

Dodecyl Methacrylate Polymerization under Nanoconfinement: Reactivity and Resulting Properties

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ABSTRACT: The effect of nanoconfinement on the free radical polymerization of dodecyl methacrylate (DMA) with di-*tert*-butyl peroxide (DtBP) initiator is investigated over a wide temperature range from 110 to 190 °C using differential scanning calorimetry. The reaction shows a distinct induction time, which decreases as temperature increases, with an activation energy that is the same, albeit, of opposite sign, as that for dissociation of the initiator. The rate of reaction increases with increasing temperature and is higher in nanopores than in bulk conditions, with an Arrhenius temperature dependence at temperatures lower than 160 °C and an activation energy that is approximately 10% lower in the nanoconfined cases than for bulk. The higher reaction rate and lower activation energies in the nanopores are presumably due to specific interactions between the monomer and the native silanol groups on the pore surface. The enhancement of the reaction rate is found to be inversely related to the length of the alkyl group and the water contact angle compared data for several poly(*n*-alkyl methacrylate) studied previously. For bulk and nanoconfined DMA polymerizations, the



molar mass increases as temperature decreases with a cross-linked product obtained at temperatures below 170 $^{\circ}$ C. The gel fraction increases as temperature decreases and is nearly 80% at 110 $^{\circ}$ C. In the nanopores, the molar mass is smaller compared to that in bulk conditions at high temperatures. The results can be described by a simplified recursive model.

1. INTRODUCTION

Nanoconfinement is known to affect the reaction kinetics, thermodynamics, and resulting properties of polymerizations, including molar mass and polydispersity. In previous work from our laboratory, 1-7 nanoconfined polymerization of *n*-alkyl methacrylates was performed in controlled pore glasses (CPGs) for methyl-, ethyl-, and butyl-methacrylates. Nanoconfinement was found to increase the initial reaction rates and to decrease the apparent activation energy, with effects particularly strong in native or unfunctionalized CPG due to interaction between the monomer and the silanol groups on the pore surface. In addition, autoacceleration was found to occur at shorter times and at lower conversions for the nanoconfined alkyl methacrylate polymerizations, presumably due to a decrease in the rate of termination arising from decreased diffusivity under nanoconfinement.^{1,2} For the case of poly(methyl methacrylate), the polymer synthesized under nanoconfinement displays an increase in molar mass and a decrease in dispersity (D) relative to the polymer synthesized in bulk.^{4,7,8} Similar behavior has been observed for the nanoconfined free radical polymerization of styrene,9 vinyl esters,¹⁰ and ε -caprolactone¹¹ monomers.

The effect of synthesis under nanoconfinement on the molar mass for longer *n*-alkyl methacrylate monomers is not as straightforward, however. In the particular case of *n*-dodecyl methacrylate, chain transfer to the polymer during the bulk polymerization leads to branching and cross-linked products, 12-15 and if such products are suppressed under

nanoconfinement, as is the case for vinyl esters in metallic organic frameworks¹⁰ and for ε -caprolactone in aluminum oxide membranes,¹¹ one might expect a decrease in molar mass for polymer synthesized under nanoconfinement. In addition to promoting chain transfer to polymer, the long alkyl side chain in the dodecyl methacrylate monomer leads to a suppression of autoacceleration,^{12,13} an increase in the propagation rate constant,^{16–18} a decrease in the rate of termination,¹⁹ and a propensity of the dodecyl groups in the polymer to crystallize.²⁰

The purpose of this work is to investigate the nanoconfined polymerization of dodecyl methacrylate in controlled pore glass over a broad temperature range by differential scanning calorimetry (DSC) to understand the influence of the long alkyl chain. In particular, we are interested in how nanoconfinement influences polymerization kinetics, including autoacceleration, induction, and chain transfer, as well as the molar mass of the synthesized polymer.

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2. EXPERIMENTAL METHODOLOGY

Disclaimer: Certain equipment, instruments, or materials are identified in this paper to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.

2.1. Materials. Dodecyl methacrylate monomer (Sigma-Aldrich, containing 500 ppm (mg/kg) 4-methoxyphenol (MEHQ) as inhibitor, 96%) was purified with a prepacked column (Sigma-Aldrich, No. 306312) to remove the inhibitor, and then was mixed with 0.5% by mass di-*tert*-butyl peroxide (DTBP, Sigma-Aldrich, 98%) initiator at room temperature to form a homogeneous solution. The premixed solutions were stored in a freezer at -20 °C with a desiccant prior to use. Less than 1% conversion accumulated during mixing and after two months of storage according to a calculation based on the reaction model.

Controlled pore glasses (CPGs, Millipore) with diameter *D* of (8.1 \pm 0.7) and (50 \pm 1.9) nm were used as the confinement media. We choose these two pore sizes with native silanol groups because in previous work,¹ we found that the initial rate varied as 1/D in native pores with little effect at 100 nm; hence, the use of the smaller 8 and 50 nm diameter pores; in addition, we used native pores because we were interested in the influence on the initial reaction rate, and that rate was unchanged in previous work on other alkyl methacrylate monomers when the native silanol was replaced by trimethylsilyl. The CPGs consisted of nanoporous borosilicate particles and have been shown to be stable with organic liquids.^{21,22} The specifications of CPGs are listed in Table 1. The pores were cleaned prior to use,

Table 1. Specifications of CPGs, as Provided by the Manufacturer

product name	mean pore diameter (nm)	pore diameter distribution (%)	specific pore volume (cm ³ /g)	specific surface area (m²/g)
CPG75C	8.1 ^{<i>a</i>}	9.0	0.49	197
CPG00500B	50.0	3.7	1.10	51

^aCPG75C is the catalogue number for the 8.1 nm diameter CPG product, and for this reason, it was erroneously referred to as having 7.5 nm diameter pores in reference 7, Figure 5.

following the procedures from Jackson and McKenna²³ using nitric acid (Mallinckrodt Chemicals, 68 to 70% by mass) at 110 °C, and then rinsed with deionized water (Barnstead Nanopure Infinity System, by Thermo Scientific) until neutral pH, followed by drying under vacuum (740 mm Hg) at 285 °C for 24 h. The CPGs were stored under the desiccant prior to use to minimize the effect of moisture.

The CPG was filled with monomer/initiator solution by imbibement, which occurs in seconds due to the capillary forces. In this procedure, the CPG was first placed at the bottom of a 20 μ L hermetic DSC pan under a nitrogen blanket pan. Then, a prespecified volume of the monomer/initiator solution was added on top using a syringe such that the pore fullness (volume fraction of pores filled with monomer) ranged from 70 to 95% based on the ratio of the volume of monomer added relative to the pore volume, the latter being obtained from the CPG manufacturer's specification. There was no monomer or resin outside of the CPG based on inspection of the sample after reaction; in other words, the CPG was still free-flowing, and there were no fused or aggregated CPG particles; hence, complete imbibement of the monomer into the CGP occurred. It is also noted that the monomer/initiator solution is anticipated to fill the CPG pores as a plug, as discussed by Jackson and McKenna²⁴ for the case of nonwetting liquids, such as dodecyl methacrylate in native pores, and hence, there should be no influence on pore fullness on the measurements. In prior work for the CPG-nanoconfined polymerization of cyanate ester, pore fullness was indeed found to not influence either T_g values or trimerization reaction kinetics.^{25,2}

2.2. DSC Measurements. A Mettler Toledo DSC 1 with an ethylene glycol cooling system and nitrogen purge gas were used to study the polymerization kinetics. Indium and the liquid crystal, (+)-4-*n*-hexylophenyl-40-(20-methylbutyl)-biphenyl-4-carboxylate (CE-3), were used to calibrate the DSC temperature at 10 K/min, and enthalpy was calibrated using only indium. An isothermal calibration²⁷ was performed with indium at 0.1 K/min for isothermal conditions. An indium check was performed daily to minimize systematic errors.

The polymerization reaction was carried out in 20 μ L hermetic pans under isothermal temperatures ranging from 110 to 190 °C. Although reactions were performed at lower temperatures in previous work in our laboratory^{1,6} for AIBN-initiated MMA polymerization and for DTBP-initiated EMA and BMA polymerizations, the induction times for the DTBP-initiated DMA polymerizations carried out in the present work are longer (as shown later), and as a consequence, the lowest reaction temperature examined is 110 °C; at this temperature, the reactions are run for as long as 10 h.

Repeat runs were made for most reaction temperatures for the reaction kinetics; the raw data is shown in the Supporting Information. After the isothermal run to determine the reaction kinetics, a dynamic scan of 10 K/min was performed on selected samples to check for residual heat, which was zero in all cases. Less than 1% mass loss was observed based on measurements of the sample mass before and after runs.

2.3. Gel Permeation Chromatography (GPC). The polymer products from some of the nanoconfined DSC reaction samples were extracted from the CPG beads by immersion in high-performance liquid chromatography (HPLC)-grade tetrahydrofuran (THF) for 48 h, and then the CPG was filtered out with a Nylon Millex syringe filter (0.20 μ m pore size, 13 mm diameter, Millex-GN Nylon membrane, hydrophilic), as in previous published work.⁴ The molar mass data for the samples synthesized in bulk and most of those synthesized in 8 nm pores (i.e., all samples at 120, 160, 170, 190 °C and one sample each at 175 and 180 °C) were obtained on a Tosoh EcoSEC system with differential refractive index (RI) detection coupled to a Wyatt DAWN Heleos II multiangle light scattering detector (18°), and a Wyatt Visco Star III differential viscometer THF was used as mobile phase at 35 °C, and the stationary phase was a set of two Tosoh mixed pore columns (2× TSKgel GMHHR-H). Data were collected using Astra 7, and molar masses were determined using light scattering data with a Zimm plot method,²⁸ and secondary calibrations were checked with poly(methyl methacrylate). The calibrated results from PMMA standards yielded errors of less than 5% in molar mass. The differential refractive index increment (dn/dc) values were measured from offline batch injections. The molar mass data for samples synthesized in 50 nm pores and the rest of those for 8 nm pores were characterized using Tosoh HLC-8320GPC with TSKgel SuperH-H and two TSKgel SuperHM-H columns coupled with a refraction index (RI) detector. The calibration results used PMMA standards, and errors were less than 4% in molar mass. Reproducibility between the two instruments was checked at two reaction temperatures, resulting in an average difference in logarithmic molar mass of 5% and a maximum difference of 10%.

2.4. Gel Fraction Determination and Thermogravimetric Analysis (TGA). After extraction of the soluble portion of the reaction product, thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA2 under nitrogen purge to determine the gel fraction, if any, in the samples synthesized under nanoconfinement. A given sample was first dried at 160 °C for 1 h in the TGA to ensure complete removal of the solvent used for extraction, and then a TGA run was performed from 100 to 500 °C at 10 K/min to determine the amount of polymer remaining in the CPG. This amount was attributed to cross-linked polymer. For the bulk samples, after reaction, the soluble portion of the sample was extracted by immersion in HPLC-grade tetrahydrofuran (THF) for 48 h, and then the remaining insoluble portion was collected by filtration and dried to determine the gel fraction.

3. RESULTS

Conversion (x) vs time (t) data during the isothermal polymerization are obtained by integrating the DSC heat flow (\dot{Q})

$$x = \frac{1}{\Delta H_{\rm p}} \int_{t_0}^t \dot{Q} \,\mathrm{d}t \tag{1}$$

where the enthalpy of reaction ΔH_p is found to be (222 ± 8) J/g from bulk polymerization at 110 °C, in good agreement with literature value²⁰ of (217.2 ± 3) J/g. Representative data for three polymerization temperatures are shown in Figure 1



Figure 1. Conversion versus time of isothermal polymerization for representative bulk and nanoconfined samples at three reaction temperatures. The solid line represents samples reacted in bulk condition, the dotted line represents samples reacted in 50 nm pores, and the dashed line represents samples reacted in 8 nm pores.

for both bulk and nanoconfined samples as a function of time after subtracting the induction time (t_{ind}) , which is obtained from the intersection of the DSC baseline and a linear fit through the heat flow at the initial stage of the reaction. Before further analyzing the data in Figure 1, we note that the induction time is independent of confinement and decreases as temperature increases, as shown in an Arrhenius plot in Figure 2 with an activation energy of (-147 ± 3) kJ/mol. Also shown in the inset of Figure 2 is a typical heating scan from which the induction time can be clearly identified. The activation energy obtained from the temperature dependence of the induction time is identical to the reported value of the activation energy



Figure 2. Natural logarithm of the induction time vs reciprocal temperature. The line is the best Arrhenius fit through all of the data. The inset shows a typical run for the bulk sample at 110 $^{\circ}$ C showing the induction time at approximately 20,000 s.

for dissociation of the DTBP initiator (147 kJ/mol),²³ albeit with the opposite sign. Thus, the time scale of induction is inversely related to the rate constant for initiator dissociation. This relationship can be rationalized by noting that the length of the induction phase depends on the concentration of adventitious radical scavengers, such as oxygen, that are initially present in the monomer/initiator solution, as well as the time that it takes for these to be consumed. The concentration of radical scavengers initially present may be considered to be independent of confinement size and to depend on the solubility of, for example, oxygen in the solution, whereas the time scale of consumption is proportional to the time scale for initiator dissociation, which is reciprocally proportional to the rate constant for dissociation. Thus, the time scale of induction (t_{ind}) is inversely related to $k_{\rm d}^{29}$

$$t_{\rm ind} = [A]_{\rm o}/2fk_{\rm d}[I]_{\rm o} \tag{2}$$

where $[A]_{o}$ and $[I]_{o}$ are the initial concentrations of radical scavengers and initiator in the solution. In the case where the initiator dissociation rate constant k_{d} and initiator efficiency f are unaffected by confinement, the apparent activation energy for induction is expected to be the negative of the activation energy for initiator dissociation $(-E_{d})$, as is found here.

The initial reaction rate, indicated by the initial slope (dx/dt) of the conversion versus time curves in Figure 1, increases with increasing temperature, as expected. Autoacceleration, which is observed as a dramatic increase in slope at intermediate conversions in the case of methyl methacrylate polymerization,¹ is almost entirely suppressed for the dodecyl methacrylate monomer with only subtle increases in the slope (of between 20–90%) at around 40% conversion at 120 °C for bulk and nanoconfined samples. Even at 110 °C, which is the lowest temperature studied, the increase in the rate at the onset of autoacceleration was a maximum of only $(125 \pm 12)\%$ for the sample in 8 nm CPG. The suppression of autoacceleration in DMA is consistent with reports in the literature, although the origin of the phenomenon is under debate. Vizovišek and co-workers³⁰ attribute it to the ease of rotation of the PDMA chain, which causes a delay in the onset of autoacceleration and its suppression, whereas Borsig and co-workers¹³ attribute it to the presence of chain transfer from the growing radical to the alkyl group of the ester. Nevertheless, the fact that autoacceleration is weak in PDMA polymerization suggests that the effects of chain diffusion in this polymerization are not very significant; furthermore, the fact that there is little effect of confinement on autoacceleration suggests that chain diffusion is not significantly affected by the confinement conditions used here. This is very different from the polymerization of methyl-, ethyl-, and butyl-methacrylates where autoacceleration and chain diffusion effects are enhanced in confinement.^{1,c}

The influence of nanoconfinement on the reaction rate can also be observed in Figure 1. The effective rate is highest in the nanopores and lowest in the bulk condition at temperatures lower than 140 °C, but the increase in rate under nanoconfinement is considerably less pronounced for dodecyl methacrylate than was observed for methyl-, ethyl-, and butylmethacrylates.^{1,6} Similar to our previous work,^{1,6} we suggest that the increase in rate under nanoconfinement is due to specific interactions between the monomer and the native silanol groups on the pore surface. The effective initial rate constants can be obtained from the conversion versus time data, considering both propagation and depropagation reactions $^{\rm 6}$

$$-\ln(x_{\infty} - x) = k_{\text{eff}}t \tag{3}$$

where x_{∞} is the conversion at equilibrium, k_{eff} is the effective rate constant, which, in the absence of autoacceleration and transfer reactions and at the initial stage of reaction, is equal to

$$k_{\rm eff} = k_{\rm p} \left(\frac{fk_{\rm d}}{k_{\rm t}} [I]_0 \right)^{1/2} \tag{4}$$

where k_p , k_d , and k_t are the specific reaction rate constants for propagation, initiator dissociation, and termination, respectively, *f* is the initiator efficiency, and $[I]_0$ is the initial initiator concentration. For all of the temperatures studied, the firstorder model fits the data well at low conversions, from 5 to 10%. The reaction is kinetically controlled in this conversion range, as was validated in our previous study for BMA;⁶ in addition, the rate of free radical generation was calculated based on the initiator dissociation rate constant and activation energy in the literature²⁹ and found to decrease by less than 7% relative to the initial rate at 10% conversion for reaction at 160 °C and to decrease less than 29% at 190 °C, thus indicating sufficient initiator to maintain first-order kinetics over the conversion range used to perform the analysis.

The influence of nanoconfinement on the effective reaction rate (k_{eff}) is shown versus reciprocal absolute temperature in Figure 3, with the standard deviation in k_{eff} estimated to be



Figure 3. Natural logarithm of the effective reaction rate constant at the initial stages of the reaction vs reciprocal absolute temperature for bulk and nanoconfined DMA. Black circles represent samples reacted in the bulk condition, blue squares are samples reacted in 50 nm pores, and red diamonds are samples reacted in 8 nm pores. The lines are Arrhenius fits up to 140 °C, with the solid line representing the bulk, the dotted line representing samples in 50 nm pores, and the dashed line representing samples in 8 nm pores. View in color for best clarity.

10% based on results where three or more runs were made. The effective rate constants show an Arrhenius temperature dependence at temperatures lower than 160 °C, with the apparent activation energy E_{app} of the bulk being (95 ± 3) kJ/mol and that in 50 and 8 nm pores being approximately 10% lower at (84 ± 6) and (86 ± 5) kJ/mol, respectively. The higher rate and lower activation energy under nanoconfinement is attributed to interactions between the methacrylate group on the DMA monomer and the silanol groups on the pore surface as was observed for MMA, EMA, and BMA

polymerization in native pores,^{1,6} although the interactions are presumed to be weaker for DMA due to its higher hydrophobicity. This suggestion is backed up by a correlation between the acceleration of the reaction rate over the bulk as a function of alkyl chain length and water contact angle on the corresponding polymer (PEMA, PBMA, and PDMA), as shown in Figure 4, where the ratio k_{nano}/k_{bulk} for DTBP-



Figure 4. Ratio of the effective rate constant at the initial stages of the reaction in 8 nm nanoconfined and in bulk *n*-alkyl methacrylate polymerizations, $k_{\text{nano}}/k_{\text{bulk}}$, versus the water contact angle on the poly(*n*-alkyl methacrylate) at 120 and 140 °C (black circles and red squares, respectively). The data for ethyl- and butyl-methacrylate DTBP-initiated polymerization in 8 nm native pores are taken from ref 6, and the data for the water contact angle is taken from ref 31. Error bars are assumed to be 10% of the value based on measurements where multiple runs were made.

initiated polymerizations at 120 and 140 °C are found to decrease approximately linearly with increasing water contact angle, with the latter taken from the literature.³¹ It is noted that the water contact angle on n-alkyl methacrylates increases approximately linearly with increasing length of the *n*-alkyl chain to an alkyl length of 14, and a similar trend was found for the contact angle of water on n-alkyl functionalized diatomaceous earth.³² Hence, as the length of the alkyl group increases, the hydrophobicity also increases, resulting presumably in a decrease in the interaction between the native silanol groups and the methacrylate moiety of the monomer, which is speculated to involve >C=O...HO-Si-, an interaction observed by Achilias and Siafaca³³ in an investigation of 2hydroxyethyl methacrylate polymerization with nanosilica particles, where interestingly, nanosilica reduced the reaction rate presumably due to interruption of the hydrogen bonding between monomers (which does not occur in our system). In our PDMA polymerization, how the silanol group enhances the reaction rate is unknown, although earlier work by O'Driscoll and co-workers attributed an increase in the effective rate constant for MMA polymerization with increasing concentration of benzyl alcohol solvent to stabilization of the MMA monomer by complexation by solvent.^{34,35} We note that a simple argument might anticipate that the size of the monomer relative to the pore size should be the important variable in determining changes in rate; however, this is not the case for this series of *n*-alkyl methacrylates. Similarly, this was not the case for nanoconfined trimerization of cyanate esters, where a smaller monomer showed a larger acceleration in the

trimerization rate, presumably due to better packing and a higher local concentration of functional groups. 36

Returning to the results in Figure 3, at temperatures above 160 $^{\circ}$ C, the effective forward reaction rate clearly decreases relative to the Arrhenius expectation, and this effect is due to depropagation. Figure 5 shows the ratio of the depropagation



Figure 5. Ratio of the rates of depropagation to propagation at the initial stages of the reaction vs reciprocal absolute temperature for bulk and nanoconfined DMA. Black circles represent samples reacted in the bulk condition, blue squares are samples reacted in 50 nm pores, and red diamonds are samples reacted in 8 nm pores. The lines are independent Arrhenius fits to each set of data yielding a ceiling temperature of (198 ± 1) °C. View in color for best clarity.

rate over the propagation rate as a function of reciprocal temperature at the initial stages of the reaction, where

$$\frac{K_{\rm dp}}{R_{\rm p}} = 1 - \frac{k_{\rm eff}}{k_{\rm Ar}} \tag{5}$$

and k_{Ar} is the Arrhenius rate constant from Figure 3 for the low temperatures. The ratio of the rates of depropagation to propagation will be essentially zero at low temperatures and increases to a value of 1.0 at the ceiling temperature. Fitting each set of data in Figure 5 independently with an Arrhenius temperature dependence yields the same ceiling temperature of (198 ± 1) °C (471 K) for the bulk and nanoconfined samples. The activation energy in the fit is the difference between the effective activation energy for the forward and backward reactions; in the case of the bulk, this value is (56.8 ± 5.7) kJ/ mol, which, as expected, is consistent with the value of the enthalpy of the reaction (56.5 kJ/mol). For the 50 nm case, the data differ significantly from the bulk data, and the value is larger (see Supporting Information for statistical analyses); a similar effect was observed for nanoconfined ethyl- and butylmethacrylate polymerizations.⁶ For the 8 nm case, however, the data are not statistically distinguishable from the bulk.

The ceiling temperature can also be determined from the temperature-dependent equilibrium conversion x_{∞} , which is plotted in Figure 6 on the right-hand axis. On the left is plotted the measured enthalpy of reaction, and the two variables are related by $x_{\infty} = 1 - \Delta H/\Delta H_{\rm p}$, where $\Delta H_{\rm p}$ is the total enthalpy for complete reaction (222 J/g). For bulk polymerization, the equilibrium conversion is unity at low temperatures (≤ 110 °C), and as the reaction temperature increases, the equilibrium conversion decreases as the ceiling temperature (T_c) is approached. The ceiling temperature (T_c) based on the bulk x_{∞} data is (193 ± 2) °C determined from the thermodynamic



Figure 6. Heat of reaction and equilibrium conversion x_{∞} as a function of reaction temperature for dodecyl methacrylate reacted in both bulk and nanoconfined conditions. The black circles represent the samples reacted in bulk condition, the blue squares represent the sample reacted in 50 nm pores, and the red solid diamonds represent the samples reacted in 8 nm pores. The line is the fit of eqs 5 and 6 to the bulk data.

relationship between the equilibrium constant K and the activity of the monomer $\hat{a}_{\rm M}$

$$K = \exp \frac{-\Delta G}{RT} = \frac{1}{\hat{a}_{\rm M}} \tag{6}$$

where the Gibbs free energy $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the enthalpy and entropy change on reaction, respectively. Often, the activity of the monomer is taken to be the equilibrium conversion, but the mixture of monomer and polymer is not an ideal mixture. Consequently, the Flory–Huggins model is a better description

$$\ln \hat{a}_{\rm M} = \ln(1 - \varphi_{\rm p}) + \left(1 - \frac{1}{r}\right)\varphi_{\rm p} + \chi \varphi_{\rm p}^{2}$$
(7)

where r represents the number of repeating units in the polymer molecule (obtained from the molecular weight of the polymer synthesized at a given temperature), χ is Flory-Huggins parameter (taken to be 0.5 here), and the volume fraction of polymer $\varphi_{\rm p}$ is taken to be equal to the equilibrium conversion x_{∞} in this work because there is little volume contraction on polymerization of dodecyl methacrylate. The equilibrium conversion data for the bulk is fitted to eqs 5 and 6 using the experimental value of $\Delta H = (222 \pm 8) \text{ J/g} = (56.6 \pm 10) \text{ J/g}$ 2.0) kJ/mol. The result gives $T_c = (193 \pm 2)$ °C (466 K), consistent with the results shown in Figure 5, and $\Delta S = (-121)$ \pm 5) J mol⁻¹ K⁻¹, consistent with literature values for methyl methacrylate^{37,38} and ethyl methacrylate,³⁹ which fall in the range of -115 to -125 J mol⁻¹ K⁻¹. We note that the literature values reported for the ceiling temperatures of *n*-alkyl methacrylates are somewhat higher than the value found here, being (209 ± 29) °C for MMA³⁷ and (212 ± 32) °C for EMA.³⁹ Hutchinson and co-workers¹⁸ also studied DMA polymerization up to 180 °C, and they conclude that different analysis methods lead to different T_c values, ranging from 199 to 204 °C. Of importance is the fact that we incorporate the Flory-Huggins theory to determine the activity of the monomer, \hat{a}_{M} , instead of assuming $\hat{a}_{M} = 1 - x_{\infty}$, and this affects the steepness of the curvature at high temperatures and low equilibrium conversions, making the curve more steep and the determined T_c lower than when the approximation of ideal monomer/polymer solution is used.

In the case of nanoconfinement, the equilibrium conversion data follow the same trend as the bulk data and have the same ceiling temperature. However, at a given temperature, the equilibrium conversion is statistically lower (as shown in the Supporting Information) for material synthesized in 8 nm pores compared to data in the bulk or in 50 nm pores. We suggest that the decrease in x_{∞} in 8 nm-confinement is because the entropy of polymerization is a larger negative number due to the loss of entropy by the confined polymer, resulting in a smaller (negative) ΔG in eq 5, a higher activity \hat{a}_{M} , and a lower x_{∞} ; this entropy loss depends on chain length, and at T_{c} where the degree of polymerization is 1.0, there is no difference in the entropy of the reaction. Hence, T_c is not expected to change under nanoconfinement, although the approach (slope) will be less steep in the nanoconfinement case. However, the decrease in equilibrium conversion due to nanoconfined polymerization that we observe here in 8 nm pores is less pronounced than in previous MMA work in 13 nm pores,⁵ presumably due to the larger flexibility of the PDMA chain and the lower relative degree of confinement.

The effects of nanoconfinement on the number-average molar mass, $M_{\rm n}$, mass-average molar mass, $M_{\rm w}$, and gel fraction are shown as a function of polymerization temperature or reciprocal temperature in Figure 7. Molar mass increases as the reaction temperature decreases, and the gel fraction increases below 170 °C. The latter is consistent with the literature and attributed to chain transfer to polymer.^{12,13} For reactions carried out under nanoconfinement, mass-average molar



Figure 7. (a) Dependence of number-average molar mass $(M_{n\nu}$ left) and mass-average molar mass $(M_{w\nu}$, right) on polymerization temperature for dodecyl methacrylate in both bulk and nanoconfined pores. (b) Dependence of the gel fraction vs reciprocal polymerization temperature. The black filled circles represent the samples reacted in bulk conditions, the blue squares represent the samples reacted in 50 nm pores, and the red diamonds represent the samples reacted in 8 nm pores. Lines are model fits.

masses are lower than for bulk reactions at temperatures of 170 °C and above, suggesting that the nanoconfined termination reaction is faster relative to propagation under nanoconfinement at high temperatures. The result differs from our previous work on MMA,⁴ where molar mass was found to increase in nanoconfined polymerization due to earlier autoacceleration. Schmidt and co-workers¹⁰ also found that increased monomer size can lead to a decrease of molar mass in free radical and reversible addition fragmentation chain transfer (RAFT) polymerization of vinyl esters in the metalorganic-framework (MOF), and they attributed lower molar mass upon confinement to be due to the limited amount of monomer in the small pore as a result of confinement environment and decreased diffusivity of the large monomer in the nanochannels. They also found suppression of chain transfer, as did Tarnacka and co-workers, who reported the suppression of both hydrolysis and chain transfer by transesterification under nanoconfinement in the ring-opening polymerization of ε -caprolactone in nanoporous aluminum oxide (AAO) membranes.¹¹ In this work here, we find the same gel fraction, independent of confinement, indicating that the ratio of propagation to chain transfer to polymer is similar at temperatures below 170 °C where gelation occurs. The reasons for the differences in behavior are not understood.

Insights may be gained by estimating the molar mass and the gel fraction using the recursive method of Miller and Macosko,^{40,41} making some simplifying assumptions. Namely, in determining the mass-average molar mass and the gel fraction, we assume that when the chain transfer to polymer reaction occurs, a branch point occurs, and we ignore that one chain is terminated. The result is a slight overestimation of the molar mass but not appreciably since we account for the increasing molar mass of the branched chain, which is most important. In addition, in this statistical modeling, the effects of chain diffusion cannot be accounted for, but as previously mentioned, chain diffusion effects are not very strong in PDMA polymerization. Following the notation of Miller and Macosko, the probability of a finite chain looking out of monomer A is given by

$$P(F_{\rm A}^{\rm out}) = x P(F_{\rm A*}^{\rm out}) + 1 - x$$
(8)

where A^* indicates an A that has been activated and is part of a chain. The activated A^* will terminate and be finite looking out if it terminates (rather than propagating or transferring), whereas if the chain propagates, its probability of being finite is dictated by the net probability of propagation. In the case of chain transfer to polymer, a branch point is made, and now the probability of being finite is that of being finite looking out of two A^*s

$$P(F_{A*}^{out}) = (1 - q - q_{tr}) + q P(F_{A*}^{out}) + q_{tr} P(F_{A*}^{out})^{2}$$
(9)

where the probability of net propagation q is given by

$$q = \frac{(R_{\rm p} - R_{\rm dp})}{(R_{\rm p} - R_{\rm dp}) + R_{\rm t} + xR_{\rm tr}}$$
(10)

where R_p is the rate of propagation, R_{dp} is the rate of depropagation, R_t is the rate of termination, and xR_{tr} is the rate of chain transfer to polymer, where the conversion x is included since the probability of transfer to polymer is the probability of the presence of a polymer (x) times the probability of the A* undergoing the transfer reaction. The

probability of transfer q_{tr} is simply xR_{tr} divided by the denominator in eq 9. Solving, we get

$$P(F_{A^*}^{out}) = 1/q_{tr} - q/q_{tr} - 1$$
(11)

The weight fraction of sol and the weight fraction gel are then given by

$$w_{\rm sol} = P(F_{\rm A*}^{\rm out})^2 \tag{12}$$

$$w_{\rm gel} = 1 - P(F_{\rm A*}^{\rm out})^2 \tag{13}$$

The number-average molar mass is independent of chain transfer to polymer and only depends on the probability of termination since chain transfer to polymer results in one chain growing at the expense of another, and hence, only changes the molar mass distribution, not the number-average molar mass

$$M_{\rm n} = M_{\rm A}/q_{\rm t} \tag{14}$$

where $M_{\rm A}$ is the molar mass of the monomer. The massaverage molar mass, on the other hand, is given by the following for termination by disproportionation

$$M_{\rm w} = M_{\rm A} \left(\frac{q + 2q_{\rm tr}}{1 - q - 2q_{\rm tr}} \right) \tag{15}$$

The model, even with its simplifying assumption, reasonably captures the data in Figure 7 using the data from Figures 3 and 4, along with several adjustable parameters shown in Table 2,

Table 2. Fitting Parameters Used in Recursive Model

	bulk	50 nm	8 nm
$R_{\rm t}/R_{\rm p}$ at 160 °C	0.0015	0.0028	0.0059
$R_{\rm tr}/R_{\rm t}$ at 160 °C	1.22	1.18	1.19
$E_{\rm t} - E_{\rm p} (\rm kJ/mol)$	-15.8	-4.2	-10.4
$E_{\rm tr} - E_{\rm t} (\rm kJ/mol)$	-14.1	-14.1	-14.1

namely, the ratios R_t/R_p and R_{tr}/R_t at 160 °C and the values of the difference in the activation energies of termination to propagation $(E_t - E_p)$ and the difference in the activation energies of transfer to termination $(E_{tr} - E_t)$. The other parameters in the model are obtained from the data (e.g., R_p/R_{dp} and $E_p - E_{dp}$). The fitting parameter values suggest that the rate of chain transfer to polymer is similar under nanoconfinement relative to the bulk, consistent with the data showing that the gel fractions are indistinguishable and that the rate of termination increases with nanoconfinement relative to propagation at high temperatures. More in-depth kinetic modeling without simplifying assumptions will be performed in the future to further test these findings.

CONCLUSIONS

The DTBP-initiated free radical polymerization of dodecyl methacrylate has been investigated in bulk and CPG native nanopore conditions at reaction temperatures from 110 to 190 °C. The initial reaction rate increases with increasing temperature for all cases. The induction time is found to decrease with increasing temperature with an activation energy that is the same, albeit with a negative sign, for initiator dissociation. Autoacceleration is strongly suppressed in dodecyl methacrylate polymerization compared to previous work on methyl-, ethyl-, and butyl-methacrylate, including under nanoconfinement. At temperatures lower than 160 °C,

the effective rate shows an Arrhenius temperature dependence and is highest in nanopores and lowest in bulk condition, with the nanoconfined reactions showing an activation energy that is 10% lower than that of the bulk polymerization. The increased reaction rate and decreased activation energy are attributed to interactions between the methacrylate moiety and the silanol groups on the pore wall surface. A comparison with prior data for polymerization of ethyl- and butyl-methacrylate indicates that the enhancement of rate under nanoconfinement decreases with increasing alkyl chain length and increasing hydrophobicity, varying approximately linearly with the water contact angle on the resulting polymer. Molar mass increases as the temperature decreases below the ceiling temperature of (193 ± 2) °C and is lower in the nanoconfined samples relative to the bulk. For all samples, cross-linked polymer with infinite molar mass starts to form at temperatures below 170 °C, and the gel fraction increases to 80% at 110 °C for all samples. A recursive model with simplifying assumptions is able to capture the trends in molecular weight and gel fraction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c01724.

DSC heat flow data and corresponding conversion data vs time; statistical *t*-test analysis for rate constants at 110, 120, and 130 °C: bulk vs nanoconfined; difference between bulk model and bulk and nanoconfined data for $R_{\rm dp}/R_{\rm p}$ vs 1000/*T* and x_{∞} vs *T* and corresponding statistical analysis (PDF)

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Notes

The authors declare no competing financial interest.

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Article

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