Effects of Pressure and Temperature on the Kinetics of L-Lactide Polymerization in Supercritical Chlorodifluoromethane

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ABSTRACT: The ring-opening polymerization of L-lactide initiated by 1-dodecanol/stannous 2-ethylhexanoate (DoOH/Sn(Oct)$_2$) was carried out in supercritical chlorodifluoromethane at pressures ranging from 180 to 360 bar and at temperatures ranging from 100 to 130 °C. Increasing the pressure resulted in an accelerated polymerization rate. The activation volume for $[DoOH]_0/[Sn]_0 = 0$ was determined to be -50 cm^3/mol. The partial bond formation in the transition state contributed to the negative value of the activation volume and the pressure-induced acceleration in the rate of L-lactide polymerization, i.e., by producing a four-center transition state and a lower partial molar volume. A further stabilization of the transition state in terms of the activation volume of -61 cm^3/mol by the use of DoOH ($[DoOH]_0/[Sn]_0 = 1.0$) can be explained by sterically crowded transition state. A computational study using semiempirical methods showed the transition state is subject to weak electrostriction effects. The observed activation energy (88.7 kJ/mol), which is higher than that in bulk, reflects a partial blocking of the active coordinate site by chlorodifluoromethane.

Introduction

Supercritical carbon dioxide (scCO$_2$) has been shown to be a promising alternative solvent medium for polymerization by Desimone and others,[1−3] but its practical use has been limited because of the need for high CO$_2$ pressure to dissolve even small amounts of polar, amphiphilic, organometallic, or high-molecular-mass compounds,[2,4−7] which reduces the number of possible homogeneous polymerizations to an extremely narrow range. In many cases, either unrealistically high pressures or expensive "CO$_2$-philic" materials (substance with a high affinity for CO$_2$ solution at lower pressures) are needed. Thus, most studies have focused on heterogeneous-phase polymerizations and on the development of new "CO$_2$-philic" materials.[8] Beckman et al.[2] introduced a new strategy for designing CO$_2$-philic materials from readily available components, which overcomes some of the oldest prejudices concerning the solvent properties of CO$_2$. Moreover, the literature reflected an increasing interest in the ring-opening polymerization (ROP) of cyclic (di)esters in scCO$_2$.[9−13] Recently, we have reported for the first time that supercritical chlorodifluoromethane (scR22) can be successfully utilized as the homogeneous solvent for the ring-opening polymerization of L-lactide (L-LA).[14] This polymerization system could also be followed by the in situ preparation of poly(L-lactide) (PLLA) microspheres, in the absence of residual monomer or solvent, by using a continuous supercritical antisolvent process. An attractive feature of R22 is that it has lower ozone depleting potential than chlorofluorocarbons[15] as to be used in medical applications.

Increasing interest in the synthesis of environmentally friendly materials, particularly the biodegradable ones, has created new scientific interest in the understanding of the kinetics and the mechanism of cyclic (di)ester polymerization. Stannous(II) 2-ethylhexanoate (Sn(Oct)$_2$) is one of the most commonly used compounds for initiating the ROP of cyclic (di)esters. Two different mechanisms have been proposed concerning the role of Sn(Oct)$_2$: the activated monomer mechanism[16] and the coordination insertion mechanism.[17−20] In the former mechanism, Sn(Oct)$_2$ is considered to form an activated donor−acceptor complex with a monomer, which, in turn, is subject to the nucleophilic attack of growing hydroxyl ended macromolecular chain resulting in the ring-opening propagation process. In the latter mechanism, however, a compound containing a hydroxyl group like an alcohol is believed to react first with Sn(Oct)$_2$ to form the actual initiator, i.e., an alkoxide covalently bound to tin. Recent investigations[19,20] on Sn(Oct)$_2$ systems are more supporting the coordination−insertion mechanism because the presence of a tin−alkoxide complex is directly confirmed by MALDI−TOF mass spectrometry. We have also found that the same mechanism is operative in the polymerization of L-LA in scR22.[21] A theoretical study on the ROP of L-LA using density functional methods supports the coordination−insertion mechanism as well.[18]

To be more convinced of the coordination−insertion mechanism in the ROP of cyclic (di)esters, however, specific knowledge on the transition state and activated complex is very essential. Unfortunately, the literature has paid little attention to the transition state of the coordination−insertion mechanism.[18,22] Recently, Jérôme and co-workers[9,10] have reported upon the kinetics of ϵ-caprolactone polymerization initiated by dibutyltin

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dimethoxide and also upon the effect of pressure on its transition state in $scCO_2$. Except these papers, we do not find any significant works dealing with the kinetic and mechanistic investigations based on the transition state characteristics in the ROP of cyclic (di)ester in bulk or in supercritical fluid.

In this paper, we focus on the effects of pressure (P) and temperature (T) on the kinetics of L-LA polymerization initiated by $Sn(Oct)_2$ in scR22 to get a better understanding of the coordination−insertion polymerization process.

Experimental Section

Materials. L-Lactide (L-LA) was purchased from Purac Biochem BV (Gorinchem, The Netherlands) and was recrystallized from ethyl acetate and dried in a vacuum (0.2 mmHg) over P_4O_{10}. Stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) (Sigma Chemical Co., St. Louis, MO, 99%) and 1-dodecanol (DoOH) (Aldrich, 99.5%) were purified by distillation under reduced pressure and dissolved in dry toluene. R22 of a certified purity of 99.99 wt % was purchased from the Solvey Gas Co. and was used as received. Toluene was dried by refluxing over the benzophenone−Na complex and distilled in a nitrogen atmosphere just prior to use.

Polymerization Procedure in Supercritical R22. Polymerization was conducted in a variable volume stainless steel high-pressure cell equipped with a magnetic stirring bar and an electrical heating mantle. L-LA (3.0 g), DoOH solution (0.9 mL of a 0.11 M solution in toluene; 1.0×10^{-4} mol of DoOH), and $Sn(Oct)_2$ solution (0.42 mL of a 0.24 M solution in toluene; 1.0×10^{-4} mol of $Sn(Oct)_2$) were added to the cell. After removing toluene under vacuum, the reactor was heated to 50 °C and purged with nitrogen for 5 min. After cooling the reactor to room temperature, it was evacuated for 2 h using a liquid nitrogen cooled trap and then purged with nitrogen for an additional 10 min. The cell was then disconnected from the nitrogen line, evacuated, and connected to the R22 feed system. The cell was filled with liquid R22 to ca. 30 bar at 50 °C by using an air-driven gas compressor (Maximator Schmidt Kranz & Co. GmbH), gradually heated to 110 °C to achieve the predetermined pressure, and then polymerization was allowed to proceed for the predetermined time. After cooling the reactor down to room temperature, R22 was vented through a needle valve into chloroform to collect both the unreacted monomer and polymer. To quantify the conversions of L-LA, the cell was rinsed with chloroform to dissolve traces of polymer and monomer. Both of these chloroform solutions were then poured into a large volume of cold methanol, and the precipitated PLLA was recovered by filtration and dried under vacuum at room temperature to constant weight. Monomer conversion was determined gravimetrically.

Polymer Characterization. Molecular weights (MWs) and molecular weight distributions (MWDs) were determined by gel permeation chromatography (GPC) using a Waters 510 fluid unit, a Waters 717 plus autosampler, and a Waters 410 differential refractometer with a combination of three Shodex microstyragel columns with molecular weight exclusion limits of 1500/70 000/400 000 g/mol. The column was eluted with $CHCl_3$ (flow rate of 1.0 mL/min at 30 °C) and calibrated with polystyrene standards over a MW range of 1000−350 000.

Computational Method. Semiempirical calculations were carried out using the Mopac 2002 program implemented in the CAChe package (Fujitsu Limited). The 2-ethylhexanoate ligand of $Sn(Oct)_2$ was simplified to an acetyloxy group (Oct′) to simplify the calculation. Geometries in different microenvironments were obtained using the PM3 parameter and the COSMOS solvation method by employing various dielectric constants.

Results and Discussion

Effect of Pressure on the Reaction Kinetics. Two series of L-lactide (L-LA) polymerizations initiated by $Sn(Oct)_2$ in the absence and presence of 1-dodecanol (DoOH) were carried out at pressures ranging from 180 to 360 bar at a constant temperature of 110 °C (see entries 1−8 in Table 1). In all of these experiments, the ratio of monomer (L-LA) to R22 was held constant at 12.4 wt %. To keep this ratio constant at different pressure condition, polymerization pressure was varied by adopting separate reactors with different cell volumes. The polymerization rate constant, k_p, was determined according to a previously reported standard procedure,[21] and the results are listed in the last column of Table 1.[23] The kinetic plot showed a linear relationship in the semilogarithmic coordinates (i.e., $\ln k_p$ vs P) within experimental error (Figure 1). It is noted that the higher pressure resulted in the higher polymerization rate. Additionally, it is importantly noted that the slope in $\ln k_p$ vs P plot gets much steeper when DoOH is intentionally added into the polymerization system ($[DoOH]_0/[Sn]_0 = 1.0$). The volume of activation, which provides quantitative information concerning the transition state, must be known to determine the effect of pressure on the reaction kinetics. The effect of pressure on a rate constant is given by[24]

$$\left(\frac{d \ln k}{dP}\right)_T = \frac{-\Delta V^{\neq}}{RT} \tag{1}$$

where $\Delta V^{\ddagger}$ is the volume of activation, i.e., the difference in the partial molar volumes (cm^3/mol) between reactants and the transition state ($\bar{V}^{\ddagger} - \sum_{rcts}\bar{V}$). A negative

Table 1. Measured Propagation Rate Constants of L-LA Polymerization Initiated by DoOH/Sn(Oct)₂ in scR22 at Various Pressures[a]

entry	$[DoOH]_0/[Sn]_0$	P (bar)	T (°C)	$k_p \times 10^4$ (s^{-1})
1	0	180	110	0.72
2	0	250	110	0.83
3	0	300	110	0.88
4	0	360	110	0.97
5	1.0	180	110	0.80
6	1.0	250	110	0.96
7	1.0	300	110	1.06
8	1.0	360	110	1.14

[a] $[LA]_0 = 0.4$ mol/L, $c_{R22} = 40.8\%$ w/v, and $[LA]_0/[Sn]_0 = 210$. $[LA]_0$ is the initial L-lactide concentration, $[DoOH]_0$ the initial DoOH concentration, $[Sn]_0$ the initial $Sn(Oct)_2$ concentration, and c_{R22} the R22 concentration.

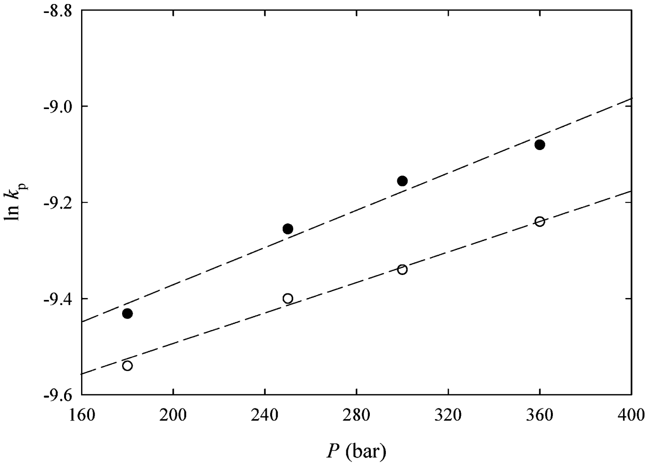


Figure 1. Pressure dependence of the polymerization rate constant, k_p, for L-LA polymerization initiated by DoOH/Sn(Oct)₂ in scR22. Conditions of polymerization: $[LA]_0 = 0.4$ mol/L at 110 °C; $[DoOH]_0/[Sn]_0$ was (○) 0 and (●) 1.0.

value of $\Delta V^{\ddagger}$ corresponds to lower transition state volume than the total volume of the reactants and indicates that an increase in pressure causes an increase in the reaction rate.[25] The volume of activation has normally been regarded as the sum of two terms: $\Delta V_i^{\ddagger}$, an "intrinsic" term, and $\Delta V_s^{\ddagger}$, a "solvation" term. $\Delta V_i^{\ddagger}$ is related to the intrinsic change in volume of reacting molecules and results from an alternation in interatomic distances during the formation of the activated complex. $\Delta V_s^{\ddagger}$ is the volume change due to interaction between the solvent and the activated complex.[26] The formation of a bond between two molecules is accompanied by a reduction in intrinsic volume, and conversely, bond cleavage causes an increase.[25] The polymer generally has a lower volume per monomeric unit fraction than the monomer. Figure 1 is very typical of the reaction with a negative activation volume. According to eq 1, the activation volume for $[\mathrm{DoOH}]_0/[\mathrm{Sn}]_0 = 0$, i.e., in the absence of DoOH, was determined to be -50 cm^3/mol. The negative value of $\Delta V^{\ddagger}$ indicates that the transition state corresponds to a volume contraction, i.e., the transition state occupies a smaller volume than the total volume of reactants, and as a consequence the rate of polymerization increased with increasing pressure.

In the coordination−insertion mechanism of $\mathrm{Sn(Oct)_2}$-initiated L-LA polymerization, a compound containing a hydroxyl group (an alcohol or H_2O) is believed to react with $\mathrm{Sn(Oct)_2}$ to form the actual initiator, i.e., an alkoxide or hydroxide covalently bound to tin.[17] Our previous study[21] on the polymerization of L-LA initiated by $\mathrm{Sn(Oct)_2}$ in scR22 has provided direct spectroscopic evidence for the covalent bonding between tin and the growing polyester chain end (−Sn−OR). Therefore, the proposed coordination−insertion mechanism in the ROP of cyclic (di)esters involves covalent tin−alkoxide bond formation, coordination of the monomer to the tin−alkoxide bond, and monomer insertion into the tin−alkoxide bond by the cleavage of the acyl−oxygen bond of the monomer. It has been proposed that the rate-determining step in the coordination−insertion mechanism involves nucleophilic attack by the tin−alkoxide on the carbonyl carbon of the monomer.[18] On the basis of these reports, our important observation in this work, i.e., the negative values of activation volume and the pressure-induced increase in the rate of L-LA polymerization (Figure 1), can be explained all together by the formation of chemical bonds in the transition state, which implies the production of a transition state with a lower partial molar volume than the reactants (see **1** and **TS** in Scheme 1). In the **TS**, the alkoxy (or hydroxy) group nucleophilically attacks the monomer's carbonyl carbon, and a new C−O bond is formed between the monomer and the alkoxy (or hydroxy) group via a four-center transition state.[18] This activation volume is quantitatively similar to that of cycloaddition, which lies in the range -30 to -50 cm^3/mol. Moreover, it is more negative than that of vinyl acetate radical polymerization[27] ($\Delta V^{\ddagger} = -10.2 \pm 0.9$ cm^3/mol) and styrene[28] ($\Delta V^{\ddagger} = -11.3 \pm 1.1$ cm^3/mol) in $\mathrm{scCO_2}$, which may be due to the formation of the four-center cyclic transition state during the coordination−insertion mechanism. It should also be noted that the cyclic compounds have smaller partial molar volumes than their acyclic analogues.[26] Jérôme et al.[10] observed that the polymerization of ϵ-caprolactone initiated by dibutyltin dimethoxide in $\mathrm{scCO_2}$ was slowed down by pressure. They attributed their result to the formation of carbonate tin−alkoxide species, resulting in a positive volume of activation.

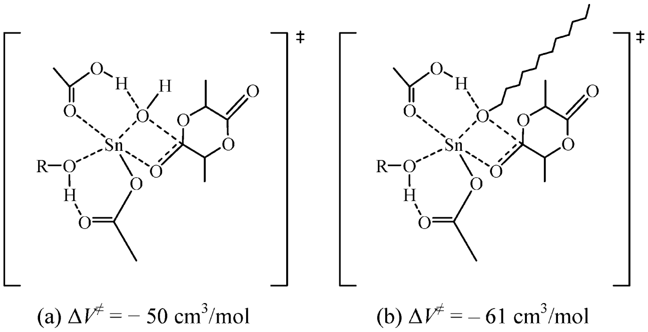
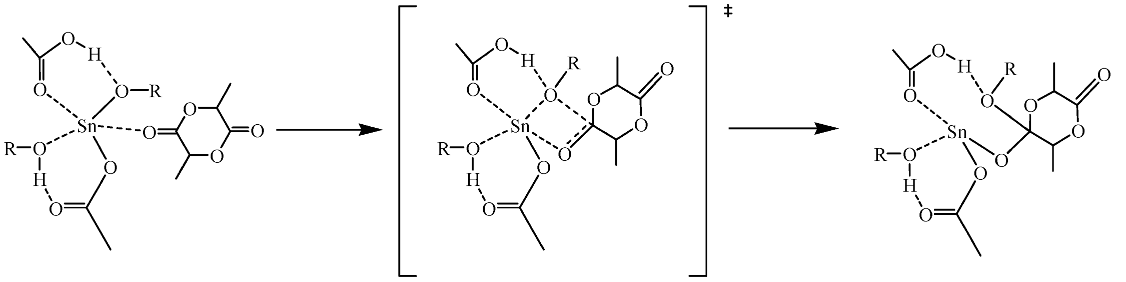


Figure 2. Transition states and the corresponding activation volumes of the coordination−insertion mechanism of L-LA polymerization initiated by (a) $\mathrm{Sn(Oct)_2}$ and (b) $\mathrm{DoOH/Sn(Oct)_2}$ ($[\mathrm{DoOH}]_0/[\mathrm{Sn}]_0 = 1.0$).

In addition, the activation volume for $[\mathrm{DoOH}]_0/[\mathrm{Sn}]_0 = 1.0$, i.e., in the presence of DoOH as co-initiator, was determined to be -61 cm^3/mol (see Figure 1). Thus, the polymerization rate was even more accelerated by pressure than that of $[\mathrm{DoOH}]_0/[\mathrm{Sn}]_0 = 0$. A further stabilization of the transition state in terms of the reduced activation volume (11 cm^3/mol) by the use of DoOH ($[\mathrm{DoOH}]_0/[\mathrm{Sn}]_0 = 1.0$) can be explained by a sterically crowded transition state. A growing chain with a dodecyloxy end group in the ROP of L-LA initiated by $\mathrm{DoOH/Sn(Oct)_2}$ has been observed by MALDI−TOF mass spectrometry (see Figure 2, (b) in comparison to (a)).[21] Sterically crowded compounds usually have greater densities than their unhindered isomers, and thus, it is reasonable to suppose that hindered transition states would similarly have smaller volume requirements than the unhindered ones from which they are formed.[29] If this is so, hindered reactions should be accelerated more than their unhindered analogues by the reduced activation volume. Evidence for this has been reported by several groups.[30] An example of this effect is found in

Scheme 1. Coordination−Insertion Mechanism of L-Lactide Polymerization; Coordination of the Monomer to the Tin−Alkoxide Bond (1), the Four-Center Transition State (TS), and Monomer Insertion into the Tin−Alkoxide Bond (2)[18,21]



1 **TS** **2**

Table 2. Measured Propagation Rate Constants of L-LA Polymerization Initiated by DoOH/Sn(Oct)$_2$ in scR22 at Various Temperatures[a]

entry	T (°C)	P (bar)	$k_p \times 10^4$ (s^{-1})
9	100	250	0.41
10	110	250	0.96
11	120	250	1.51
12	130	250	4.10

[a] $[LA]_0/[Sn]_0 = 210$ and $[DoOH]_0/[Sn]_0 = 1.0$. $[LA]_0$ is the initial L-lactide concentration, $[DoOH]_0$ the initial DoOH concentration, $[Sn]_0$ the initial Sn(Oct)$_2$ concentration.

the report of Gonikberg;[31] the activation volume for reaction of methyl iodide with 2,6-lutidine is 3.4 cm^3/mol more negative than that with pyridine, and the reaction of the lutidine with isopropyl iodide has a more negative $\Delta V^‡$ by 6−7 cm^3/mol than the reaction of pyridine with ethyl iodide.

When an ion is created in a liquid medium composed of dipolar molecules, strong electrostatic forces tend to pull solvent molecules close around the charge and thus effect a volume reduction; this effect is known as electrostriction.[26] Hamann et al.[32] showed that the solvation term, $\Delta V_s^‡$, is a large contribution for some reactions, in which a change in charge is accompanied by the formation of a transition state. On the other hand, cycloadditions show weak electrostriction effects due to the lack of charge development in the cyclic transition state.[25] By applying the Kirkwood model[33] to the relationship between the electrostatics and solution properties, $\Delta V_s^‡$ is given by[34]

$$\Delta V_s^{\neq} = -N_0\left(\frac{\mu_M^{\,2}}{r_M^{\,3}} - \frac{\mu_A^{\,2}}{r_A^{\,3}} - \frac{\mu_B^{\,2}}{r_B^{\,3}}\right)\frac{\partial}{\partial P}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) \qquad (2)$$

where N_0 is Avogadro's number, r the radius of the spherical cavity, ϵ the dielectric constant, and m the dipole moment. A and B are reagents, and M is a transition state. The nature and reactivity of the metal−alkoxide bond, i.e., its electrophilic or nucleophilic character, have been studied by Jérôme and co-workers.[35] However, the electrostriction effect of the transition state of Sn(Oct)$_2$-initiated polymerization has not been studied. To calculate the dipole moment of the **TS**, a computational study was performed on the ROP of L-lactide in the presence of Sn(Oct)$_2$.[23] Details of the semiempirical methods used are given in the Experimental Section. The dielectric constant (ϵ) of R22 increases from 3.6 to 4.2 between 180 and 360 bar at 110 °C.[36] The dipole moments of L-LA, Sn(OH$_2$Oct′)$_2$, and of the **TS** were calculated to be ca. 3.0, 2.7, and 5.2 D, respectively; from the relationship between electrostatics and solution properties (eq 2), $\Delta V_s^‡$ was calculated to be ca. −7 cm^3/mol, showing that the **TS** may be associated with a weak electrostriction effect in scR22 at pressures ranging from 180 to 360 bar.

Effect of Temperature on Reaction Kinetics. The effect of temperature on the polymerization rate was investigated in a series of polymerizations conducted at temperatures ranging from 100 to 130 °C and at a constant pressure of 250 bar (see Table 2).[23] In all of these experiments, the ratio % of monomer to R22 was held constant at 12.4 wt %. As shown in the Arrhenius plot in Figure 3, the polymerization rate increased with increasing temperature. According to the relationship $\partial(\ln k)/\partial(1/T) = -E_a/R$, the activation energy was calculated to be 88.7 kJ/mol, which is higher than the value obtained for the ROP of L-LA initiated by Sn(Oct)$_2$ in bulk (70.9 ± 1.5 kJ/mol).[37] As was pointed out in our previous study,[21] the slower kinetics in scR22 is attributed to the competition between R22 and the monomer for coordination to the active coordinate site. In this sense, the higher activation energy also reflects a partial blocking of the active coordinate site by R22.

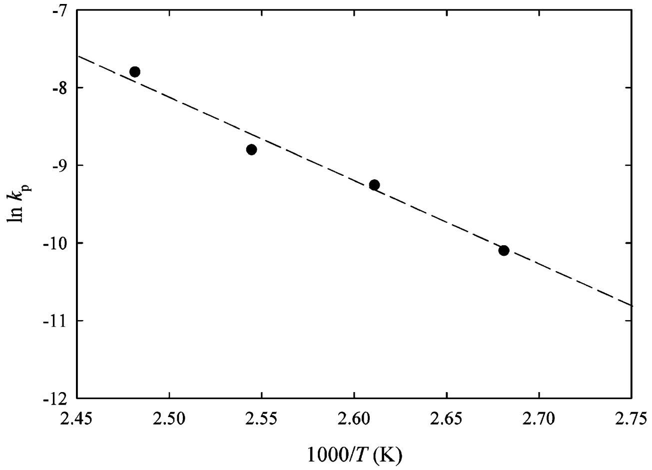


Figure 3. Arrhenius plot of the propagation rate constant, k_p, for L-LA polymerization at 250 bar in scR22.

Conclusions

A study of pressure and temperature effects on the kinetics of L-LA polymerization in scR22 was undertaken to gain more detailed information about the coordination−insertion mechanism. The kinetic plot of ln k_p vs P was typical of a reaction with a negative volume of activation. The negative values of $\Delta V^‡$ (−50 to −61 cm^3/mol) indicated that the transition state was contracted by reactants moving into the transition state. In the transition state, the alkoxy group nucleophilically attacks the monomer's carbonyl carbon, and a new C−O bond is formed between the monomer and the alkoxy group via a four-center transition state. This activation volume is quantitatively similar to that of cycloaddition and has a more negative than the radical polymerization of vinyl acetate and styrene in scCO$_2$, which may be due to the formation of four-center cyclic type transition state. A computational study using semiempirical methods showed that the transition state may be associated with weak electrostriction effects. The observed activation energy (88.7 kJ/mol), which is higher than the value recorded in bulk, reflects a partial blocking of the active coordinate site by chlorodifluoromethane.

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Supporting Information Available: Table giving details of the polymerization conditions and results in scR22 and table of changes in dipole moments according to the dielectric constant and its contribution to the solvation term. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Canelas, D. A.; DeSimone, J. M. *Adv. Polym. Sci.* **1997**, *133*, 103.

(2) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature (London)* **2000**, *405*, 165.

(3) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543.

(4) Consani, K. A.; Smith, R. D. *J. Supercrit. Fluids* **1990**, *3*, 51.

(5) O'Shea, K. E.; Kirmse, K. M.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1991**, *95*, 7863.

(6) Johnston, K. P.; Lemert, R. M. In *Encyclopedia of Chemical Processing and Design*; McKetta, J. J., Ed.; Dekker: New York, 1996; Vol. 56, pp 1−45.

(7) (a) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. *Nature (London)* **1996**, *373*, 313. (b) Leitner, W. *Nature (London)* **2000**, *405*, 129.

(8) (a) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356. (b) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745. (c) Christian, P.; Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Major, R. C.; Howdle, S. M. *Macromolecules* **2000**, *33*, 9222. (d) Shiho, H.; DeSimone, J. M. *Macromolecules* **2001**, *34*, 1198. (e) Wood, C. D.; Cooper, A. I. *Macromolecules* **2001**, *34*, 5. (f) Fehrenbacher, U.; Ballauff, M. *Macromolecules* **2002**, *35*, 3653.

(9) Stassin, F.; Halleux, O.; Jérôme, R. *Macromolecules* **2001**, *34*, 775.

(10) Stassin, F.; Jérôme, R. *Chem. Commun.* **2003**, *2*, 232.

(11) Hile, D. D.; Pishko, M. V. *Macromol. Rapid Commun.* **1999**, *20*, 10, 511.

(12) Mingotaud, A. F.; Cansell, F.; Gilbert, N.; Soum, A. *Polym. J.* **1999**, *31*, 5, 406.

(13) Bratton, D.; Brown, M.; Howdle, S. M. *Macromolecules* **2003**, *36*, 5908.

(14) Pack, J. W.; Kim, S. H.; Park, S. Y.; Lee, Y.-W.; Kim, Y. H. *Macromolecules* **2003**, *36*, 7884.

(15) Because of their oxidation in the troposphere, R22 has a lower half-life than chlorofluoromethanes (CFCs) and therefore a lower ozone depletion potential. See: (a) Ravishankara, A. R.; Turnipseed, A. A.; Jensen, N. R.; Barone, S.; Mills, M.; Howard, C. J.; Solomon, S. *Science* **1994**, *263*, 71. (b) First Review Meeting of Parties to the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, London, June 1990, and Copenhagen, 1992. (c) Powell, R. L. *J. Fluorine Chem.* **2002**, *114*, 237 and references therein.

(16) (a) Du, Y. J.; Lemstra, P. J.; Nijenhuis, A. J.; van Aert, H. A. M.; Bastiaansen, C. *Macromolecules* **1995**, *28*, 2124. (b) Schwach, G.; Coudane, J.; Engle, R.; Vert, M. *J. Polym. Chem., Part A: Polym. Chem.* **1997**, *35*, 3431. (c) Kricheldorf, H. R.; Kreiser-Saunders, I.; Boettcher, C. *Polymer* **1995**, *36*, 1253. (d) In't Veld, P. J. A.; Velner, E. M.; van de Witte, P.; Hamhuis, J.; Dijkstra, P. J.; Feijen, J. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 219.

(17) (a) Storey, R. F.; Taylor, A. E. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 723. (b) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39* (2), 74. (c) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567. (d) Duda, A.; Penczek, S.; Kowalski, A.; Libiszowski, J. *Macromol. Symp.* **2000**, *153*, 43. (e) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964. (f) Kricheldorf, H. R.; Kreiser-Saunders, I.; Stricker, A. *Macromolecules* **2000** *33*, 702. (g) Storey, R. F.; Sherman, J. W. *Macromolecules* **2002**, *35*, 1504.

(18) Ryner, M.; Stridsberg, K.; Albertsson, A.-C.; von Schenck, H.; Svensson, M. *Macromolecules* **2001**, *34*, 3877.

(19) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689.

(20) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 7359.

(21) Pack, J. W.; Kim, S. H.; Park, S. Y.; Lee, Y.-W.; Kim, Y. H. *Macromolecules* **2003**, *36*, 8923.

(22) Eguiburu, J. L.; Fernandez-Berridi, M. J.; Cossio, F. P.; San Roman, J. *Macromolecules* **1999**, *32*, 8252.

(23) See Supporting Information.

(24) Clifford, A. A. *Fundamentals of Supercritical Fluids*; Oxford University Press: Oxford, 1998; pp 189−190.

(25) (a) Asno, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. (b) van Eldik, R.; Asno, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(26) Isaacs, N. S. *Liquid-Phase High-Pressure Chemistry*; John Wiley and Sons: New York, 1981; pp 136−353.

(27) Beuermann, S.; Buback, M.; Nelke, D. *Macromolecules* **2001**, *34*, 6637.

(28) Beuermann, S.; Buback, M.; Isemer, C.; Lacik, I.; Wahl, A. *Macromolecules* **2002**, *35*, 3866.

(29) LeNoble, W. J.; Ogo, Y. *Tetrahedron* **1970**, *26*, 4119.

(30) (a) Okamoto, Y.; Shimizu, H. *J. Am. Chem. Soc.* **1968**, *90*, 6145. (b) Ewald, A. H. *Trans. Faraday Soc.* **1959**, *55*, 792.

(31) Gonikberg, M. G. *Russ. J. Phys. Chem. (Engl. Transl.)* **1963**, *37*, 248.

(32) Buchanan, J.; Hamann, S. D. *Trans. Faraday Soc.* **1953**, *49*, 1425.

(33) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.

(34) Mccabe, J. R.; Ecker, C. A. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 168.

(35) (a) Degée, P.; Dubois, P.; Jérôme, R. *Macromol. Chem. Phys.* **1997**, *198*, 1973. (b) Ropson, N.; Dubois, P.; Jérôme, R.; Teyssié, P. *Macromolecules* **1992**, *25*, 3820. (c) Dubois, P.; Ropson, N.; Jérôme, R.; Teyssié, P. *Macromolecules* **1995**, *28*, 1965.

(36) Franck, E. U. *Fluid Phase Equilib.* **1983**, *10*, 211.

(37) Witzke, D. R.; Narayan, R.; Kolstad, J. J. *Macromolecules* **1997**, *30*, 7075.

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