 - 1 \times 10^7$) using THF as the eluent at a flow rate of 1 mL/min at 40 °C. Samples taken directly from the polymerization mixture were analyzed. The number-average MWs were calculated using narrow dispersity PMMA standards. The MWs obtained using PMMA standards were recalculated using the universal calibration curve and the parameters values $k = 1.3 \times 10^{-4}$ dL g^{-1}, $\alpha = 0.688$ (PMMA) [S6] and $k = 1.395 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.786$ (polycaprolactone).[S7] [In the calculation of C_M for PS, MWs obtained using PMMA standards were recalculated using the equation $M_n(\text{PMMA}) = 0,644\ M_n^{1.019}(\text{PS})$. [S8]]

^1H NMR spectra were recorded on the Bruker Avance-400 spectrometer at ambient temperature. Chemical shifts are reported on the δ-scale in parts per million relative to the residual solvent peak ($CHCl_3$: δ_H 7.25) as internal standard.

Table 1. MW-characteristics of poly(MDO) obtained under various experimental conditions.

Initiator (I)	[I] (mol %)	Temperature (°C)	Conversion (%)	M_n (10^3)	M_w/M_n	Refs
Irgacure 184	0.25[a]	RT (UV)	32	23.9	1.4	S9
Irgacure 184	0.25[a]	RT (UV)	89	88.5	1.9	S9
Diethyl 2,2'-azobis(2-methylpropionate)	3	50	55	8.4	4	S10
	3	70	69	8.8	6	S10
AIBN	0.042	65		7.7	1.8	S3
AIBN	0.044	65		6.7	2.0	S3
AIBN	0.08	65		7.5	1.6	S3
AIBN	0.13	65		13.2	1.9	S3

AIBN	0.26	65		13.2	2.2	S3
AIBN	0.36	65		7.8	2.7	S3
AIBN	1.2	85	97	5		S11
AIBN	2	50	70	42	1.7	S12
AIBN	20	60	18	11	2.7	S13
DTBP	3	120	69	8.7	4	S10
DTBP	3	150	97	9.4	20	S10
DTBP	0.5-3	120	90	30-35	10-13	S14

[a] Concentration of radical initiator is indicated in wt %;

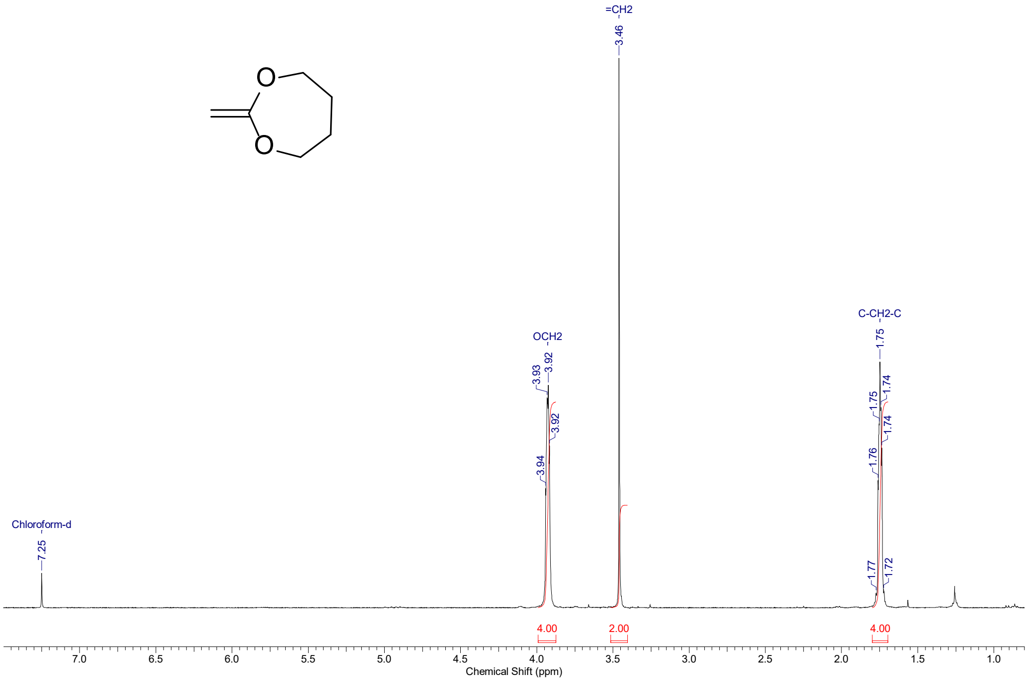

Figure 1. ^{1}H NMR spectrum of MDO with peak assignment.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.75 (m, 4H, C-CH_2-C), 3.46 (s, 2H, =CH_2), 3.931 (m, 4H, OCH_2).

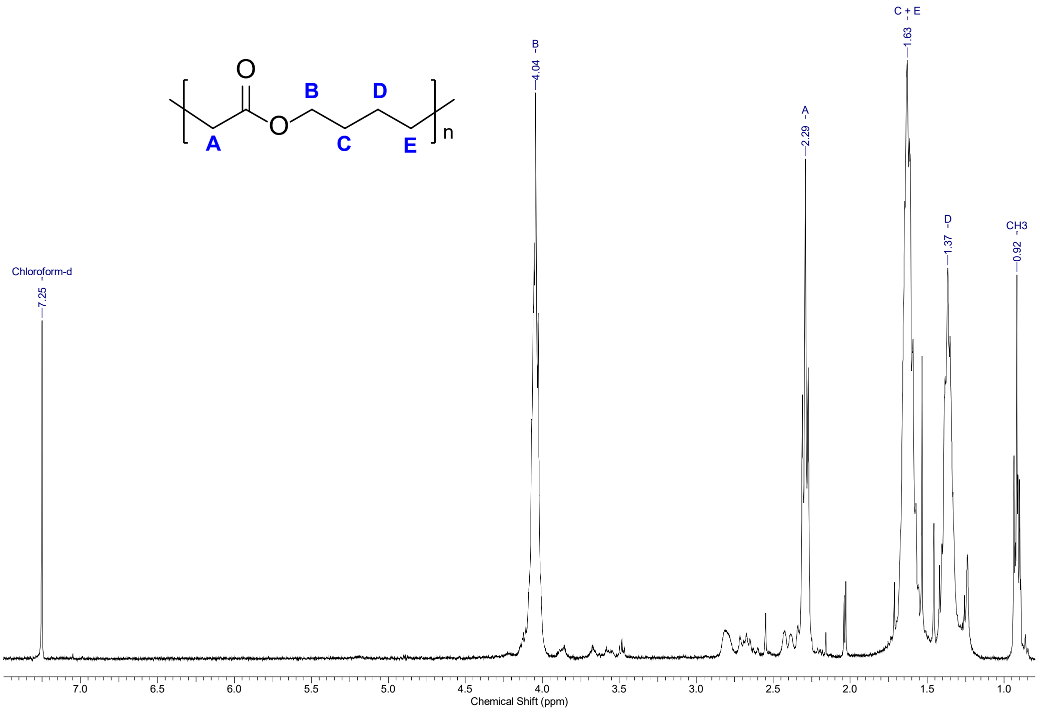

Figure S2. ^{1}H NMR spectrum of poly(MDO) ([AIBN] = 0.17 M, 70 ºC) with peak assignment. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, CH_3), 1.37 (m, 2H, $C(O)OCH_2CH_2CH_2$), 1.55–1.67 (m, 4H, $C(O)OCH_2CH_2$ and $CH_2CH_2C(O)O$), 2.29 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, $CH_2C(O)O$), 4.04 (m, 2H, $C(O)OCH_2$).

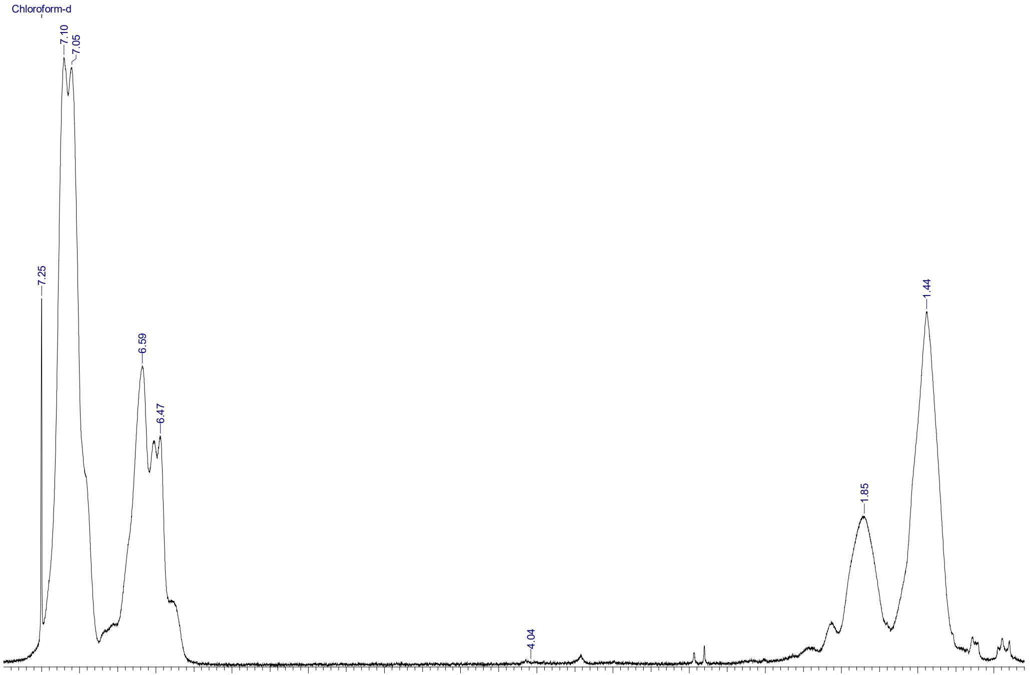

Figure S3. ^{1}H NMR spectrum for the "copolymer" of MDO and styrene at f_{MDO} = 0.25. The absence of a substantial signal around 4.04 ppm, corresponding to the methylene protons $C(O)OCH_2$ in the poly(MDO) structure, indicates the actual absence of MDO units in the main chain of the polymer.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19-1.68 (br. s, 2H, CH_2 (polystyrene)), 1.68-2.03 (br. s, 2H, CH (polystyrene)), 6.29-7.22 (br. m, 5H, CH_{Ph} (polystyrene)).

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