

Supporting Information for Atom Transfer Radical Polymerization of Isobornyl Acrylate: a Kinetic Modeling Study

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1 Diffusional and (population weighted) apparent rate coefficients

In this section the calculation of the center-of-mass diffusion coefficients for the diffusional rate coefficients is discussed. A distinction is made between the center-of-mass diffusion coefficient of the non-macromolecules, such as the monomer and initiator molecules, and the macromolecules. Next, the calculation of the reaction diffusion coefficient for macroradicals and the collision radius for the diffusional rate coefficients is explained. Finally, the center-of-mass contributions to the diffusional rate coefficients and the (population weighted) apparent rate coefficients for propagation and activation are discussed.

1.1 The calculation of the center-of-mass diffusion coefficients

1.1.1 Center-of-mass diffusion coefficient of a non-macromolecule

The center-of-mass diffusion coefficient of a non-macromolecule A (D_A) is calculated as a function of polymerization conditions and conversion based on the Vrentas and Duda free volume theory (equation (1);^{1,3}).

$$D_A = D_{0,A}^{av} \exp \left(-V_A^* M_{j,A} \frac{\sum_{B=1}^{n_{rc}} \frac{w_B}{M_{j,B}}}{\frac{V_{FH}}{\gamma}} \right) \quad (1)$$

In equation (1), $D_{0,A}^{av}$ is an average pre-exponential factor, V_A^* the specific critical hole free volume required for a diffusional jump of A , $M_{j,A/B}$ the molar mass of a jumping unit of the (reaction) component A/B , w_B the mass fraction of the (reaction) component B , and n_{rc} the number of (reaction) components (i.e., non-macromolecules and macromolecules).

Furthermore, in equation (1) V_{FH} is the specific hole free volume of the reaction system and γ an average overlap factor used to correct for the same free volume being available for several jumping units. However, as the sum of the mass fraction of the monomer (m), of the solvent (s), of the internal standard (is) and of the polymer (p) is close to unity during the whole

polymerization process equation (1) can be simplified into:

$$D_A = D_{0,A}^{av} \exp \left(-V_A^* M_{j,A} \frac{\frac{w_m}{M_{j,m}} + \frac{w_s}{M_{j,s}} + \frac{w_{is}}{M_{j,is}} + \frac{w_p}{M_{j,p}}}{w_m \frac{V_{FH,m}}{\gamma_m} + w_s \frac{V_{FH,s}}{\gamma_s} + w_{is} \frac{V_{FH,is}}{\gamma_{is}} + w_p \frac{V_{FH,p}}{\gamma_p}} \right), \quad (2)$$

in which $V_{FH,A}$ ($A=m, s, is, p$) is the specific hole free volume of the pure component A to γ_A ($A=m, s, is, p$) the overlap factor in pure A . The ratio of $V_{FH,A}$ and γ_A ($A=m, s, is, p$) can be calculated via:

$$\frac{V_{FH,A}}{\gamma_A} = \frac{K_{1A}}{\gamma_A} (K_{2A} - T_{g,A} + T_{pol}), \quad (3)$$

in which $\frac{K_{1A}}{\gamma_A}$ and $K_{2A} - T_{g,A}$ ($A=m, s, is, p$) are parameters to be estimated from experimental data of the pure dynamic viscosity as a function of temperature. For the polymer, $T_{g,p}$ corresponds to its glass transition temperature. For the non-macromolecules, $T_{g,A}$ is a formally analogous temperature.

Hence, to calculate the center-of-mass diffusion coefficient of a non-macromolecule A (D_A), the following free volume parameters have to be known: $D_{0,A}^{av}$, V_A^* , $M_{j,B}$ ($B=1, \dots, n_{rc}$), $\frac{K_{1A}}{\gamma_A}$ and $K_{2A} - T_{g,A}$ ($A=m, s, is, p$). In what follows, the calculation of each free volume parameter is discussed.

Diffusional jump related free volume parameters For each non-macromolecule A , the specific critical hole free volume required for a diffusional jump (V_A^*) is calculated via group contributive methods.⁴⁻⁶ The obtained values for V_A^* are listed in Table 1.

The molar mass of the jumping unit of each non-macromolecule A ($M_{j,A}$) is taken equal to the molar mass of the non-macromolecule. These molar masses are also presented in Table 2. For the polymer $M_{j,p}$ (with p referring to polymer) is taken equal to the corresponding value for the monomer.

Average pre-exponential factor of a non-macromolecule The average pre-exponential factor of a non-macromolecule ($D_{0,A}^{av}$) should ideally be obtained from regression of equation (2) to experimental diffusion data.^{7,8} However, if no such diffusion data are available, the average

Table 1: Specific critical hole free volume required for a diffusional jump of a non-macromolecule A (V_A^*), the molar mass of the jumping unit of a non-macromolecule A ($M_{j,A}$), the average pre-exponential factor ($D_{0,A}^{av}$) of a non-macromolecule A and the value of the center-of-mass diffusion coefficient of a non-macromolecule A (D_A) at $T_{pol} = 335$ K, $w_m=w_s=w_p=0.33$ and $w_{is}=0.01$; equation (3)

A	name	V_A^* ($\text{m}^3 \text{ kg}^{-1}$)	$M_{j,A}$ (kg mol^{-1})	$D_{0,A}^{av}$ ($\text{m}^2 \text{ s}^{-1}$)	D_A^a ($\text{m}^2 \text{ s}^{-1}$)
1	iBoA	$8.42 \cdot 10^{-4}$	0.280	$3.3 \cdot 10^{-9} \text{ }^b$	$2.32 \cdot 10^{-10}$
2	MBP	$5.10 \cdot 10^{-4}$	0.167	$5.23 \cdot 10^{-7} \text{ }^c$	$3.49 \cdot 10^{-8}$
3	M(.)P ^d	$7.89 \cdot 10^{-4}$	0.087	$1.27 \cdot 10^{-7} \text{ }^c$	$1.84 \cdot 10^{-8}$
4	[Cu(I)BrPMDETA] ^d	$6.91 \cdot 10^{-4}$	0.317	$6.27 \cdot 10^{-7}$	$1.06 \cdot 10^{-8}$
5	[Cu(II)Br ₂ PMDETA] ^e	$6.08 \cdot 10^{-4}$	0.397	$3.82 \cdot 10^{-7}$	$4.60 \cdot 10^{-9}$
6	ethyl acetate	$7.27 \cdot 10^{-4}$	0.088	$5.23 \cdot 10^{-7} \text{ }^c$	$1.98 \cdot 10^{-8}$
7	<i>n</i> -decane	$1.082 \cdot 10^{-3}$	0.142	$5.22 \cdot 10^{-8} \text{ }^c$	$5.08 \cdot 10^{-9}$

^a evaluated at $T_{pol} = 335$ K, $w_m=w_s=w_p=0.33$ and $w_{is}=0.01$

^b based on Kobuchi et al.¹¹ and evaluated at $T_{pol} = 335$ K

^c from Hong et al.¹⁰

^d initiating radical from MBP

^e from D'hooge et al.⁹ with $D_{0,A}^{av}$ evaluated at $T_{pol} = 335$ K

pre-exponential factor of a non-macromolecule having a similar chemical structure and/or mobility can be used. In this work, the data reported by D'hooge et al.⁹ are used for the calculation of the average pre-exponential factor of the activator and the deactivator, whereas for the solvent, the initiator and the initiating radical the by Hong et al.¹⁰ value reported for the average pre-exponential factor of the similar molecules methyl acetate, methyl methacrylate, and again methyl acetate are used. At the average temperature of 335 K, the values listed in Table 1 result for these average pre-exponential factors

For the calculation of the average pre-exponential of the monomer ($D_{0,m}^{av}$), the semi-empirical equation (4) proposed by Kobuchi et al.¹¹ derived for diffusion in (poly)acrylic systems is used (evaluated at the average temperature of 335 K and for a volume fraction of monomer equal to 0.5):

$$D_{0,m}^{av} = 0.25(1 - 2.901 + 7.160 \cdot 10^{-5} E_{coh_m}) (1.835 \cdot 10^{-7} MM_m - 7.753 \cdot 10^{-9}) \exp\left(\frac{0.1252 E_{coh_m} - 2537}{2785}\right) \quad (4)$$

In equation (4), MM_m is the molar mass of the monomer ($MM_m = 0.2803 \text{ kg mol}^{-1}$) and E_{coh} the cohesive energy of the monomer (i.e., the increase in the internal energy of the monomer per mole, if all intramolecular forces are eliminated). The cohesive energy of the monomer is calculated via the group additivity method of Fedors¹² ($E_{coh} = 44.9 \text{ kJ mol}^{-1}$) leading to a value of $3.30 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for $D_{0,m}^{av}$ (see also in Table 2).

Hole free volume parameters In this work, the dynamic viscosity of iBoA and piBoA are measured at temperatures ranging from 280 to 350 K and at temperature above $T_{g,p}$, respectively, allowing an accurate calculation of the corresponding hole free volume contributions. The latter approach has been proven successful for several non-macromolecules.^{3,7,8,10} For a detailed description, the reader is referred to the manuscript.

1.1.2 Center-of-mass diffusion coefficient of a macromolecule

The center-of-mass diffusion coefficient of a macromolecule with chain length i ($D_{p,i}^{com}$) is calculated by the universal scaling law proposed by Griffiths et al.:¹³

$$D_{p,i}^{com} = \frac{D_m^{com}}{i^{0.664+2.02w_p}}, \quad (5)$$

in which D_m^{com} is the center-of-mass diffusion coefficient of the monomer and w_p the mass fraction of the polymer. For $w_p \rightarrow 0$ (i.e., at low conversions) equation (5) approaches the Stokes-Einstein model for the diffusion of a polymer molecule in a dilute solution (i.e., an $i^{-0.5}$ dependence of $D_{p,i}^{com}$).¹⁴ On the other hand, for $w_p \rightarrow 1$ (i.e., at high conversions) equation (5) is related to the reptation theory, in which an i^{-2} dependence of $D_{p,i}^{com}$ is predicted for the diffusion of a polymer molecule in a polymer melt or a highly concentrated solution of polymer molecules.¹⁵

1.2 The calculation of the reaction diffusion coefficient

As indicated in the manuscript, the diffusional contribution $k_{l,diff}$ for reaction steps involving macroradicals is calculated based on the sum of the center-of-mass and reaction diffusion

coefficient. The reaction diffusion coefficient of a macroradical with chain length i ($D_{p,i}^{rd}$) is calculated via:¹⁶

$$D_{p,i}^{rd} = \frac{1}{6} k_{p,\text{chem}} M a^2, \quad (6)$$

in which a is the root-mean-square end-to-end distance per square root of the number of monomer units in a polymer molecule and M the monomer concentration. It should be noted that accounting for the reaction diffusion coefficient mainly influences the apparent termination reactivity at high conversion, as for termination no non-macromolecules are involved.

The mean-square end-to-end distance ($\langle R^2 \rangle$) can be approximately calculated from:¹⁷

$$K = \phi \left(\frac{\langle R^2 \rangle}{1000 M_n} \right)^{3/2}, \quad (7)$$

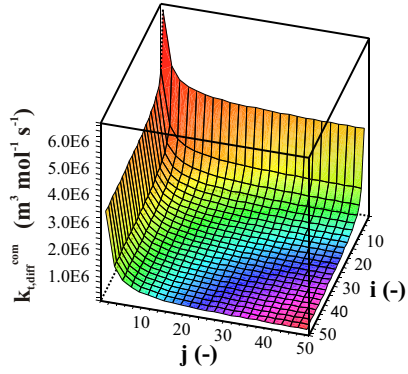
in which K is the first Mark Houwink constant for the studied polymer-solvent pair in dl g^{-1} , ϕ the Flory universal hydrodynamic constant ($\phi=2.5 \cdot 10^{21} \text{dl mol}^{-1} \text{cm}^{-3}$) and M_n the number average molar mass of the polymer in kg mol^{-1} . The first Mark Houwink constant K for piBoA in tetrahydrofuran (THF) was measured by Dervaux et al.¹⁸ and found equal to $5 \cdot 10^{-5} \text{dl g}^{-1}$. If the same value is assumed for solvent ethyl acetate used on this work a value of $3.9 \cdot 10^{-10} \text{m}$ is obtained for a , consistent with typical values reported for other (meth)acrylates.^{16,19}

1.3 Collision radius for the calculation of the diffusional rate coefficients

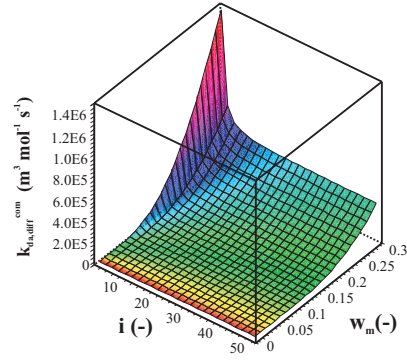
The collision radius σ is considered equal to the Lennard Jones diameter of the monomer (σ_m), which is calculated from:²⁰

$$\sigma_m = 1.18 \cdot 10^{-10} V_{b,m}^{\frac{1}{3}}, \quad (8)$$

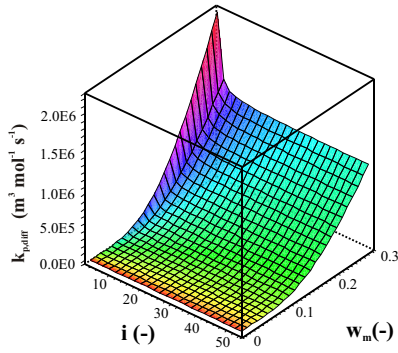
in which $V_{b,m}$ is the Le Bas molar volume of the monomer at the normal boiling point. Using the data of Brodkey and Hershey,²⁰ a value of $0.27 \text{m}^3 \text{mol}^{-1}$ is obtained for $V_{b,m}$ leading to a value of $7.46 \cdot 10^{-9} \text{m}$ for the Lennard Jones diameter of the monomer.



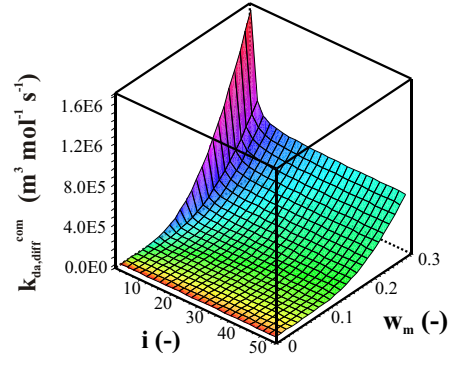
(a)



(b)



(c)



(d)

Figure 1: (a) The center-of-mass contribution to the diffusional rate coefficient for termination ($k_{t,diff}^{com}$) as a function of the chain length of the macroradicals (i, j) at 335 K for a monomer and solvent mass fraction of 0.30 and a mass fraction of internal standard equal to 0.05 (b) the center-of-mass contribution to the diffusional rate coefficient for deactivation ($k_{da,diff}^{com}$) as a function of the chain length of the macroradical (i) and the monomer mass fraction (w_m) (c) the center-of-mass contribution to the diffusional rate coefficient for propagation ($k_{p,diff}^{com}$) as a function of the chain length of the macroradical (i) and the monomer mass fraction (w_m) and (d) the center-of-mass contribution to the diffusional rate coefficient for activation ($k_{a,diff}^{com}$) as a function of the chain length of the dormant polymer molecule (i) and the monomer mass fraction (w_m) at 335 K for a solvent mass fraction of 0.30 and a mass fraction of internal standard equal to 0.05

1.4 Center-of-mass contribution to the diffusional rate coefficients

From the calculated center-of-mass diffusion coefficients the potential importance of diffusional limitations on the ATRP process can already be assessed. Based on equation (5) diffusional limitations can be expected to become important during the polymerization process for reactions involving macromolecules. In Figure 1(a), the center-of-mass contribution to the diffusional rate coefficient for termination ($k_{t,\text{diff}}^{\text{com}}$) is given as a function of the macroradical chain length at 335 K for a monomer and solvent mass fraction of 0.30 and a mass fraction of internal standard of 0.05. This center-of-mass contribution follows from equation (2) in the manuscript, evaluated using the appropriate center-of-mass diffusion coefficients. It follows from Figure 1(a) that $k_{t,\text{diff}}^{\text{com}}$ decreases strongly as a function of chain length, indicating that diffusional limitations on termination are highly likely to occur during the ATRP.

Furthermore, in Figure 1(b), 1(c) and 1(d) the center-of-mass contribution to the diffusional rate coefficient for deactivation ($k_{da,\text{diff}}^{\text{com}}$), for propagation ($k_{p,\text{diff}}^{\text{com}}$) and for activation ($k_{a,\text{diff}}^{\text{com}}$) are presented as a function of the macroradical/dormant polymer molecule chain length and the monomer mass fraction at 335 K for a solvent mass fraction of 0.30 and a mass fraction of internal standard equal to 0.05. From these figures, it is clear that, for (de)activation and propagation, diffusional limitations might be expected to become significant at relatively high conversions only. However, it should be reminded that also the value of the chemical intrinsic rate coefficient determines whether diffusional limitations might become important or not, as explained in the manuscript.

1.5 (Population weighted) apparent rate coefficients for activation and propagation with end/mid-chain macroradicals

Figure 2(a) and 2(b) present the apparent rate coefficient for activation and propagation with mid-chain macroradicals as a function of chain length and the monomer mass fraction at 335 K for a solvent mass fraction of 0.30 and a mass fraction of internal standard equal to 0.05. It can be seen in both figures that the effect of diffusional limitations is very limited (as already shown for the end-chain radicals in the manuscript). Only at conversions almost equal to complete

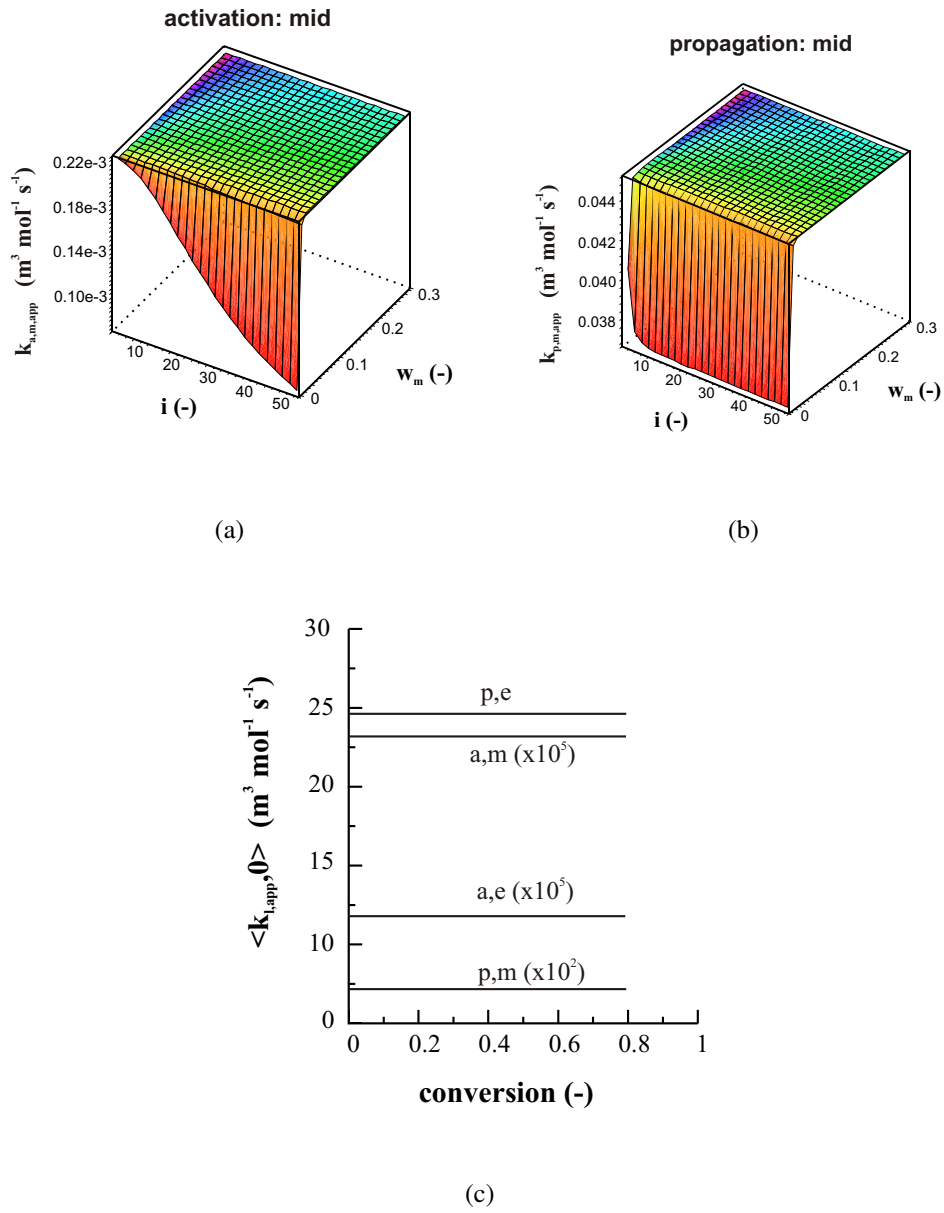


Figure 2: (a) The apparent rate coefficient for propagation with mid-chain macroradicals ($k_{p,app}$) as a function of the chain length of the macroradical (i) and the monomer mass fraction (w_m) and (b) for activation with mid-chain dormant polymer molecules ($k_{a,app}$) as a function of the chain length of the dormant polymer molecule (i) and the monomer mass fraction (w_m) at 335 K for a solvent mass fraction of 0.30 and a mass fraction of internal standard equal to 0.05 (c) the corresponding population weighted apparent rate coefficients (m) as a function of conversion; also shown for end-chain macroradicals (e); scale factors as indicated in figure

conversion a significant decrease of the apparent reactivities is observed. Indeed, from Figure 2(c) it follows that the corresponding population weighted apparent rate coefficient for activation and propagation remain equal to the corresponding intrinsic chemical rate coefficients during the ATRP. In the latter figure also the population weighted apparent rate coefficient for activation and propagation with end-chain macromolecular species are shown. Analogously, the effect of diffusional limitations on these reactions is found to be unimportant.

2 Regression analysis: determination of Arrhenius and thermodynamic parameters for reactions involving secondary end-chain macroradicals

As indicated in the manuscript, the Arrhenius parameters for activation, deactivation and termination involving end-chain macromolecular species for the ATRP of iBoA in ethyl acetate with copper bromide as transition metal, PMDETA as ligand and MBP as initiator can be obtained by regression of the experimental data at the lower temperatures investigated (i.e., at 323 and 333 K). Six parameters (b_i , $i = 1, \dots, 6$) were estimated: the pre-exponential factors and the activation energies for termination by recombination and activation with end-chain macroradicals ($A_{t,e}$, $A_{a,e}$, $E_{A,t,e}$ and $E_{A,a,e}$) and the standard reaction enthalpy and entropy for the activation-deactivation process with end-chain macromolecular species ($\Delta_{r,a,e}^0 H$ and $\Delta_{r,a,e}^0 S$). Note that the latter two parameters determine the equilibrium coefficient of the activation deactivation process with end-chain macromolecular species ($K_{eq,e}$):

$$K_{eq,e} = \frac{k_{a,e,chem}}{k_{da,e,chem}} = \exp\left(-\frac{\Delta_{r,a,e}H^0 - T_{pol}\Delta_{r,a,e}S^0}{RT_{pol}}\right) \quad (9)$$

It should be noted that the Arrhenius parameters for propagation with end-chain macroradicals are taken as reported by the recent pulsed laser polymerization study of Dervaux et al.¹⁸

For each sample i withdrawn from the reaction system ($i = 1, \dots, n$ with n the total number of samples), three responses are measured: the (monomer) conversion x_m , the average chain length of the polymer molecules (x_n^{pol}), and the polydispersity index of the MMD of the polymer (PDI^{pol}). A weighted nonlinear least-squares regression is performed using a multi-response Levenberg-Marquardt algorithm.²¹⁻²³ As merit function ($S(\mathbf{b})$; equation (10)) is used:

$$S(\mathbf{b}) = \sum_i^n (\mathbf{y}_i - \hat{\mathbf{y}}_i)^T \mathbf{W}_i (\mathbf{y}_i - \hat{\mathbf{y}}_i), \quad (10)$$

in which \mathbf{y}_i and $\hat{\mathbf{y}}_i$ ($i = 1, \dots, n$) are the vector representation of the observed and calculated response values of the i -th sample (both having a dimension equal to the number of responses (i.e., $m=3$)) and in which \mathbf{W}_i ($i=1, \dots, n$) is a ($m \times m$) matrix consisting of the weights of regression for the i -th sample. A detailed description of the estimation of these weights of regression can be found in De Roo et al.²⁴

An F -test, based on the weighed sum of squares of the calculated response values and the weighted residual sum of squares and their degrees of freedom, is used to verify the statistical global significance of the regression.²³ The statistical significance of the individual parameters is validated by the calculation of the individual confidence intervals at the 95 % level of confidence.

For the studied system, the statistical global significance of the regression is found to be high (i.e., the calculated F -value is found to be significantly higher than the tabulated one) and all parameters, except the activation energy for termination by recombination with end-chain macroradicals, are estimated statistically different from zero.

3 Calculation of the volume of the reaction system and correlations for the dynamic viscosity of the monomer and the solvent

The volume of the reaction system V is calculated from:

$$V = \frac{m_0(1 - x_m)}{\rho_m} + \frac{m_0 x_m}{\rho_p} + \frac{s_0}{\rho_s} + \frac{is_0}{\rho_{is}}, \quad (11)$$

in which x_m is the (monomer) conversion, m_0 , s_0 and is_0 are the initial mass of the monomer (m), the solvent (s) and the internal standard (is), and ρ_k ($k = m, s, is, p$) is the density of the component k . The conversion x_m is obtained from:

$$x_m = 1 - \frac{MV}{M_0 V_0}, \quad (12)$$

in which V_0 is the initial volume of the reaction system and M_0 the initial monomer concentration.

Table 2: Density (ρ_A) and dynamic viscosity (η_A) of the monomer (m ; η_m : measured (this work)) and solvent (s) and the density of the internal standard (ρ_{is}) and the polymer (ρ_A) as a function of temperature (T_{pol}); T_{pol} range: see Table 1; with 95% confidence intervals for η_m

k	ρ_k/η_k	correlation (kg m ⁻³ / Pa s)	reference
m	ρ_m	946 -0.88 (T_{pol} - 273.15)	18
	η_m	$(6.40 \pm 0.03) \cdot 10^{-3} + (1.62 \pm 0.004) \cdot 10^{-2} par$ $par = \exp(-\frac{T_{pol}-273.15}{24.51 \pm 0.098})$	this work
		79.16	
s	ρ_s	$0.25856^{(1+(1-\frac{T_{pol}}{523.3})^{0.278})}$	25
	η_s	$1.377 \cdot 10^{-6} T_{pol}^2 - 1.261 \cdot 10^{-4} T_{pol} + 2.986$	based on ²⁷
		142.29	
is	ρ_{is}	$0.42831^{(1+(1-\frac{T_{pol}}{617.7})^{0.2891})}$	25
p	ρ_p	$1197 \frac{1.42T_{g,p}+44.7}{1.42T_{g,p}+0.15T_{pol}}$	based on ²⁶

The data reported by Dervaux et al.¹⁸ and Perry and Green²⁵ are used for the calculation of the density of the monomer (ρ_m), of the solvent (ρ_s), and of the internal standard (ρ_{is}). The corresponding correlations are given in Table 2. The density of the polymer ρ_p is obtained based

on;²⁶

$$V_p(T) = V_p(298K) \frac{1.42T_{g,p} + 0.15T}{1.42T_{g,p} + 44.7}, \quad (13)$$

in which $V_p(T)$ is the molar volume of the polymer at temperature T . Equation (13) is valid for $T < T_{g,p}$ and $T_{g,p} \geq 298$ K, as is the case in this work. The molar volume of the polymer at 298 K (i.e., $V_p(298K)$) can be calculated from a structural unit of the polymer, due to its repetitive character.²⁶ A value of $0.17 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ is obtained. The corresponding correlation for ρ_p is given in Table 2. For piBoA at 298 K, a density of 1197 kg m^{-3} results from the calculations. Finally, it should be noted that in Table 2 in addition to the densities the used correlations for the dynamic viscosity of the monomer and the solvent are given.

4 Extension of the kinetic modeling methodology for ATRP to reactions involving tertiary mid-chain macroradicals

As indicated in the manuscript, in this work the methodology successfully tested by D’hooge et al.⁹ for the kinetic modeling of the atom transfer radical polymerization (ATRP) of methacrylates was extended for the ATRP of acrylates. This methodology is related to the method of moments and allows simulating the conversion and important polymer properties, such as the polymer end group functionality, the averages of the molar mass/chain length distribution (MMD/CLD) of the polymer and the MMD of the dormant polymer, as a function of polymerization time and conditions. Diffusional limitations are systematically accounted for by population weighted apparent rate coefficients obtained based on a convergence test. As explained in the manuscript, the apparent rate coefficients are mainly obtained using the Vrentas and Duda free volume theory.^{1,3}

In this section a brief overview is given of the three most important extensions related to the introduction of mid-chain macroradicals: (i) due to the consideration of mid-chain macroradicals new population weighted apparent rate coefficients have to be introduced. In particular, for the studied system, these new population weighted apparent rate coefficients are:

$$\langle k_{a,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{a,m,\text{app}}^i R_{i,m} X}{\sum_{i=3}^{\infty} i^s R_{i,m} X} \quad (14)$$

$$\langle k_{da,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{da,m,\text{app}}^i R_{i,m}}{\sum_{i=3}^{\infty} i^s R_{i,m}} \quad (15)$$

$$\langle k_{p,m,\text{app}}, s \rangle = \frac{\sum_{i=4}^{\infty} i^s k_{p,m,\text{app}}^{i-1} R_{i-1,m}}{\sum_{i=4}^{\infty} i^s R_{i-1,m}} \quad (16)$$

$$\langle k_{p2,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{p,m,\text{app}}^i R_{i,m}}{\sum_{i=3}^{\infty} i^s R_{i,m}} \quad (17)$$

$$\langle k_{pm,e,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} \sum_{j=1}^{i-2} i^s k_{pm,e,\text{app}}^{j,i-j} R_{j,e} M_{i-j}}{\sum_{i=3}^{\infty} \sum_{j=1}^{i-2} i^s R_{j,e} M_{i-j}} \quad (18)$$

$$\langle k_{pm,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} \sum_{j=1}^{i-2} i^s k_{pm,m,\text{app}}^{j,i-j} R_{j,m} M_{i-j}}{\sum_{i=3}^{\infty} \sum_{j=1}^{i-2} i^s R_{j,m} M_{i-j}} \quad (19)$$

$$\langle k_{pm2,e,\text{app}}, s \rangle = \frac{\sum_{i=2}^{\infty} \sum_{j=1}^{\infty} i^s k_{pm,e,\text{app}}^{j,i} R_{j,e} M_i}{\left[\sum_{i=2}^{\infty} i^s M_i \right] \left[\sum_{j=1}^{\infty} R_{j,e} \right]} \quad (20)$$

$$\langle k_{pm2,m,\text{app}}, s \rangle = \frac{\sum_{i=2}^{\infty} \sum_{j=3}^{\infty} i^s k_{pm,m,\text{app}}^{j,i} R_{j,m} M_i}{\left[\sum_{i=2}^{\infty} i^s M_i \right] \left[\sum_{j=3}^{\infty} R_{j,m} \right]} \quad (21)$$

$$\langle k_{bb,e,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{bb,e,\text{chem}}^i R_{i,e}}{\sum_{i=3}^{\infty} i^s R_{i,e}} \quad (22)$$

$$\langle k_{\beta C1,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{\beta C1,m,\text{app}}^i R_{i,m}}{\sum_{i=3}^{\infty} i^s R_{i,m}} \quad (23)$$

$$\langle k_{\beta C12,m,\text{app}}, s \rangle = \frac{\sum_{i=4}^{\infty} i^s k_{\beta C1,m,\text{app}}^i R_{i,m}}{\sum_{i=4}^{\infty} i^s R_{i,m}} \quad (24)$$

$$\langle k_{\beta C13,m,\text{app}}, s \rangle = \frac{\sum_{i=2}^{\infty} i^s k_{\beta C2,m,\text{app}}^{i+2} R_{i+2,m}}{\sum_{i=2}^{\infty} i^s R_{i+2,m}} \quad (25)$$

$$\langle k_{\beta C2,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{\beta C2,m,\text{app}}^i R_{i,m}}{\sum_{i=3}^{\infty} i^s R_{i,m}} \quad (26)$$

$$\langle k_{\beta C22,m,\text{app}}, s \rangle = \frac{\sum_{i=4}^{\infty} i^s k_{\beta C2,m,\text{app}}^i R_{i,m}}{\sum_{i=4}^{\infty} i^s R_{i,m}} \quad (27)$$

$$\langle k_{\beta C23,m,\text{app}}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{\beta C2,m,\text{app}}^{i+3} R_{i+3,m}}{\sum_{i=3}^{\infty} i^s R_{i+3,m}} \quad (28)$$

$$\langle k_{tc,mm,\text{app}}, s \rangle = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} i^s k_{tc,mm,\text{app}}^{ij} R_{i,m} R_{j,m}}{\left[\sum_{i=3}^{\infty} i^s R_{i,m} \right] \left[\sum_{j=3}^{\infty} R_{j,m} \right]} \quad (29)$$

$$\langle k_{tc,em,\text{app}}, s \rangle = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} i^s k_{tc,em,\text{app}}^{ij} R_{i,e} R_{j,m}}{\left[\sum_{i=1}^{\infty} i^s R_{i,e} \right] \left[\sum_{j=3}^{\infty} R_{j,m} \right]} \quad (30)$$

$$\langle k_{tc,me,\text{app}}, s \rangle = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} i^s k_{tc,me,\text{app}}^{ij} R_{i,m} R_{j,e}}{\left[\sum_{i=3}^{\infty} i^s R_{i,m} \right] \left[\sum_{j=1}^{\infty} R_{j,e} \right]} \quad (31)$$

$$\langle k_{tc,em^0,app}, s \rangle = \frac{\sum_{i=3}^{\infty} i^s k_{tc,em,app}^{0i} R_{i,m}}{\sum_{i=3}^{\infty} i^s R_{i,m}} \quad (32)$$

$$\langle k_{tc,mm,app}, e_1 \rangle = \frac{\sum_{i=3}^{\infty} \sum_{j=3}^{\infty} i j k_{tc,mm,app}^{ij} R_{i,m} R_{j,m}}{\left[\sum_{i=3}^{\infty} i R_{i,m} \right]^2} \quad (33)$$

$$\langle k_{tc,mm,app}, e_2 \rangle = \frac{\sum_{i=3}^{\infty} \sum_{j=3}^{\infty} i j^2 k_{tc,mm,app}^{ij} R_{i,m} R_{j,m}}{\left[\sum_{i=3}^{\infty} i R_{i,m} \right] \left[\sum_{j=3}^{\infty} j^2 R_{j,m} \right]} \quad (34)$$

(ii) for the transition of the continuity equations of the reaction components mentioned in the manuscript to the corresponding moment equations using the population weighted apparent rate coefficients, the reader is referred to D'hooge et al.⁹ It should be noted that new moment equations are introduced for the mid-chain macroradicals, their dormant counterparts and the macromonomers. (iii) as carefully explained by D'hooge et al.,⁹ the population weighted apparent rate coefficients in the moment equations are obtained from the integration of a set of differential algebraic equations. The algebraic part results from the application of the quasi-steady state approximation to the macroradicals. The differential equations correspond to the dormant polymer molecules, which are not intermediate reactive species such as the macroradicals. Convergence is required for the obtained averages of the CLD/MMD of the macroradicals and dormant polymer via the corrected moment equations and the averages of these MMDs as used to calculate the related population weighted apparent rate coefficients. Via this demand of convergence, the evolution of the MMD of the dormant polymer can be simulated. Note that, as in the studied ATRPs, the chain length domain is limited and the dormant polymer constitutes the dominant fraction, in addition also the MMD of the dead polymer, and hence, the full polymer MMD, could be calculated based on the obtained radical distributions. In this work, the number of differential equations to be integrated is doubled, due to the presence of both

end- and mid-chain macroradicals.

5 Calculation of the short chain branching and CC double bond content

As indicated in the manuscript, the short chain branching and CC double bond content are expressed as a mol% per average number monomer units. For short chain branching, the content at a polymerization time t is obtained by integrating the sum of the production rates (i.e., the sum of the (volumetric) reaction rates multiplied by the volume) of reactions with mid-chain macroradicals leading to short chain branching (i.e, propagation and termination) with respect to time up to t followed by division by the mole of macromolecules (i.e, the total concentration of the macromolecules multiplied by the volume) and the average chain length at t . Analogously, the CC double bond content at t is obtained by dividing the integrated difference of the production rate for β C-scission of mid-chain macroradicals and addition to macromonomers up to t by the mole of macromolecules and average chain length at t .

Notation

a	root-mean-square end-to-end distance per square root of the number of monomer units in a polymer molecule [m]
A_a	pre-exponential factor for activation [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
A_t	pre-exponential factor for termination [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
b_k	k -th parameter in \mathbf{b} [kJ mol^{-1} or $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ or $\text{m}^3 \text{kg}^{-1}$ or K or $-$]
D_A	self-diffusion coefficient of the (reaction) component A [$\text{m}^2 \text{s}^{-1}$]
$D_{0,A}^{av}$	average pre-exponential factor for the center-of-mass diffusion coefficient of the reaction component A [$\text{m}^2 \text{s}^{-1}$]
E_A	activation energy [kJ mol^{-1}]
E_{coh}	cohesive energy [kJ mol^{-1}]
F	F-value [$-$]
is_0	initial mass of the internal standard [kg]
K	first Mark Houwink constant for a polymer-solvent system [dl g^{-1}]
K_{eq}	ATRP equilibrium coefficient of the activation-deactivation process [$-$]
K_{1A}	parameter for specific hole free volume of pure reaction component A [$\text{m}^3 \text{kg}^{-1} \text{K}^{-1}$]
$K_{2A} - T_{g,A}$	parameter for specific hole free volume of pure reaction component A [K]
k	rate coefficient [$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$]
L	ligand [$-$]
l	reaction step [$-$]
M	monomer (concentration) [(mol m^{-3})]
M_n	number average molar mass of the polymer [kg mol^{-1}]
M_q	macromonomer (concentration); q : its chain length [(mol m^{-3})]
MM_A	molar mass of the (reaction) component A [kg mol^{-1}]
$MM_{j,B}$	molar mass of the jumping unit of the (reaction) component B [kg mol^{-1}]
$M_t^n L_y X$	activator (concentration) [(mol m^{-3})]
$M_t^{n+1} L_y X_2$	deactivator (concentration) [(mol m^{-3})]
m	number of responses [$-$]

m_0	initial mass of the monomer [kg]
n	number of samples (related to the polymerization experiments) [–]
n_A	number of dynamic viscosity experiments for the (reaction) component A [–]
par	parameter in the correlation for η_m [–]
P_i	dead polymer molecule with chain length i ($i > 0$) [–]
R	universal gas constant [J mol ^{−1} K ^{−1}]
$\langle R^2 \rangle$	mean-square end-to-end distance [m ²]
R_i	macroradical with chain length i ($i > 0$) [–]
s_0	initial mass of the solvent [kg]
S	merit function [–]
T	temperature [K]
T_{pol}	(polymerization) temperature [K]
$T_{g,p}$	glass transition temperature of the polymer [K]
T_i	temperature of the i -th dynamic viscosity experiment [K]
t	polymerization time [s]
X	halogen atom / end group functionality [–]
V	volume of the reaction system [m ³]
V_b	Le Bas molar volume [m ³ mol ^{−1}]
V_A^*	the specific critical hole free volume required for a diffusional jump of A [m ³ kg ^{−1}]
V_{FH}	specific hole free volume of the reaction system [m ³ kg ^{−1}]
$V_{FH,A}$	specific hole free volume of pure component A [m ³ kg ^{−1}]
V_p	molar volume of the polymer [m ³ mol ^{−1}]
w_B	mass fraction of the (reaction) component B [–]
x_m	(monomer) conversion [–]

Greek symbols

γ	average overlap factor for the reaction system [–]
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γ_A	average overlap factor for pure component A $[-]$
$\Delta_{r,a}H^0$	standard reaction enthalpy for the activation deactivation process [kJ mol ⁻¹]
$\Delta_{r,a}S^0$	standard reaction entropy for the activation deactivation process [J mol ⁻¹ K ⁻¹]
ϕ	Flory universal hydrodynamic constant [dl mol ⁻¹ cm ⁻³]
η_A	measured dynamic viscosity of the (reaction) component A [Pa s]
$\hat{\eta}_A$	calculated dynamic viscosity of the (reaction) component A [Pa s]
ρ	density [m ³ kg ⁻¹]
σ	Lennard Jones diameter [m]

Subscripts

a	activation
app	apparent
$calc$	calculated
$chem$	chemical intrinsic
da	deactivation
e	end-chain (macro)radical
$diff$	diffusional
i, j, q	chain length (macromolecule: $i, j > 0$; initiator related $i, j=0$; $q \geq 2$)
is	internal standard
l	reaction step
m	monomer/mid-chain
$n(+1)$	oxidation number
p	propagation
pm	propagation with macromonomer
s	solvent
t	termination
tab	tabulated

tc	termination by recombination
y	number
0	initial
βC	βC reaction

Superscripts

com	center-of-mass
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Abbreviations

ATRP	atom transfer radical polymerization
CLD	chain length distribution
MBP	methyl 2-bromopropionate
M(.)BP	initiating radical from methyl 2-bromopropionate
MMD	molar mass distribution
PMDETA	N,N,N',N'',N'''-pentamethyldiethylenetriamine

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