

Supporting Information

Observing Depolymerization of a RAFT Polymer by Time-Resolved Small-Angle X-ray Scattering

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Materials and Methods

Materials. Benzyl methacrylate (BzMA) was purchased from Tokyo Chemical Industry (Tokyo, Japan), 2-cyano-2-propyl benzodithioate was obtained from Sigma–Aldrich, Merck (Darmstadt, Germany), and *p*-xylene and 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65) were acquired from FUJIFILM Wako Pure Chemical (Osaka, Japan). BzMA was passed through a column filled with activated alumina to remove a polymerization inhibitor. The other materials were used without any purification.

Synthesis of PBzMA. BzMA (7.00 g, 39.7 mmol), V-65 (6.74 mg, 0.0271 mmol), 2-cyano-2-propyl benzodithioate (57.8 mg, 0.261 mmol), toluene (3.53 g), and a stirrer bar were placed into a brown glass vial with a rubber cap. After purging with nitrogen for 20 min, this solution was placed into an oil bath maintained at 56 °C and stirred for 4 hours. The reaction was stopped by cooling in an ice bath and exposure to air. The monomer conversion was 53%, as determined by ¹H NMR spectroscopy. The product was poured into a water–methanol mixture (1 to 9 volume ratio), and the precipitate was recovered by filtration. Water and methanol were then removed under vacuum at *ca.* 25 °C. This precipitation process was repeated three times.

SAXS measurements. Small-angle X-ray scattering (SAXS) measurements were conducted in the BL40B2 beamline at SPring-8 (Sayo, Japan). We used a PILATUS 2M detector (Dectris, Baden, Switzerland) with a sample-to-detector distance of 4.2 m. PBzMA was dissolved in *p*-xylene in a brown glass vial sealed with a rubber septum. Unless otherwise stated, nitrogen purging was performed to remove oxygen. A 30 μL aliquot of the solution was loaded into a quartz capillary (diameter ~ 2.0 mm, wall thickness ~ 0.01 mm) and sealed with a double layer of epoxy resin (first layer) and silicone resin (second layer) inside a nitrogen-filled glovebox. The capillary was then

placed in a thermostat on the beamline, which was set to 120 °C to initiate depolymerization; the target temperature was reached within *ca.* 1.5 min. X-ray exposures were repeated with a wavelength of 0.1 nm, a photon flux of 7×10^9 photons/s, and an exposure time of 180 s each. The resulting two-dimensional scattering patterns were azimuthally averaged, and the background scattering from the cell and *p*-xylene was subtracted. The intensity and scattering angle were calibrated by standard samples (water and silver behenate, respectively).

The weight-average molecular weight (M_w) and z-average radius of gyration ($R_{g,z}$) were obtained from Berry plots with the following equation:^{S1}

$$\sqrt{\frac{K_e c}{I(q)}} = \frac{1}{\sqrt{M_w}} \left[1 + \frac{1}{6} R_{g,z}^2 q^2 + O(q^4) \right] \quad (S1)$$

where $O(x)$ is the Landau symbol, and K_e is a constant regarding the X-ray contrast, defined as^{S2}

$$K_e = N_A r_e^2 \left(\frac{n_e}{M_1} - \bar{v} \rho_{\text{solv}} \frac{n_{e,\text{solv}}}{M_{\text{solv}}} \right)^2 \quad (S2)$$

where N_A stands for the Avogadro's constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), r_e is the classical electron radius ($2.818 \times 10^{-13} \text{ cm}$), n_e and M_1 are the number of electrons (94) and the molar mass (176.2 g/mol) of the monomer unit, respectively, and $n_{e,\text{solv}}$ and M_{solv} are the number of electrons (58) and the molar mass (106.2 g/mol) of the solvent, respectively. \bar{v} denotes the partial specific volume of the polymer, and ρ_{solv} represents the mass density of the solvent. A high-precision density meter (DMA 4500 M, Anton Paar, Graz, Austria) was used to determine the \bar{v} and ρ_{solv} values. The densitometry was performed for the PBzMA/*p*-xylene solutions at various concentrations and pure *p*-xylene at 25, 80, 90, and 100 °C, and the values at 120 °C were estimated by the extrapolation, since the highest temperature for this density meter is 100 °C. The reason we did not measure directly at

120 °C is that the density meter, like other similar instruments, has a maximum operation temperature of 100 °C. The parameters for calculating K_e are listed in Table S1.

Table S1. Parameters for Calculating K_e

Temperature / °C	$\rho_{\text{solv}} / \text{g cm}^{-3}$	$\bar{v} / \text{cm}^3 \text{g}^{-1}{}^a$	$K_e / \text{mol cm}^2 \text{g}^{-2}$
25	0.857	0.830	1.01×10^{-3}
80	0.808	0.849	-
90	0.799	0.852	-
100	0.790	0.854	-
120	0.771 ^a	0.860 ^a	1.40×10^{-3}

^aExtrapolated values.

¹H NMR spectroscopy. The PBzMA/*p*-xylene solution was divided into five brown glass vessels with rubber caps. After purging with nitrogen, four vessels were simultaneously placed in an oil bath set to 120 °C. The remaining vessel was designated as the initial state ($t = 0$). The four heated vessels were sequentially taken off, placed in an ice bath, and exposed to air. Approximately 90% of the xylene was then evaporated off, and dimethyl sulfoxide (DMSO)-d₆ was added for the NMR measurements, where the solute concentration was about 0.1 wt%. The ¹H NMR measurements were done using a ECA 400 or ECA600 spectrometer (JEOL, Akishima, Japan) at 25 °C.

Computations. The models of scattering functions and the kinetic models were calculated by Microsoft Excel 16.90. When numerically solving the differential equations (eqs 4–6), the results tended to diverge or oscillate near the equilibrium state. To prevent this instability, smoothing of the molecular weight distribution function was employed by

averaging the neighbouring data points at each time step in the late stage (near equilibrium). The effects of smoothing on the calculated M_w and $R_{g,z}$ values of asymptotic behaviors were imperceptible.

Molecular Characteristics of PBzMA (Initial State)

The ^1H NMR spectrum for the purified PBzMA in DMSO- d_6 is shown in Figure S1; the monomer content was less than 1%.

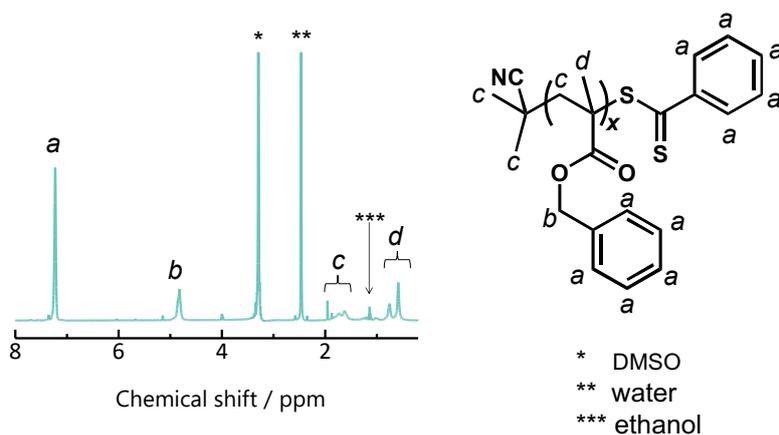


Figure S1. ^1H NMR spectrum for PBzMA (initial state) in DMSO- d_6 .

Size-exclusion chromatography (SEC) was conducted using a Prominence system (Shimadzu, Kyoto, Japan) equipped with two columns in series (GF-7M HQ, Shodex, Showa Denko, Tokyo, Japan) and a refractive index detector (RID-20A). *N,N*-dimethyl formamide containing 0.2 M LiBr was used as the eluent at a flow rate of 0.5 mL/min. The temperature around the columns and the detector was 40 °C. Standard samples of poly(methyl methacrylate) (Agilent Technologies, Santa Clara, CA) were used for calibration. The results were fitted by a log-normal distribution, expressed as^{S3}

$$w dM = \frac{1}{\sqrt{\pi}} \exp(-y^2) dy \quad (\text{S3})$$

with

$$y \equiv \left[\frac{\ln(M/\sqrt{M_w M_n})}{2 \ln(M_w/M_n)} \right]^2 \quad (\text{S4})$$

Here, w denotes the weight fraction, M is the molecular weight, and M_w and M_n are the weight- and number-average molecular weight, respectively. The SEC result with the fitted curve, showing $D (= M_w/M_n)$ of 1.12, is represented in Figure S2.

In addition, the SAXS measurements were performed at 25 °C for PBzMA in *p*-xylene. M_w was determined from the Berry plot (Figure S3) with eqs S1 and S2.

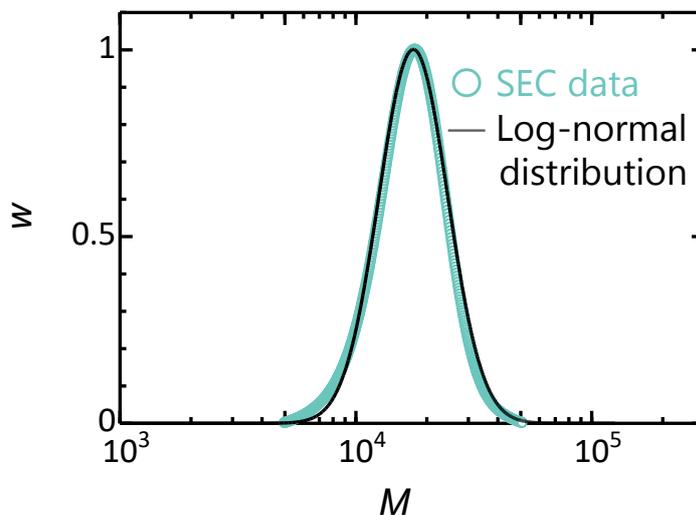


Figure S2. SEC data as the weight fraction (w) plotted against the molecular weight (M). The circles and solid curve represent the experimentally obtained data and the calculated value of the log-normal distribution with $D = 1.12$. Please note that M represents the relative molecular weight here.

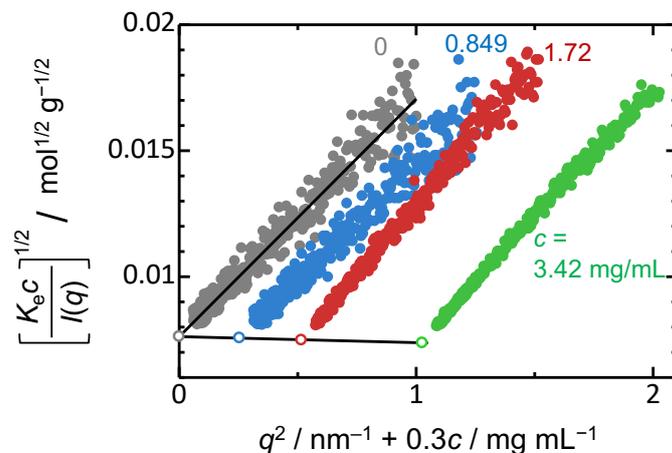


Figure S3. Berry plot for PBzMA in *p*-xylene at 25 °C. The blue, red and green symbols represent the data for $c = 0.849$, 1.72 , and 3.42 mg/mL, respectively. The grey symbols indicate the extrapolated values as c becomes zero at each q . The unfilled symbols represent the extrapolated values as q becomes zero at each c .

The livingness or end-group fidelity (L) was calculated by^{S4}

$$L = \frac{[\text{CTA}]}{[\text{CTA}] + 2f[\text{I}](1 - e^{-k_1 t}) \left(1 - \frac{f_c}{2}\right)} \quad (\text{S5})$$

where $[\text{CTA}]$ denotes the initial molar concentration of CTA, $[\text{I}]$ is the initial concentration of the initiator, f represents the efficiency of the initiator (set to 0.5, typical for diazo-type initiators), and f_c is the coupling factor (0 for the termination solely by disproportionation and 1 for the termination solely by combination). k_1 is the rate constant of the initiator's decomposition. The k_1 value was calculated to be 0.00224 min^{-1} from the nominal value of the 10-hour half-life temperature (51 °C) and the activation energy (117.8 kJ/mol) for V-65 in toluene. Therefore, L was estimated to range from 96% ($f_c = 0$) to 98% ($f_c = 1$). These results are summarised in Table S2.

Table S2. Molecular Characteristics of PBzMA Used in this Study

$M_w / 10^3$ ^a	x_w ^b	$M_n / 10^3$ ^c	x_n ^d	\bar{D} ^e	$L / \%$ ^f
17.2	97.7	15 ^g (14 ^h)	87 ^g (81 ^h)	1.12	96–98

^aWeight-average molecular weight determined by SAXS. ^bWeight-average degree of polymerization calculated by M_w/M_1 with $M_w = 1.721 \times 10^4$ and M_1 denoting the molecular weight of the monomer (= 176.2). ^cNumber-average molecular weight. ^dNumber-average degree of polymerization. ^eDispersity index (= M_w/M_n) determined by SEC. ^fLivingness calculated by eq S4. ^gCalculated by M_w/\bar{D} or x_w/\bar{D} . ^hCalculated from the monomer conversion, determined by ¹H NMR (before purification).

Models of the Scattering Form Factor

To fit the SAXS profile at 5.17 min, we used the Gaussian chain model:

$$\frac{I(q)}{I(0)} = \frac{2[\text{Exp}(-q^2 R_g^2) - 1 + q^2 R_g^2]}{q^4 R_g^4} \exp\left(-\frac{q^2 d^2}{16}\right) \quad (\text{S6})$$

where d denotes the cross-sectional diameter. Regarding the fitting at $t = 45.7$ min, a coexistence model was used, which is expressed as

$$\begin{aligned} \frac{I(q)}{I(0)} = & (1 - z) \frac{2[\text{Exp}(-q^2 R_g^2) - 1 + q^2 R_g^2]}{q^4 R_g^4} \exp\left(-\frac{q^2 d^2}{16}\right) \\ & + z \frac{2[\text{Exp}(-q^2 R_{g,s}^2) - 1 + q^2 R_{g,s}^2]}{q^4 R_{g,s}^4} \exp\left(-\frac{q^2 d^2}{16}\right) \quad (\text{S7}) \end{aligned}$$

Here, the first and second terms on the right-hand side correspond to the original and the smaller components, respectively. $R_{g,s}$ represents the radius of gyration of the smaller component, and z represents the fraction of the smaller component. The parameters obtained are summarized in Table S3.

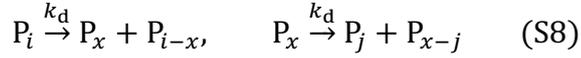
Table S3. Parameters Obtained in the Fitting of the Form Factor

	R_g / nm	d / nm	$R_{g,s} / \text{nm}$	z
$t = 5.17 \text{ min}$	3 ± 0.05	1 ± 0.1	-	-
$t = 45.7 \text{ min}$	3^a	1^a	1.2 ± 0.5	0.035 ± 0.01

^aAssumed values

Kinetic Model of the Random Scission

The kinetics of the random scission may be expressed as^{S5}



Eq 3 in the main text was also considered, but the reverse reactions of eq S8 were not taken into account for simplicity. Thus, we have

$$\frac{dC_x}{dt} = k_d \sum_{i=x+1}^{\infty} C_i - (x-1)k_d C_x - \tilde{k}C_x \quad (x \geq 2) \quad (\text{S9})$$

$$\frac{dC_1}{dt} = k_d \sum_{i=2}^{\infty} C_i \quad (x = 1) \quad (\text{S10})$$

and eq 6. These differential equations were solved numerically to obtain M_w and $R_{g,z}$ at each time point (Figure S7).

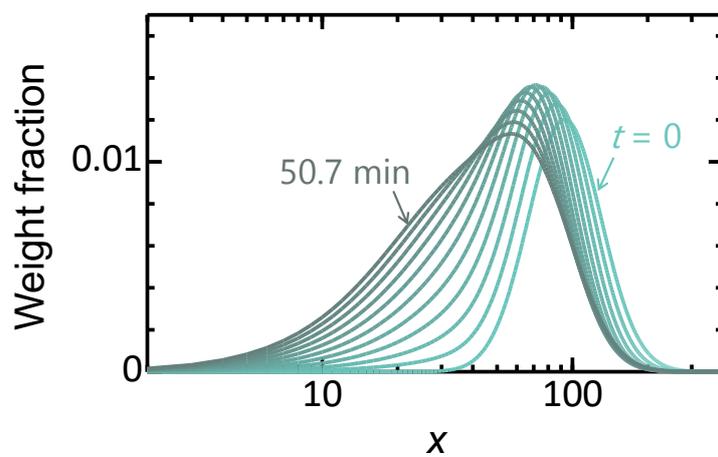


Figure S4. Calculation results of the random scission model as the distribution function of x , including the living and dead chains.

Supplementary figures

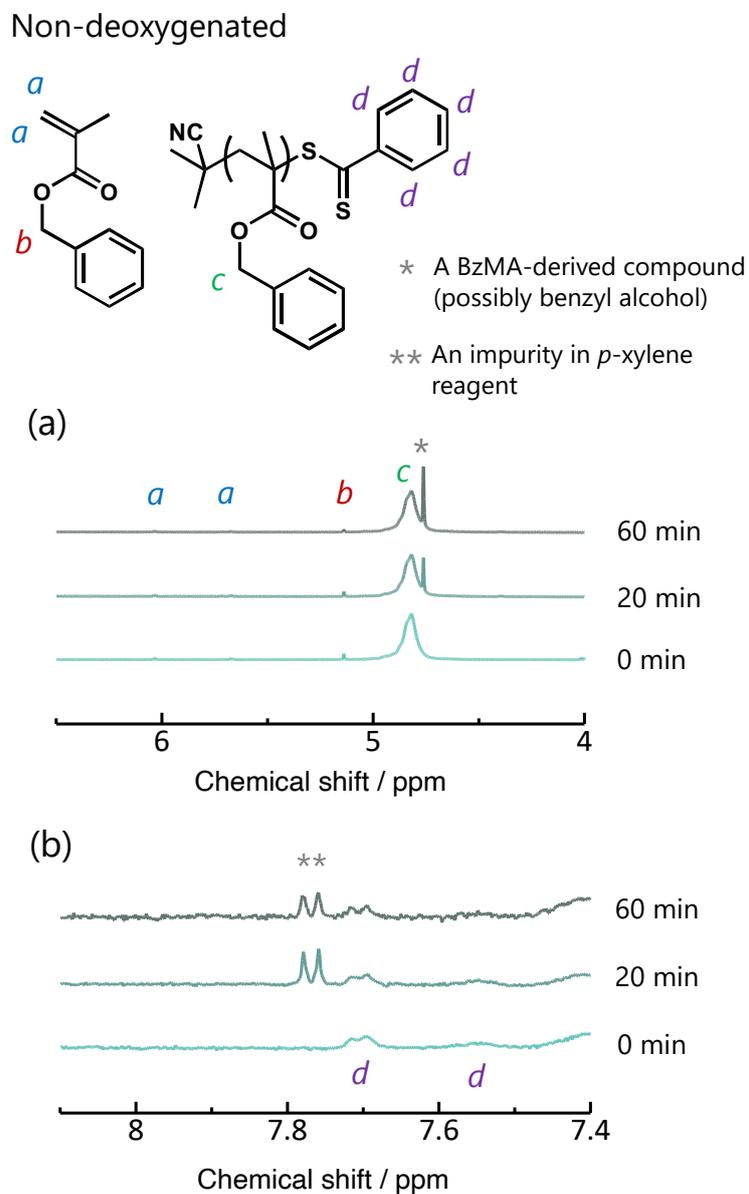


Figure S5. Time-evolution of the ^1H NMR spectrum for non-deoxygenated PBzMA at the chemical shift range of 6.5 to 4 ppm (a) and 8.1 to 7.4 ppm (b). The depolymerization was performed in *p*-xylene at $c = 0.2\text{wt}\%$, and the ^1H NMR measurements were carried out in DMSO- d_6 .

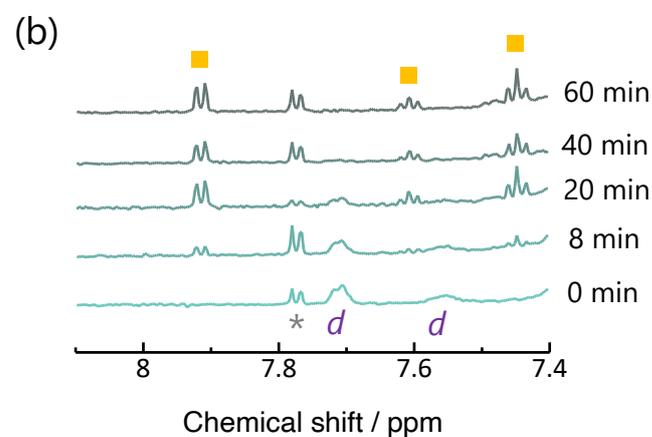
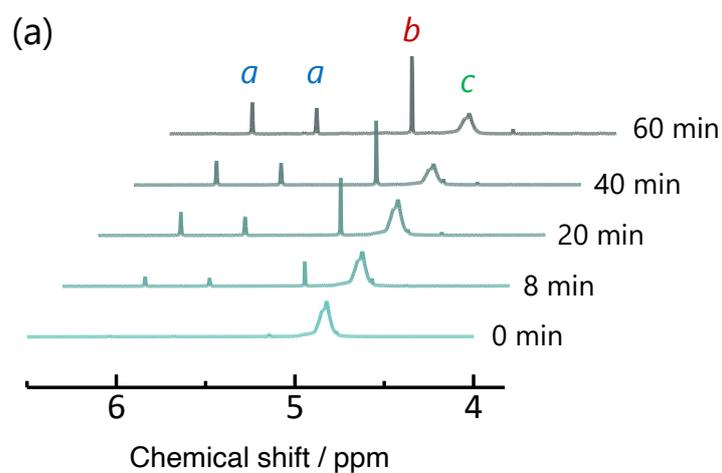
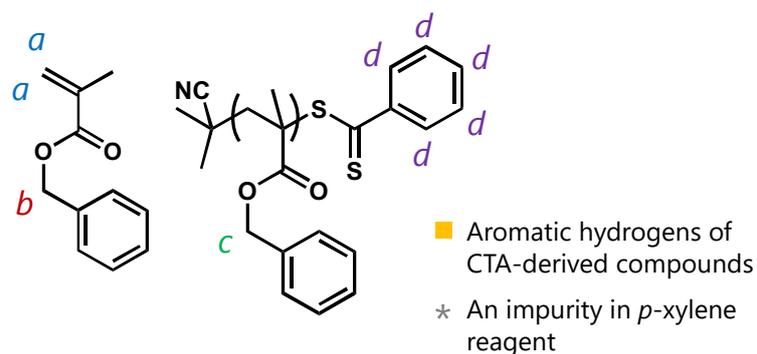


Figure S6. Time-evolution of the ^1H NMR spectrum for deoxygenated PBzMA at the chemical shift range of 6.5 to 4 ppm (a) and 8.1 to 7.4 ppm (b). The depolymerization was performed in *p*-xylylene at $c = 0.2\text{wt}\%$, and the ^1H NMR measurements were carried out in DMSO- d_6 .

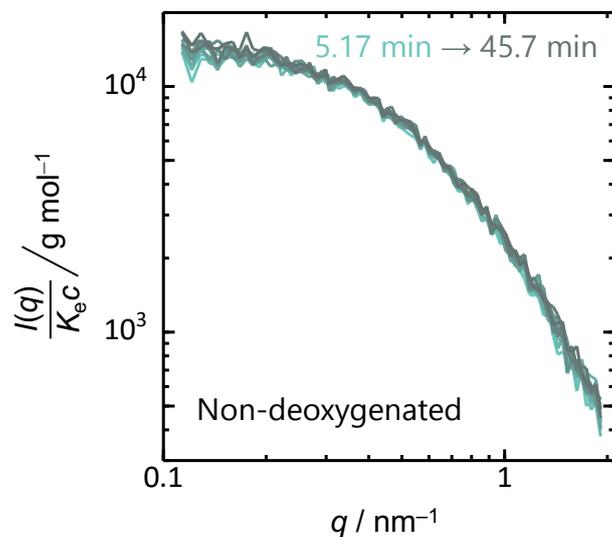


Figure S7. Effect of deoxygenation: Time evolution of the SAXS profiles of PBzMA in *p*-xylene, where the solution was not deoxygenated, at $c = 0.1$ wt% at 120 °C.

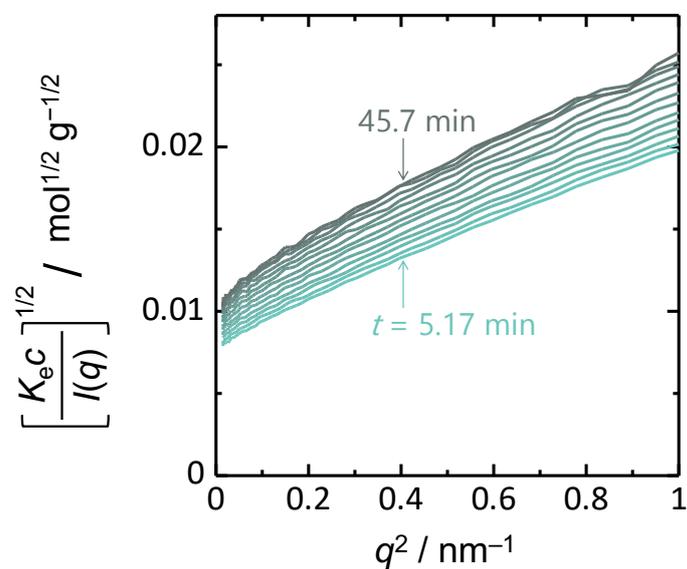


Figure S8. Berry plots during the depolymerization of PBzMA in *p*-xylene at $c = 0.1$ wt% at 120 °C.

References

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