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Individual Rate Coefficients for 1*H*,1*H*,2*H*,2*H*-Tridecafluorooctyl Methacrylate Radical Polymerizations

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ABSTRACT: Kinetic data for radical polymerizations of 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate (TDFOMA) in bulk is reported. Pulsed laser initiated polymerizations yield propagation rate coefficients, k_p, which are by a factor of 1.9 higher than methyl methacrylate k_p. The activation energy of TDFOMA k_p is not significantly different from that of alkyl methacrylates. Chain-length averaged termination rate coefficients were estimated from chemically initiated polymerizations with in-line FT-NIR spectroscopic monitoring of monomer conversion. Up to 30% of monomer conversion TDFOMA termination rate coefficients are only slightly below MMA low conversion values. The result is suggested to be due to less interactions between the macroradicals compared to nonfluorinated systems.

Introduction

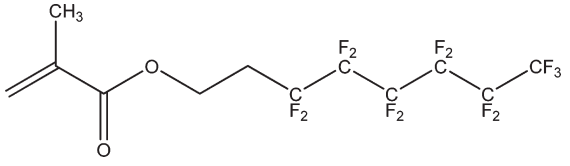
Polymers containing (meth)acrylate units that carry fluorinated ester groups are of great interest for various technical applications due to the unique properties of the fluorinated groups. For example, fluorinated monomers are contained in various coatings recipes due to low surface tension[1] or they may lead to the formation of aggregates from block copolymers due to the incompatibility with hydrocarbon based entities.[2,3] Moreover, applications in membranes, as polymeric materials with low dielectric constants in the electronic industry or as additives in lubricants were reported.[4−6] Despite their technical importance so far only little is known about the polymerization kinetics of fluorinated (meth)acrylates in radical polymerizations. Previously, it was reported that polymerizations of these monomers proceed rather slowly compared to nonfluorinated monomers.[7] Moreover, for monomers of type CH_2=$CHCOO-(CH_2)_n-C_mF_{2m+1}$ it was demonstrated that n has a significant influence on the reactivity of the monomer.[8] To provide kinetic data for modeling and optimization of polymerization reactions it seemed important to determine individual rate coefficients for the propagation and termination reaction, k_p and k_t, respectively. To the best of our knowledge these data are not yet available. Here, for the first time individual rate coefficients for 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate (Scheme 1) are reported.

To determine k_p pulsed laser initiated polymerizations (PLP) in combination with polymer analysis via size-exclusion chromatography (SEC) were carried out. This technique was recommended as the method of choice for the determination of k_p by the IUPAC Working Party on "Modeling of Polymerization Kinetics and Processes".[9] k_p is derived according to eq 1:

$$L_i = i k_p c_M t_0, \quad i = 1, 2, 3, ... \tag{1}$$

L_1 refers to the number of propagation steps between two pulses and is calculated according to $L_1 = M_1/M_{mon}$, where M_1 is identified by the first inflection point of the molecular weight distribution[10] and M_{mon} is the molar mass of the monomer. c_M is the monomer concentration and t_0 the time between two successive laser pulses. The existence of a second or even a third inflection point at degrees of polymerization around $L_2 = 2L_1$ and $L_3 = 3L_1$ indicates that the shape of the molecular weight distribution (MWD) is controlled by the pulsed initiation of the polymerization and serves as a consistency criterion for k_p determination via PLP−SEC.[11,12] In addition to the knowledge of reliable k_p data, modeling of polymerization processes requires information on the termination kinetics. Here, chain-length averaged termination rate coefficients, $<k_t>$ were derived from conversion time data obtained from in-line Fourier transform near infrared (FTNIR) spectroscopy applied to chemically initiated polymerizations.

Scheme 1



Experimental Section

Materials. The monomer 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate (TDFOMA, Aldrich, 97%) was passed through a column filled with aluminum oxide (Aldrich) before use to remove the inhibitor and stored unter nitrogen atmosphere at 2 °C. Hexafluoroisopropanol (Fluorochem, 99%) with potassium trifluoroacetate (Fluka, 99%) used as eluent for SEC as well as the photoinitiator, 2-methyl-4′-(methylthio)-2-morpholinopropiophenone (MMMP, Aldrich, 98%) and the chain transfer agent *n*-dodecyl mercaptan (DDM, Merck, 99.5%) were used as received. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization from methanol prior to use in chemically initiated polymerizations.

Size-Exclusion Chromatography. Molecular weight distributions were obtained by size-exclusion chromatography (SEC) using an Agilent 1200 isocratic pump, an Agilent 1200 refractive index detector, a viscosity detector (ETA 2010, WEG Dr. Bures), and two PSS PFG columns (7 μm, 8 × 300 mm, pore sizes 100 and 300 Å). Hexafluoroisopropanol containing 0.05 mol·L^{-1} potassium trifluoroacetate at 35 °C and a flow rate

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Table 1. Reaction Conditions, Dispersity Index, *PDI*, and Number Average Molecular Weights Based on PMMA Calibration, M_n*, of TDFOMA Polymers Used for SEC Calibration[a]

sample	c_{AIBN}/ mol·L^{-1}	c_{DDM}/vol %	t/ min	M_n*/ g·mol^{-1}	$M_{n,TDFOMA}$/ g·mol^{-1}	*PDI*
P1	0.05	2.5	48	8000	31 000	1.5
P2	0.05	0.5	42	40 000	208 000	1.5
P3	0.2	0.7	32	31 000	153 000	1.4
P4	0.1	0.9	54	11 000	45 000	1.5

[a] $M_{n,TDFOMA}$, was obtained with eq 2, using $K = 0.0162$ mL·g^{-1} and $a = 0.709$ for PMMA and $K = 0.0248$ mL·g^{-1}, and $a = 0.444$ for TDFOMA.

of 1 mL·min^{-1} was used as eluent. The SEC setup was calibrated against PMMA standards of narrow dispersity (molecular weights between 500 and 1×10^6 g·mol^{-1}, PSS). Determination of K and a values was carried out with precisely known polymer concentrations between 4 and 5 mg·mL^{-1}.

Viscosity Measurements. Viscosities of bulk TDFOMA and methyl methacrylate were measured at 25 °C with a rotational rheometer (Bohlin Gemini, Malvern) equipped with a 1° 40 mm cone−plate system with a gap of 30 μm. For both monomers two measurements were carried out with (*i*) variation in shear rate from 0.001 to 1000 Hz and (*ii*) variation in shear stress between 0.003 and 3 Pa.

Chemically Initiated Polymerizations. Polymers for determination of Mark−Houwink parameters were obtained from chemically initiated TDFOMA bulk polymerizations at 60 °C with AIBN as initiator and dodecyl mercaptan as chain transfer agent. The reactions were carried out under nitrogen atmosphere in sample vials placed in a heating block. The concentrations of AIBN, c_{AIBN}, and of DDM, c_{DDM}, as well as reaction time, t, number-average molecular weights, M_n*, and dispersity, *PDI*, are given in Table 1. M_n* and *PDI* are based on PMMA calibration. $M_{n,TDFOMA}$ gives the number-average molecular weight after transformation according to eq 2 with the K and a values given below. To separate the polymer the reaction mixture was precipitated in methanol. The liquid phase was decanted and the precipitated polymer washed with methanol several times. Then, for purification the polymer was dissolved in HFIP and precipitated in methanol several times. Finally, the polymer was dried in high vacuum.

Pulsed Laser Initiated Polymerization. Pulsed laser initiated polymerizations were carried out at temperatures ranging from 10 to 60 °C using a thermostated cuvette (Hellma 165 QS, 10 mm path length). Temperature was controlled via a thermostat with a recirculating mixture of water. The temperature was monitored during laser irradiation using a digital thermometer (Testo 735−2) equipped with a 1 mm diameter external probe placed inside the cell and located at the center of the laser beam pathway. The response time and the precision of the instrument are 1 s and ±0.1 °C, respectively. As a representative reaction temperature, the arithmetic mean of the temperatures measured prior to and after the PLP experiment was calculated. The difference between the initial and the final temperature during PLP ranges from 0.4 to 2.5 °C depending on the reaction conditions.

The polymerization was initiated using a Q−switched Nd:YAG laser (B. M. Industries, 5000 series) operating at 355 nm with a repetition rate of 10 Hz and a pulse energy of 6 mJ.

Results and Discussion

Molecular Weight Analyses. The calculation of k_p requires the precise knowledge of absolute molecular weights. Here, MWDs obtained from PLP experiments were analyzed on a SEC using the RI detector and employing the principle of universal calibration according to eq 2.[13]

$$\log(M_2) = \frac{1}{1+a_2}\log\frac{K_1}{K_2} + \frac{1+a_1}{1+a_2}\log(M_1) \qquad (2)$$

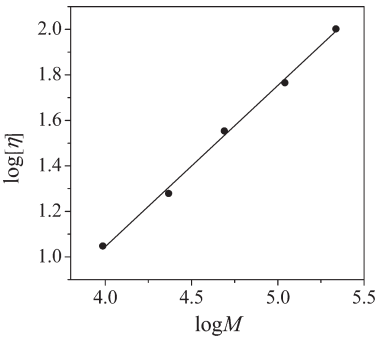

Figure 1. Mark−Houwink plot for narrow dispersity PMMA standards in HFIP.

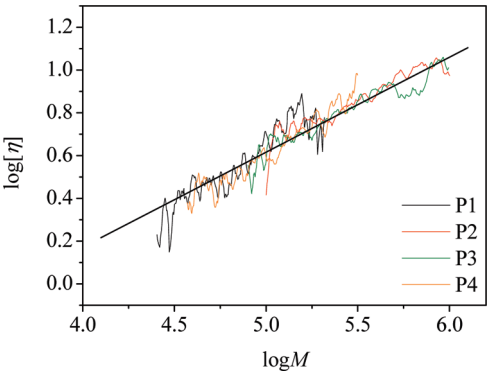

Figure 2. Variation of intrinsic viscosity with molecular weight of TDFOMA samples P1−P4 (Table 1). The full line represents a combined fit to all four samples.

Index 1 refers to the polymer used for calibration and index 2 to the polymer to be analyzed. The Mark−Houwink constants K and a for the fluorinated polymer were derived using a SEC setup with an RI and a viscosity detector based on polymers obtained via chemically initiated polymerizations. Since hexafluoroisopropanol (HFIP) containing 0.05 mol·L^{-1} potassium trifluoroacetate was used as eluent, additionally K and a of PMMA required for calibration were determined with low dispersity standards of PMMA. The Mark−Houwink plot for PMMA is given in Figure 1. According to eq 3 K and a were calculated.

$$[\eta] = KM^a \qquad (3)$$

At 35 °C the PMMA values are $K = 0.0162$ mL·g^{-1} and $a = 0.709$.

As discussed before,[13−15] for TDFOMA several polymers with varying molecular weights were used for the determination of K and a encompassing the molecular weight range of the inflection points of the PLP-derived MWDs. Details for the synthesis of polymers for calibration are given in the Experimental Section. Here, with four polymer solutions of precisely known concentration the variation of intrinsic viscosity, [η], with elution volume was measured. Using the above-mentioned calibration curve for PMMA and [η] data of the TDFOMA polymer the absolute molecular weight at every elution volume was accessible. Figure 2 gives the double logarithmic plots of [η] vs molecular weight for polyTDFOMA. A combined fit of all data yields a from the slope and K from the intercept with the y-axis. As demonstrated in Figure 2 the combined fit to all curves allows for a very good representation of all experimental data. The corresponding Mark−Houwink constants of TDFOMA are $K = 0.0248$ mL·g^{-1} and $a = 0.444$.

Table 2. Initial Monomer Concentration, c_M, Reaction Temperature, T, Absolute Molecular Weights at the First and Second Inflection Point, M_1 and M_2, Respectively, and Propagation Rate Coefficients, k_p, Calculated with M_1 for 1*H*,1*H*,2*H*,2*H*-Tridecafluorooctyl Methacrylate Bulk Polymerizations with a Pulse Repetition Rate of 10 Hz

c_M/mol·L^{-1}	T/°C	M_1/g·mol^{-1}	M_2/g·mol^{-1}	k_p/L·mol^{-1}·s^{-1}
3.54	11.3	54 400	115 000	355
3.54	12.6	54 600	115 000	357
3.48	27.0	90 700	197 000	603
3.48	27.0	88 600	183 000	589
3.43	41.2	139 000	323 000	938
3.43	41.8	137 000	301 000	926
3.36	60.5	239 000	586 000	1651
3.36	59.7	220 000	529 000	1519

Propagation Rate Coefficients. PLP experiments with bulk TDFOMA were carried out at a laser pulse repetition rate of 10 Hz, an initiator concentration of 2.5 mmol·L^{-1}, and laser pulse energies of 6 mJ between 11 and 60 °C. In all cases PLP-structured MWDs with two well resolved inflection points were obtained. For temperatures up to 42 °C the ratio of M_1/M_2 is close to 0.46, thus, fulfilling the above-mentioned consistency criterion. At the highest temperature the ratio is lowered to 0.42. This slight discrepancy may be due to the fact that the second inflection point occurs at rather high molecular weights, at the higher limit of the molecular weight range covered by the polymers used for calibration. Nevertheless, the molecular weight distributions and first derivative curves shown in Figure S1 of the Supporting Information clearly indicate that the shape of the MWD was controlled by pulse-wise chain initiation and termination. According to eq 1 k_p was calculated with L_1. The individual data are given in Table 2. c_M was calculated using the temperature dependence of the density, ρ, according to $\rho(T) = 1.550 - 1.65 \times 10^{-3}\, T/°C$. Density data were measured using an Anton Paar density meter as detailed elsewhere.[13]

The Arrhenius diagram of k_p is depicted in Figure 3. For comparison, the dashed and dotted lines representing the temperature dependence of methyl methacrylate (MMA) and dodecyl methacrylate (DMA) k_p were included. The data show that TDFOMA k_p is significantly higher than k_p for the alkyl methacrylates, whereas the slope of the lines is rather similar.

According to $\ln k_p = \ln A - E_a/(RT)$ the pre-exponential factor, A, and the activation energy, E_a, were calculated. E_a, A, and k_p at 25 °C are listed in Table 3 for TDFOMA, DMA, and MMA. As expected from Figure 3, the activation energy of TDFOMA k_p is very similar to the values for the alkyl methacrylates. Contrary, the pre-exponential of TDFOMA is significantly higher. Since the activation energy of TDFOMA k_p is not significantly different from the values for MMA and DMA it is unlikely that the reactivity of monomer and propagating radical is significantly affected by the fluorination of the ester group. This may be explained by the separation of the perfluorinated hexyl group and the carbonyl functionality by two methylene units. As pointed out by Heuts et al.[16,17] the geometry of the rotating groups in the reactants and in the transition state (TS) as well as the rotational potentials of the relevant internal motions in the transition state determine the pre-exponential factor. Thus, the finding of A being significantly enhanced compared to MMA and DMA may be assigned to a higher rotational mobility of the chain end in the TS structure, which may be caused by less intra- and intermolecular interactions involving the C_6F_{13} moiety of the ester group.

Previously, it was shown that the propagation rate may significantly be varied by the choice of the reaction media.[19]

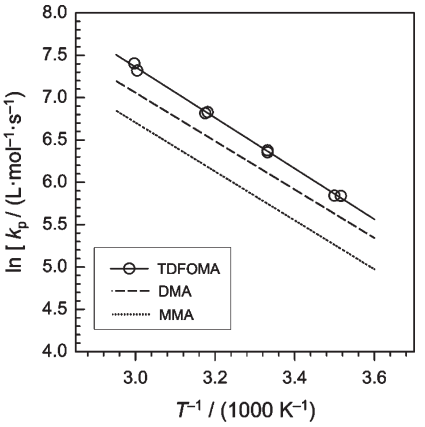

Figure 3. Temperature dependence of the bulk propagation rate coefficient for 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate (TDFOMA). Bulk data for methyl methacrylate (MMA) and dodecyl methacrylate (DMA) were taken from ref 18.

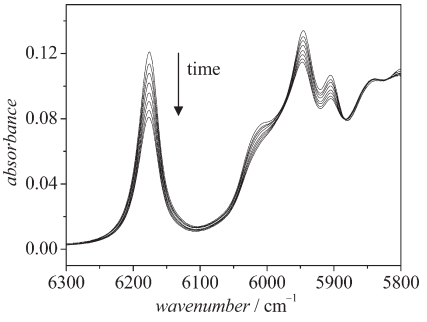

Figure 4. FT-NIR spectra series recorded during a polymerization of TDFOMA in bulk at 60 °C with 0.06 mol·L^{-1} AIBN.

Table 3. Activation Energy, E_a, Pre-Exponential Factor A, and k_p at 25 °C Calculated with the Given Values of E_a and A

monomer	E_a/ kJ·mol^{-1}	$A \times 10^{-6}$/ L·mol^{-1}·s^{-1}	k_p (25 °C)/ L·mol^{-1}·s^{-1}
TDFOMA	24.4	10.8	558
DMA[18]	23.8	6.2	422
MMA[18]	24.0	4.8	294

Depending on the type of solvent and type of interactions between solvent, monomer, and propagating radical the variations in k_p may range from a few percent to an order of magnitude. The studies into the solvent influence on k_p largely improved the understanding of the factors that determine k_p. Although polyTDFOMA solubility is poor in most conventional solvents, it seems interesting to extend the work to polymerizations in, e.g., supercritical CO_2 or ionic liquids to obtain a better understanding of the factors affecting the propagation reaction of fluorinated monomers.

Termination Rate Coefficients. Knowing the propagation rate coefficient k_p from PLP-SEC the termination rate coefficient $\langle k_t \rangle$ may be derived from the coupled parameter $k_p/\langle k_t \rangle^{0.5}$ accessible from the overall rate of polymerization, r_p, of stationary polymerizations. Here, TDFOMA bulk polymerizations carried out at 60 °C with 0.06 mol·L^{-1} AIBN were monitored by in-line FT-NIR spectroscopy. A typical spectra series is given in Figure 4.

To avoid plugging of the optical cell, the polymerizations were stopped at around 30% conversion. Within this range the polymerization proceeds in homogeneous phase. The number-average molecular weight of the polymer is around 1.7×10^6 g·mol^{-1}. The peak at 6176 cm^{-1} assigned to the

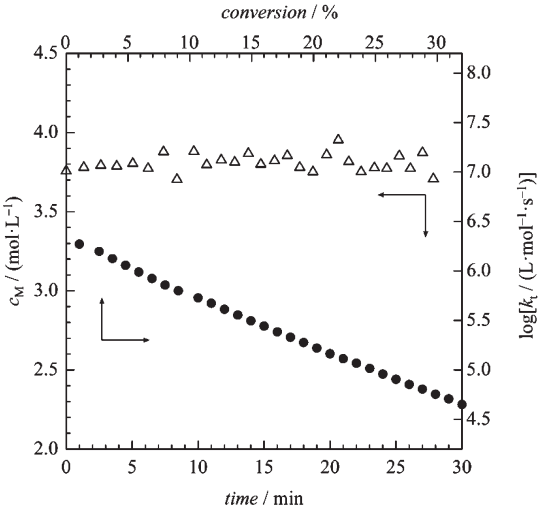

Figure 5. Monomer concentration as a function of time (circles) and conversion dependence of the chain-length averaged termination rate coefficient, $\langle k_t \rangle$, (triangles) derived from TDFOMA polymerization in bulk at 60 °C with 0.06 mol·L^{-1} AIBN.

CH-stretching vibration at the double bond decreases with time and integration of the half band from the peak maximum to 6250 cm^{-1}, against a horizontal baseline at 6300 cm^{-1}, yields monomer conversion as a function of time, which is depicted in Figure 5. The occurrence of a gel-effect was not observed. According to eq 4 r_p is related to the kinetic rate coefficients, c_M, and the initiator concentration c_I.

$$r_p = -\frac{dc_M}{dt} = \frac{k_p c_M}{\sqrt{\langle k_t \rangle}}\sqrt{f k_d c_I} \quad (4)$$

For a first estimate of $\langle k_t \rangle$ the AIBN decomposition rate coefficient, k_d, and the efficiency, f, reported for MMA were used: $f = 0.49$ and $k_d = 8.4 \times 10^{-6}$ s^{-1}.[20,21] The conversion dependence of $\langle k_t \rangle$ is depicted in Figure 5. Over the entire conversion range a constant value of $\langle k_t \rangle = 1.4 \times 10^7$ L·mol^{-1}·s^{-1} was obtained. This value is rather close to a value of 2×10^7 L·mol^{-1}·s^{-1} determined for MMA under similar conditions.[22] The finding is surprising, because generally chain-length averaged termination rate coefficients decrease with increasing length of the ester group,[23] e.g., DMA is associated with a significantly lower $\langle k_t \rangle$ of 2×10^6 L·mol^{-1}·s^{-1}.

Equation 4 shows that $\langle k_t \rangle$ is directly affected by uncertainties in f and k_d. It is known that f depends on the monomer structure. However, since the efficiency must lie between 0 and 1 the influence of uncertainties in f on $\langle k_t \rangle$ is minor. In addition, k_d depends on the environment. For example, AIBN decomposition in MMA at 60 °C is associated with a k_d value of 8.4×10^{-6} s^{-1}, whereas for decomposition in toluene or benzene a value of 9.6×10^{-6} s^{-1} was reported.[24] Obviously, the major difference between literature data and the TDFOMA system studied here is the degree of fluorination. So far, no information on the influence of fluorinated compounds on initiator decomposition are available. First studies into the decomposition of peroxide in the presence of a fluorinated solvent did not result in any differences compared to decomposition in heptane. It is a matter of priority to study AIBN k_d in a fluorinated environment in the future.

Since k_t is a diffusion controlled quantity it strongly depends on all factors influencing the mobility of the macroradical, e.g., such as radical chain length, i, and the visicosity, η, of the reaction mixture.[25−27] Generally, diffusion controlled rate coefficients, k_{diff}, may be estimated by the Smoluchowsky equation:[28]

$$k_{diff} = 2\pi N_A D_s R_c \quad (4)$$

where N_A is the Avogadro number, D_s the mutual diffusion coefficient of two reacting species, and R_c the capture radius of a reacting species. For a reaction of two radicals with identical chain length D_s may be estimated by $2D_i$, where D_i is the center-of-mass diffusion coefficient of an individual radical of chain length i. D_i may be obtained from the Stokes−Einstein equation that relates D_i to η^{-1} and r_{si}, the hydrodynamic radius of a radical of chain length i:[30]

$$D_i = \frac{k_B T}{6\pi r_{si}\eta} \quad (5)$$

with the Boltzmann constant k_B and temperature T. For methacrylate systems at low conversions the viscosity of monomer in case of bulk or of monomer/solvent mixtures in case of solution polymerizations may be used.[29,30] It was shown that frequently, e.g., for MMA or butyl methacrylate, k_t scales with the inverse of the viscosity, η^{-1}, of the initial reaction mixture. Moreover, the temperature dependence of k_t is associated with an activation energy that is close to E_a of η^{-1}, which was shown for, e.g., the chain-length averaged termination rate coefficient, $\langle k_t \rangle$, of styrene[31] and for the termination rate coefficient of two monomeric radicals, $k_t^{1,1}$. For example, just recently $k_t^{1,1}$ for MMA was determined. $E_a = 8.9$ kJ·mol^{-1} of $k_t^{1,1}$ was reported,[32] which is in excellent agreement with $E_a = 9.0$ kJ·mol^{-1} of η^{-1}.[33]

To test whether the rather similar $\langle k_t \rangle$ data for MMA and TDFOMA may be explained on the basis of viscosity data, bulk monomer viscosities were measured. Because of experimental limitations the viscosities of MMA and TDFOMA were determined at 25 °C. For MMA the viscosities measured are 0.53 mPa·s and 0.45 mPa·s, depending on whether the shear rate or shear stress were varied. These data are in excellent agreement with literature data of 0.53 mPa·s at 25 °C reported by Stickler et al.[33] For TDFOMA viscosities of 4.52 mPa·s and 4.45 mPa·s were measured upon variation of shear rate or shear stress, respectively. Since the difference in viscosity amounts to almost 1 order of magnitude, it is safe to assume that the TDFOMA viscosity at the polymerization temperature of 60 °C is still significantly higher than that of MMA. The viscosity data indicate that the slight differences in $\langle k_t \rangle$ of MMA and TDFOMA cannot be assigned to viscosity.

It is worth pointing out that for hydrocarbon systems, too, additional influences, namely shielding effects, on k_t were discussed in the past. Detailed investigations into the chain length dependence of k_t were carried out for a number of methacrylates with different ester groups, e.g., alkyl groups of different lengths and cyclic ester groups. The results suggest that viscosity is not the only determining factor. For example, MMA and DMA $k_t^{1,1}$ values of 5.8×10^8 L·mol^{-1}·s^{-1} (5 °C)[32] and 1×10^7 L·mol^{-1}·s^{-1} (0 °C),[34] respectively, were derived. As discussed in ref 34, the difference for the two monomers is too large to be explained exclusively by viscosity. In fact, besides viscosity sterical effects appear to be important. In case of DMA polymerizations it was stated "the long dodecyl groups physically block what would otherwise be successful termination encounters".[34] Thus, in case of DMA bulk $k_t^{1,1}$ viscosity and shielding effects are responsible for the rather low value of $k_t^{1,1}$. The interplay of segmental mobility, viscosity and

shielding effects was also discussed for the isomers butyl methacrylate and *tert*-butyl methacrylate.[35]

A second example for k_t not being solely controlled by viscosity are $\langle k_t \rangle$ data for polymerizations of methyl acrylate (MA) and dodecyl acrylate (DA) in solution with $scCO_2$.[23,36] For both monomers, the addition of CO_2 to the reaction mixture results in a lowering in viscosity and consequently an enhancement in $\langle k_t \rangle$ should occur. However, while the addition of 40 wt % of CO_2 led to an increase in DA $\langle k_t \rangle$ by a factor of 8, it was found that MA $\langle k_t \rangle$ is not affected by the presence of the same amount of CO_2. The finding was explained by strong sterical shielding of the radical sites by the long alkyl ester groups in case of DA. A lowering in viscosity due to the presence of CO_2 allows for higher mobility of the radical chain ends and a higher chain end encounter frequency, which causes an enhancement of k_t in the presence of CO_2. In case of MA sterical shielding of the methyl ester group is not very effective and consequently an increase in mobility has no significant influence on $\langle k_t \rangle$. It goes without saying that due to the experimental scatter of the data it cannot be excluded that there is a small influence of CO_2 and thus of viscosity on MA $\langle k_t \rangle$.

For the same reasons as discussed for DMA it is expected that the fluorinated octyl ester group of TDFOMA also leads to effective shielding of the radical sites and consequently $\langle k_t \rangle$ of TDFOMA should be significantly lower than for MMA. However, the rather similar $\langle k_t \rangle$ values for TDFOMA and MMA suggest that the shielding action of the fluorinated octyl group is less effective. The Stokes−Einstein equation relates D_i to the hydrodynamic radius of the species, too. At first sight the hydrodynamic radius of TDFOMA should be higher than that for MMA and consequently TDFOMA $\langle k_t \rangle$ should be lower. However, the hydrodynamic volume is not only given by the size of the monomer units but also by interactions of the polymer with its environment. In poor solvents smaller polymer hydrodynamic volumes are found than in good solvents. Here, polyTDFOMA in its monomer is considered. PolyTDFOMA is a partially fluorinated polymer with a perfluorinated hexyl end of the ester group on the one hand side and the nonfluorophilic polymer backbone and ester group including the first two nonfluorinated ester methylene units on the other side. It is expected that the C_6F_{13} fragment of the ester group and the polymer backbone including the carbonyl groups are not compatible, which may be envisaged as a phase separation on the molecular level. This explanation is in line with the use of highly fluorinated (meth)acrylates in block copolymers, where incompatibility and demixing leads to self-organization and, e.g., the formation of multicompartment micelles.[2] Recently, it was shown that already 1*H*,1*H*-heptafluorobutyl methacrylate monomer units in a triblock copolymer induce the formation of micelles.[3] In TDFOMA the degree of fluorination is significantly higher and incompatibility on the molecular level should occur to a larger extend. To prove this explanation, in future experiments the influence of a solvent, e.g., supercritical CO_2 or ionic luqies, on the termination kinetics will be studied. Moreover, fluorinated monomers with differing ester size and degree of fluorination will be investigated.

The results presented suggest that the termination kinetics in TDFOMA cannot solely be explained by viscosity effects. In addition, conformational changes due to the partial fluorination appear to play an important role.

Conclusions

Both kinetic rate coefficients, k_p and $\langle k_t \rangle$, for TDFOMA are significantly higher than corresponding data for nonfluorinated alkyl methacrylates. The differences for $\langle k_t \rangle$ are much more pronounced than for k_p. The findings are suggested to be due to less intra- and intermolecular interactions involving the macroradicals. The findings also suggest that previously reported very low rates of polymerization for fluorinated monomers in conventional free radical polymerizations as well as in RAFT or ATRP are not due to a low k_p value, but may be due to phase behavior issues.

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Supporting Information Available: Figure S1, showing molecular weight distributions and first derivative curves of poly(1*H*,1*H*,2*H*-tridecafluorooctyl methacrylate) obtained from pulsed laser initiated polymerizations of the bulk monomer at 20, 40, and 60°. This material is available free of charge via the Internet at http://pubs.acs.org.

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