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Homogeneous Phase Polymerization of Vinylidene Fluoride in Supercritical CO_2: Surfactant Free Synthesis and Kinetics

Sabine Beuermann, M. Imran-ul-haq*

Summary: Vinylidene fluoride (VDF) polymerizations were carried out in homogeneous phase with supercritical carbon dioxide ($scCO_2$) at 120 °C and 1500 bar. To control molecular weight perfluorohexyl iodide was used. Molecular weight analysis by size-exclusion chromatography indicates that polymers of low polydispersities ranging from 1.5 to 1.2 at the highest iodide concentration of 0.25 $mol \cdot L^{-1}$ were obtained. In addition, polymer molecular weight increases linearly with reaction time, indicating that living conditions were established. The "livingness" is based on the labile C-I bond. The weakness of the C-I bond is associated with a fast decomposition of the original hexyl iodide, thus, contributing to initiation and to a significant increase in the initiation rate in the initial phase of the polymerization.

Keywords: living radical polymerisation; polymerization kinetics; supercritical CO_2; vinylidene fluoride

Introduction

Fluorinated polymers gained large interest for technical applications due to their unique properties, such as excellent chemical, thermal, and mechanical stability as well as piezoelectric and pyroelectric properties.[1–3] These properties lead to ample technical applications, e.g., such as valves, coatings, films, cables, pipes and membranes for fuel cells.[4] Generally, these polymers are synthesized in heterogeneous phase, either in precipitation polymerizations or more frequently in emulsion polymerizations. The latter generally affords the use of fluorinated stabilizers,[5] which have a high potential for bioaccumulation.[6] Supercritical carbon dioxide ($scCO_2$) has emerged as an attractive alternate solvent. Besides being environmentally benign interesting features of $scCO_2$ for polymer applications are a reduction in viscosity and easy separation from polymeric products under mild conditions yielding dry polymer product. In addition, it may allow for a reduction in the residual monomer content.

Although fluorinated polymers show considerably higher solubility in $scCO_2$ than non-fluorinated polymers, most reports on the synthesis of fluorinated polymers in the presence of $scCO_2$ deal with heterogeneous phase reactions, either precipitation or emulsion polymerizations. In the latter frequently F-containing stabilizers are used to obtain fine particles and to avoid agglomeration upon expansion of the reaction mixture.[5] Special care has to be taken to remove these stabilizers from the product. With respect to an environmentally acceptable process and to saving resources it is advantageous to avoid the use of any stabilizers. In addition, the application of stabilizers adds more complexity to the system, such as choice of appropriate stabilizer, concentration, phase transfer processes, polymerization in different phases. Thus, it seems attractive to carry out the reaction in homogeneous phase. In addition, homogeneous phase polymerizations are advantageous for car-

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University of Potsdam, Institute of Chemistry, Karl-Liebknecht-Str. 24-25, 14476 Golm, Germany
E-mail: sabine.beuermann@uni-potsdam.de

rying out continuous polymerizations in a tubular reactor, which would allow for a reduction in reactor size and increase the inherent safety of the process.

Recently, we reported that VDF polymerizations may be carried out up to complete monomer conversion in $scCO_2$.[7] To achieve a homogeneous mixture throughout the entire reaction molecular weights (MW) below 10^4 $g \cdot mol^{-1}$ were required. Such low MW polymers may be used in coatings applications. In the first experiments MW control was achieved by the initiaton rate of di-*tert.*-butyl peroxide (DTBP). However, to yield low MW material very high initiator concentrations up to around 10 wt.% were required. With respect to a safe process the initiator concentration had to be lowered. In this publication we report about the use of perfluorohexyliodide to control MW.

Experimental Part

The monomer vinylidene fluoride (VDF, 99% *Solvay S.A.*, Tavaux, France), the initiator di-*tert.* butyl peroxide (DTBP, 99% kindly provided by *AKZO Nobel*), carbon dioxide (CO_2, grade 4.5, Messer Griesheim), the chain-transfer agent perfluorohexyliodide ($C_6F_{13}I$, Dyneon, Germany), N,N′-dimethyl acetamide (DMAc, 99% pure, *Acros*) and LiBr (*Sigma-Aldrich*, 99%) used as eluent for size-exclusion chromatography were all used as received.

The polymerization mixtures consisting of VDF monomer, CO_2, DTBP, and the chain transfer agent (CTA) were mixed, followed by stirring at 0 °C and 250 bar for one hour to obtain a homogeneous mixture. Then, the mixture is transferred into the reaction cell while keeping the pressure constant to avoid demixing. A detailed description of the set-up used to prepare the reaction mixtures and the filling procedure was given elsewhere.[7,8] Polymerizations were carried out in optical high-pressure cells[9] allowing for in-line measurement of monomer conversion by FT-NIR spectroscopy. In addition, the homogeneity of the reaction mixture may be monitored.[10]

A Bruker Vertex 70 spectrometer equipped with an InSB detector, a halogen lamp and a silicon coated CaF_2 beamsplitter is used to measure NIR spectra during the reaction. The resolution was 2 cm^{-1} and a Blackman-Harris three-term function was applied for apodization. 10 scans were used. The first overtone of the olefinic CH-stretching vibration of the monomer is used to calculate monomer concentration as a function of time. A typical spectra series recorded during a VDF polymerization at 120 °C and 1500 bar with 73 wt.% CO_2, $c_{DTBP} = 0.061$ $mol \cdot L^{-1}$ and $c_{CTA} = 0.25$ $mol \cdot L^{-1}$ is shown in Figure 1. The peak at 6303 cm^{-1} is assigned to the CH stretching vibration at the double bond. As indicated by the arrow the peak intensity decreases with reaction time. In the last spectrum no absorption is seen at 6303 cm^{-1}, showing that complete monomer conversion was reached. The reaction time was 130 min. The two small peaks at 6214 and 6332 cm^{-1} (indicated by an asterisk) refer to the absorbances of CO_2 and are unchanged. The baselines of the spectrum were not corrected and, thus, indicate that the system was homogeneous throughout the polymerization.

To determine monomer conversion as a function of reaction time the FT-NIR spectra recorded during the reactions were analyzed in the region of the first overtone of the olefinic CH stretching vibration. The half band was integrated from the peak maximum at 6303 cm^{-1} to 6450 cm^{-1} with the higher wavenumber point defining a horizontal baseline. Prior to integration the CO_2 contributions to the spectrum were subtracted using a CO_2 spectrum recorded at identical temperature and pressure. Monomer conversion x was calculated according to Equation (1):

$$x = 1 - \frac{Int(t) - Int(t=0)}{Int(t=0)} \qquad (1)$$

$Int(t=0)$ and $Int(t)$ are the integrals at time zero and at time t, respectively. After

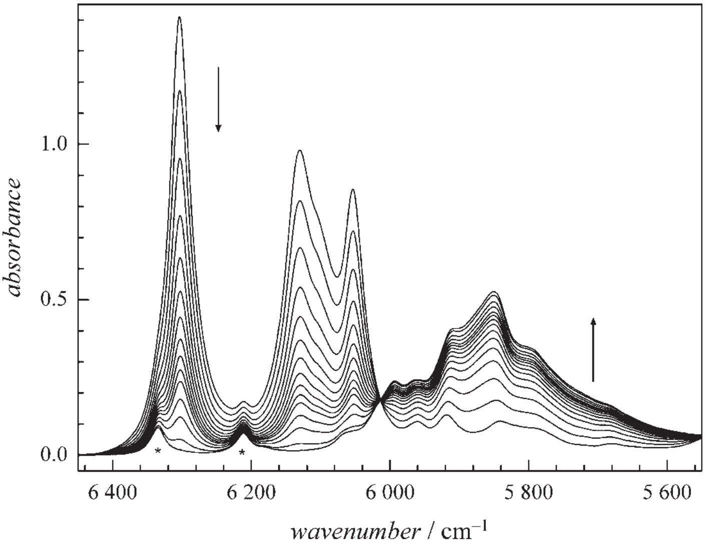

Figure 1.

NIR spectral series recorded during a VDF polymerization in the presence of 73 wt.% CO_2 at 120 °C and 1500 bar. The initial monomer concentration was 3.66 mol · L^{-1}, $c_{DTBP} = 0.061$ mol · L^{-1}, $c_{CTA} = 0.25$ mol · L^{-1}; optical path length 15 mm; final monomer conversion 98%. * indicate absorbances due to CO_2.

depressurizing the reaction cell the polymer is collected and analyzed. Molecular weight distributions (MWDs) are measured with a size-exclusion chromatography set-up consisting of an Agilent 1200 isocratic pump, an Agilent 1200 refractive index detector, and two GRAM columns (10 μm, 8 × 300 mm, pore sizes 100 and 1000) from Polymer Standards Services. N,N′-dimethylacetamide containing 0.1% LiBr was used as eluent and the column temperature was 45 °C. The SEC set-up was calibrated using low polydispersity polystyrene standards (PSS), since PVDF standards were not available.

Results and Discussion

VDF polymerizations were carried out at 120 °C and 1500 bar in the presence of $C_6F_{13}I$ concentrations ranging from 0.073 to 0.25 mol · L^{-1} to investigate the influence of chain transfer agent concentration (c_{CTA}) on molecular weight. The initial concentrations of monomer and DTBP were 3.66 mol · L^{-1} and 0.061 mol · L^{-1}. Figure 2 shows the molecular weight distributions obtained from SEC analysis. A clear shift to lower molecular weights is observed upon increasing the CTA concentration. In all cases rather narrow monomodal MWDs were obtained. The associated number average molecular weights and polydispersities are listed in Table 1, together with CTA concentrations and the monomer conversions reached.

As expected the M_n values are lowered significantly upon increasing CTA concentration. The polydispersities are all quite low ranging from 1.5 to 1.2 at the highest CTA concentration. Polydispersity values of 1.2 may not be obtained from conventional radical polymerizations and are indicative of a living radical polymerization system. To test for livingness a set of poly merizations at the same reaction conditions was carried out using 0.081 mol · L^{-1} CTA and 0.061 mol · L^{-1} DTBP. The reactions were stopped after different reaction times ranging from 15 to 166 min and MWDs of the polymers were measured. The asso-

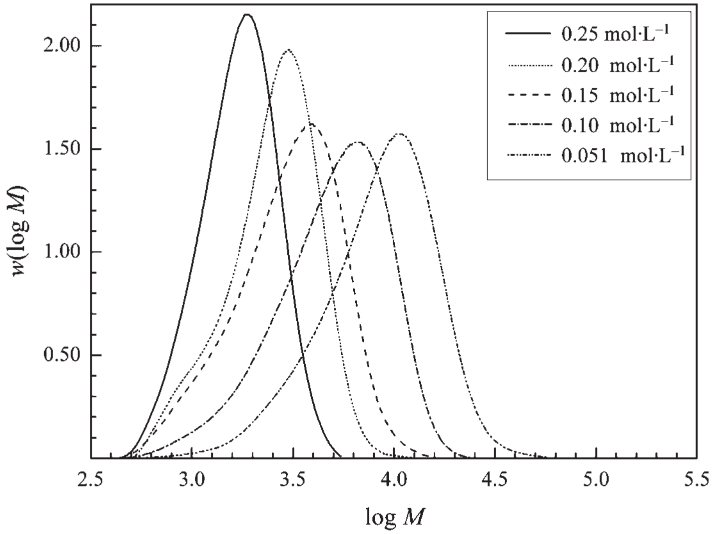

Figure 2.
Molecular weight distributions for polymer obtained from VDF poly- merization at 120 °C and 1500 bar in the presence of 73 wt.% CO_2, with 0.061 $mol \cdot L^{-1}$ DTBP, 3.66 $mol \cdot L^{-1}$ VDF and 0.05 to 0.25 $mol \cdot L^{-1}$ $C_6F_{13}I$ as indicated.

ciated M_n values are plotted as a function of monomer conversion, x, derived from the NIR spectra, in Figure 3.

The data in Figure 3 indicate already for a rather low c_{CTA} of 0.081 $mol \cdot L^{-1}$ a linear increase of M_n with monomer conversion, which is typical for living radical polymerizations. The finding of a living system is in good agreement with literature reports on iodine transfer polymerizations of VDF in acetonitrile at 75 °C employing fluorinated alkyl iodides.[11]

To study the kinetics of the VDF polymerizations the FT-NIR spectra recorded during the polymerizations were integrated as described above and monomer conversions were calculated. Figure 4 gives the variation of conversion with time for VDF polymerizations at 120 °C and 1500 bar. The data were restricted to 40% of conversion because of the pressure drop associated with the isochoric reaction cell. Up to 40% of conversion the pressure decreases from the initial value of 1500 bar to around 1300 bar. At the end of the reaction at complete monomer conversion the residual pressure was 1100 bar. Thus, the following discussion will be restricted up to conversions of 40%. We refrained from keeping the pressure constant by adding more CO_2 to the reaction cell to avoid the associated variation in mixture composition, because not only the phase behavior would have been negatively influenced, but also the kinetic analysis would have been more complicated.

Surprisingly, the conversion *vs.* time data in Figure 4 show that the polymerizations proceed faster with increasing c_{CTA}: While 40% VDF conversion were reached within 125 s at the highest c_{CTA}, 516 s were required to reach 40% conversion at the lowest c_{CTA}. Another difference is seen in the time dependence of the conversion data. At the lowest c_{CTA} of 0.05 $mol \cdot L^{-1}$ from 5 to 40% conversion a rather linear

Table 1.
Monomer conversions and molecular weight data for VDF polymerizations at 120 °C, 1500 bar with $c_{DTBP} = 0.062$ and $c_{VDF} = 3.66$ $mol \cdot L^{-1}$

$c_{CTA}/mol \cdot L^{-1}$	x	$M_n/g \cdot mol^{-1}$	M_w/M_n
0.051	90	6700	1.5
0.10	90	3900	1.5
0.15	90	2500	1.4
0.20	>97	1800	1.2
0.25	>98	1600	1.2

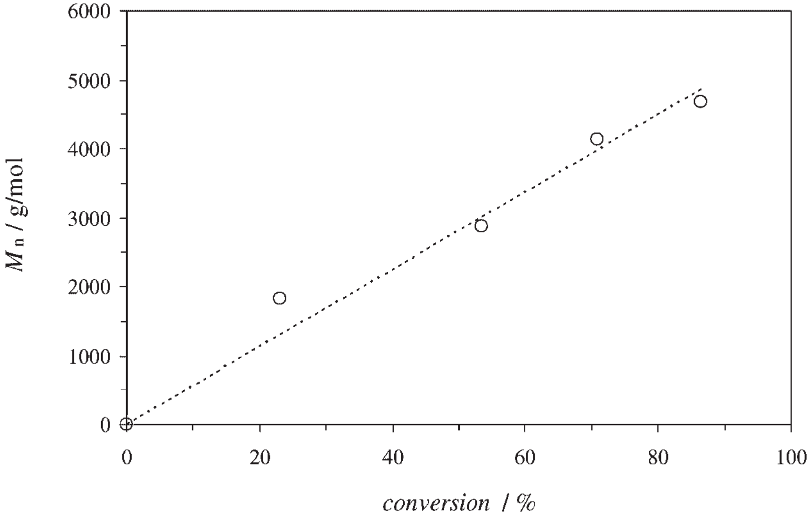

Figure 3.
M_n vs. conversion data derived from VDF polymerizations at 120 °C, 1500 bar with $c_{DTBP} = 0.061$ mol · L^{-1} and $c_{CTA} = 0.081$ mol · L^{-1}. dashed line: linear fit of the experimental data.

increase in x with time is found. This behavior is typical for living systems and is in good agreement with the molecular weight data presented in Figure 3. At the higher CTA concentrations an initial steep increase is followed by a levelling-off of the increase. The conversion – time data were used to calculate the rate of polymerization, r_p, according to $r_p = -dc_M/dt$. Figure 5 gives r_p as a function of time 5.

Within experimental uncertainty the rate of polymerization is almost constant at the lowest c_{CTA} of 0.051 mol · L^{-1}. With increasing c_{CTA} higher initial values of r_p

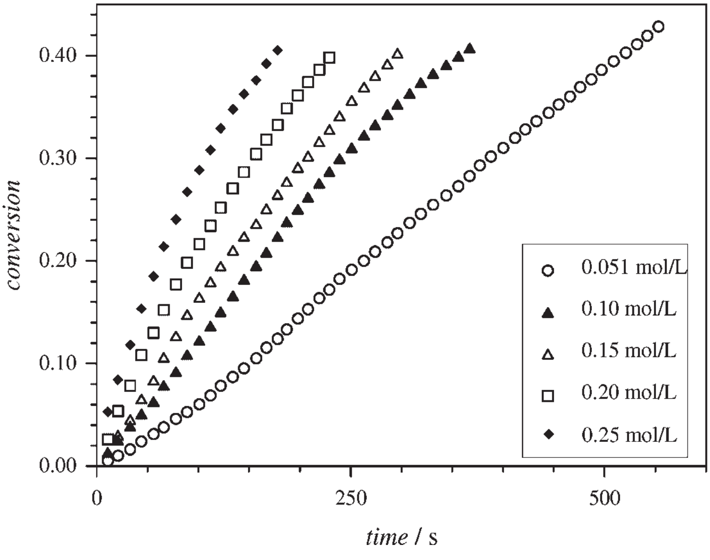

Figure 4.
Conversion-time data from VDF polymerization at 120 °C, 1500 bar with 73 wt.% CO_2, 0.061 mol · L^{-1} DTBP, 3.66 mol · L^{-1} VDF and $C_6F_{13}I$ concentrations as indicated.

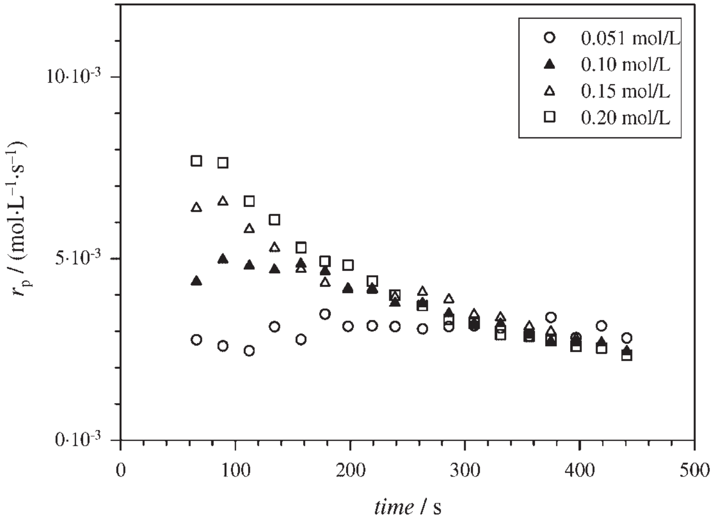

Figure 5.
Time dependence of r_p for VDF polymerizations at 120 °C and 1500 bar with $c_{VDF} = 3.66$ mol · L^{-1} and $c_{DTBP} = 0.061$ mol · L^{-1}. $C_6F_{13}I$ concentrations as indicated in the legend.

are observed. At the highest c_{CTA} of 0.25 mol · L^{-1} r_p is around a factor of 3 higher than for the lowest c_{CTA}. At higher times the r_p values approach the data for $c_{CTA} = 0.051$ mol · L^{-1}. At around 320 s no significant difference is seen in r_p of the four polymerizations. This finding may be explained considering the characteristics of living radical polymerizations. The prerequisite of successful living radical polymerizations is suppress chain-stopping events by decreasing the concentration of free radicals. To achieve this goal active propagating radicals are in an dynamic equilibrium with a larger amount of dormant species,[12] e.g., as in iodine transfer polymerizations.[13] The mechanism may be described as reversible addition fragmentation transfer and is illustrated in Scheme 1.[11]

The reversibility of the chain stopping event with an iodine atom is based on the weakness of the C-I bond. The original CTA agent also contains such a labile C-I bond, which may break at higher temperatures resulting in the formation of radical species. Thus, the CTA contributes to the initiation process and increases the initiation rate. As a consequence the rate of polymerization is enhanced. The finding that the r_p *vs.* time curves in Figure 5 coincide at around 320 s suggests that at this time already all of the original perfluorohexyl iodide is decomposed. To test for the ability of $C_6F_{13}I$ to initiate polymerization a reaction mixture without any DTBP was prepared. The concentration of the CTA was 0.073 mol · L^{-1} and the VDF concentration 3.66 mol · L^{-1} as before. At 120 °C and 1500 bar 30% of conversion were obtained in 900 min. To test whether the monomer itself may initiate the polymerization an additional reaction with CCl_3Br as CTA was carried out in the absence of any DTBP at otherwise the same conditions. Since no conversion was obtained in this control experiment it may be concluded that the perfluorohexyl iodide significantly contributes to the initiation.

$$P_n^{\bullet} + P_m\text{–I} \rightleftharpoons P_n\text{–I} + P_m^{\bullet}$$

Scheme 1.

The rate of polymerization is related to the individual rate coefficients according to Equation (2):

$$r_p = -\frac{dc_M}{dt} = \sqrt{f \cdot k_d \cdot c_I} \cdot \frac{k_p}{\sqrt{k_t}} \cdot c_M \qquad (2)$$

with the initiator efficiency, f, the initiator decomposition rate coefficient, k_d, the initiator concentration, c_I, propagation and termination rate coefficients, k_p and k_t, respectively, and the monomer concentration, c_M. From Equation (2) follows that the coupled parameter $k_p/k_t^{0.5}$ may be calculated according to Equation (3):

$$\frac{k_p}{\sqrt{k_t}} = -\frac{dc_M}{dt} \cdot \frac{1}{\sqrt{f \cdot k_d \cdot c_I}} \cdot \frac{1}{c_M} \tag{3}$$

Equation (3) only accounts for initiation by DTBP decomposition. Thus, it may only be applied at reaction times where no contribution from decomposition of the perfuorinated hexyl iodide is to be expected. Previously, it was shown that the polarity of the medium has a significant impact on k_d of peroxide initiators.[14] Thus, it is to be expected that k_d of DTBP for the VDF polymerization may be higher than k_d determined in a non-polar environment. However, decomposition data for DTBP in such polar media are not yet available. Thus, for a first analysis the k_d data published for DTBP decomposition in *n*-heptane as a function of pressure and temperature were adopted.[15] During high-pressure high-temperature ethene polymerizations the efficiency for DTBP derived radicals was determined to be 1.[15,16] This value should also hold for the system under investigation in this work.

With $k_d = 6.4 \cdot 10^{-6}$ s^{-1}, $f = 1$ and $r_p = 3.07 \cdot 10^{-3}$ mol · L^{-1} · s^{-1} at 40% conversion a value of 2.23 L$^{0.5}$ · mol$^{-0.5}$ · s$^{-0.5}$ is derived for $k_p/k_t^{0.5}$ according to Equation (3). For comparison with literature $k_p/k_t^{0.5}$ has to be estimated for 75 °C and ambient pressure. The activation volume $\Delta V^{\#}$ ($k_p/k_t^{0.5}$) = –25 cm^3/mol was taken from Mueller et al.[17] The activation energy of $k_p/k_t^{0.5}$ was estimated to be similar to the corresponding value for ethene polymerizations due to structural similarity of the monomers. The electron withdrawing F-atoms at the double bond in VDF are expected to decrease the electron density at the double to some extent and the reactivity of the monomer towards the attack of radical should be slightly enhanced compared to ethene polymerizations. Further, the electron withdrawing F-atoms will contribute to some stabilization of the propagation radical, thus, increasing the stability of the radical compared to radicals in ethene polymerizations. Thus, the activation energy of k_p, which is largely determined by radical stability and monomer reactivity should be similar to $E_A(k_p) = 34$ kJ · mol^{-1} for ethene.[18] Similarly, $E_A(k_t)$ for both monomers should differ significantly. Generally, $E_A(k_t)$ is between 0 and 10 kJ · mol^{-1}.[19] Thus, the ethene value of 5 kJ · mol^{-1} should constitute a good estimate for VDF. To estimate $k_p/k_t^{0.5}$ at 75 °C $E_A(k_p/k_t^{0.5}) = 31.5$ kJ · mol^{-1} was used. As a result $k_p/k_t^{0.5} = 0.24$ L$^{0.5}$ · mol$^{-0.5}$ · s$^{-0.5}$ is obtained at ambient pressure and 75 °C. Considering the uncertainties of the parameters used this value is remarkably close to a literature value of $k_p/k_t^{0.5} = 0.14$ L$^{0.5}$ · mol$^{-0.5}$ · s$^{-0.5}$ published for a kinetic analysis based on NMR conversion data.[20]

It goes without saying that further kinetic experiments are required to determine reliable values for $k_p/k_t^{0.5}$ and the associated activation parameters. One prerequisite for such reliable data is to understand how the polar reaction medium influences the decomposition kinetics of the initiator used. It is a matter of priority to study the influence of fluorinated compounds on initiator decomposition.

Conclusions

VDF radical polymerizations in homogeneous phase with scCO$_2$ may be carried out up to complete monomer conversion at 120 °C and 1500 bar. Excellent control of molecular weight may be achieved using perfluorohexyl iodide. In agreement with literature the linear increase in M_n with time and conversion indicates that a living radical polymerization is occurring. It is remarkable to note that polymer from reactions up to complete monomer conversion shows a polydispersity of 1.2. The monomer conversion – time data may be used to estimate the rate of polymerization and $k_p/k_t^{0.5}$. The rate data indicate that $C_6F_{13}I$ does not only control molecular weight but also significantly contributes to the initiation rate.

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