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Kinetics for free radical solution polymerization of heptadecafluorodecyl (meth)acrylate in supercritical carbon dioxide

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Abstract−Free radical solution polymerization of heptadecafluorodecyl acrylate (HDFDA) and heptadecafluorodecyl methacrylate (HDFDMA) was carried out by using 2,2'-azobisisobutyronitrile (AIBN) as the initiator in supercritical carbon dioxide ($scCO_2$). We performed solution polymerization with changing initiator concentration, temperature and polymerization time to study the polymerization kinetics. A nonlinear least square method and dead-end theory were used to determine the constant, K ($K=(k_p\sqrt{f})/\sqrt{k_d k_t}$) and initiator decomposition rate constant (k_d) from experimental data. k_d was measured as 3.77×10^{-5} s^{-1} at 62.7 °C for poly(HDFDA) and 2.71×10^{-5} s^{-1} at 62.5 °C for poly(HDFDMA), respectively, by nonlinear least square method.

Key words: Supercritical Carbon Dioxide, Heptadecafluorodecyl (meth)acrylate, Free Radical Solution Polymerization, Kinetics, Decomposition Rate Constant (k_d), Nonlinear Least Square Method, Dead-end Theory

INTRODUCTION

Supercritical fluid (SCF) technology has made enormous progress in the past decade in terms of commercial application and fundamental understanding of solution behavior [1]. SCFs have distinct properties that may improve many types of chemical process operations. An extra advantage of using SCFs stems from the fact that they may substitute for many environmentally damaging solvents currently used in industry [2,3]. $ScCO_2$, especially, has been under a spotlight and studied as an alternative polymerization medium [4], since its critical conditions are relatively mild and it is nontoxic, nonflammable and cheap. Moreover, CO_2 can be removed by simple depressurization only and the density of the solvent can be tuned by varying pressure [5-7].

Generally, $scCO_2$ is a good solvent for low molecular weight nonpolar monomers. Therefore, $scCO_2$ can replace a sizable fraction of the solvents used in a solution process. But except for amorphous perfluoropolymers and silicone polymers, CO_2 is a poor solvent for most high molecular weight polymers [5]. This phenomenon is due to the very low mixing entropy between polymer and $scCO_2$. To overcome this low mixing entropy, a specific enthalpic interaction between polymer and $scCO_2$ is demanded. In case of poly(perfluoro alkyl acrylate), $scCO_2$ dissolves abundant amounts of polymer at relatively low pressure. It is due to specific interaction between fluorine and $scCO_2$ [8]. Therefore, solution polymerization is possible for highly fluorinated acrylic ester polymers. Perfluoro alkyl acrylate polymers have been used in various industrial applications, including textile finishes, resists, protective coatings, charge control agents, optical fibers, contact lenses and surface modifiers etc. [9]. In addition, these polymers can be used as dispersant for dispersion polymerization of PMMA, PS, PVP, and so on [10].

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For free radical polymerization, generally, the elevation of pressure influences polymerization as follows: (1) increasing the concentration of gaseous monomers (such as vinyl chloride and vinylidene fluoride), (2) affecting the rate constants for initiation, propagation, termination, chain transfer, and (3) affecting the equilibrium constants for the polymerization. Consequently, reaction rate and molecular weight were increased by the elevation of pressure [11]. However, it is known that the development for reaction rate in $scCO_2$ is more complex than in the existing liquid solvent.

In this study, we focused on the free radical solution polymerization of HDFDA and HDFDMA using AIBN as initiator in $scCO_2$. In addition, polymerization kinetics was modeled with nonlinear least square method and dead-end theory.

THEORY

For free radical polymerization, various modeling methods on kinetic study have been suggested. However, there are few reports on case studies of reaction kinetics in $scCO_2$ because of the difficulties of experimental methods. Therefore, in this study, experimental results were interpreted with a relatively simple equation of modeling which consists of reactions for initiation, propagation and termination [12].

$$\ln(1-X) = 2\sqrt{[I]_0}K\exp\left(\frac{-k_d t}{2}\right) - 2\sqrt{[I]_0}K \tag{1}$$

$$\text{where, } K = \frac{k_p\sqrt{f}}{\sqrt{k_t k_d}} \tag{2}$$

k_d and K values are obtained by using nonlinear least square method after experimentally measuring conversion to time.

Another method for modeling is dead-end theory. With this theory, conversion X_t at time t is represented by

$$\ln(1-X_t) = 2\sqrt{[I]_0}K\exp\left(\frac{-k_d t}{2}\right) - 2\sqrt{[I]_0}K \quad (3)$$

Similarly, conversion X_∞ at $t\rightarrow\infty$ is represented by

$$\ln(1-X_\infty) = 2\sqrt{[I]_0}K\exp\left(\frac{-k_d t_\infty}{2}\right) - 2\sqrt{[I]_0}K \quad (4)$$

Dividing Eq. (3) by Eq. (4) gives:

$$\ln\left(1-\frac{\ln(1-X_t)}{\ln(1-X_\infty)}\right) = -\frac{k_d t}{2} \quad (5)$$

It is possible to determine k_d from the slope by plotting the left-hand side of Eq. (5).

And activation energy (E_d) and frequency factor (A_d) were determined by

$$\ln k_d = \ln A_d - \frac{E_d}{R}\frac{1}{T} \quad (6)$$

EXPERIMENTS

1. Materials

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acrylate (HDFDA, Aldrich, min. 97%) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (HDFDMA, Aldrich, min. 97%) were pretreated through alumina column to remove inhibitor (MEHQ) and dissolved oxygen was removed through nitrogen purging. 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemical, min. 98%) was purified by recrystallization from methanol. Carbon dioxide (CO_2, min. 99.99%) was purchased from Korea Industrial Gases Co.

Fig. 1 shows the chemical structures of HDFDA and HDFDMA as monomers used in polymerization.

Fig. 1. Chemical structure of monomer and polymer.

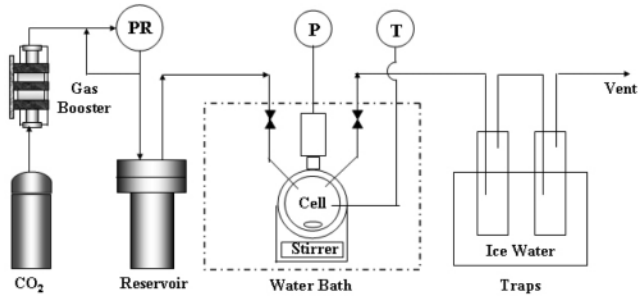

Fig. 2. Schematic diagram of supercritical polymerization apparatus.

2. Apparatus and Procedure

Fig. 2 shows a schematic diagram of a polymerization apparatus in supercritical fluid.

Free radical solution polymerization of HDFDA and HDFDMA was carried out in a 30 mL SUS 316 reactor that has two windows at both sides. CO_2 was supplied from a gas booster pump (Maxpro Technologies Inc. Model DLE 75-1). We used a 300 mL reservoir between the pump and reactor in order to minimize the fluctuation from the pump and to maintain stable feeding. Pressure was measured with pressure transducer (Data Instruments Inc. Model AB/HP, accuracy±0.25%) and indicator (Laurel Electronics Inc. L20010WM1). Temperature was measured with K(CA) type thermocouple (accuracy±0.05 K) and indicator (Hanyoung Electronics Inc. Model DX-7). A PTFE coated magnetic stirring bar was used for agitation of the reacting mixture.

Monomer (4.00 g) and AIBN (0.1, 0.5, 1.0 wt% of monomer) were introduced to the reactor. Then the reactor was purged with CO_2 several times to remove air and charge with known amount of CO_2 (28.5±0.1 g) at room temperature. Then reactor was heated up to a predetermined temperature in the water bath. Polymerization was performed at, respectively, 52.5 °C (P=205 bar), 62.5 °C (P=255 bar) and 72.5 °C (P=300 bar) (accuracy of temperature±0.5 °C, pressure±5 bar). We carried out polymerization for 1 to 168 h to investigate polymerization kinetics. After polymerization was completed, we cooled down the reactor below 10 °C. At that time pressure in the reactor was about 40 bar and vapor/liquid phase separation occurred, and then CO_2 was slowly vented from vapor phase through two glass traps. To prevent discharge of unreacted monomer to atmosphere during CO_2 venting, glass traps were filled with methanol and cooled with ice water. The resulting polymer was precipitated and washed in methanol to remove unreacted monomer. We could obtain fine powder after drying in vacuum at room temperature. Conversion was determined by the ratio of residual mass after methanol washing to initially charged monomer mass.

3. Polymer Characterization

To confirm chemical structure of polymer, ^{1}H-NMR (Bruker, 300 MHz, 3 : 2 mixture of $CDCl_3$ and CFC113 as a solvent) and FT-IR (AVATAR 360ESP) were used. In addition, residual monomer was detected by the relative intensities of polymer and monomer at the same functional group with NMR spectra. Thermal properties of polymers were investigated by using DSC (Perkin Elmer DSC7, heating and cooling rate of 10 K/min).

4. Viscosity Measurement

In the case of perfluoro alkyl acrylate polymer, it is still difficult

Table 1. Inherent viscosity of poly(HDFDA) and poly(HDFDMA)

	AIBN (wt%)	η_{inh} (dL/g)
Poly(HDFDA)	0.1	0.074[a]
	1.0	0.025[a]
Poly(HDFDMA)	0.1	0.111[b]
	0.5	0.071[b]
	1.0	0.049[b]

[a]Inherent viscosity in HFIP (0.5 g/dL) at 31 °C.
[b]Inherent viscosity in HFIP (0.5 g/dL) at 34 °C.

Table 2. Experimental result for solution polymerization of poly[perfluoroalkyl (meth)acrylate] in $scCO_2$: monomer=4.0 g, P=300±5 bar, T=72.5±0.5 °C, and reaction time=24 h

Entry	Monomer	AIBN (wt%)	Recovery ratio[a] (%)	Conversion[b] (%)	Appearance
F1	HDFDA	0.1	98.7	79.5	Fluffy solid
F2		0.5	96.1	84.9	Fluffy solid
F3		1.0	97.9	89.4	Fluffy solid
F4	HDFDMA	0.1	96.5	43.3	Fluffy solid
F5		0.5	98.2	75.3	Fluffy solid
F6		1.0	97.4	85.2	Fluffy solid

[a]Determined by the ratio of residual mass in the reactor after CO_2 separation to initially charged monomer mass.
[b]Determined by the ratio of residual mass after methanol washing to initially charged monomer mass.

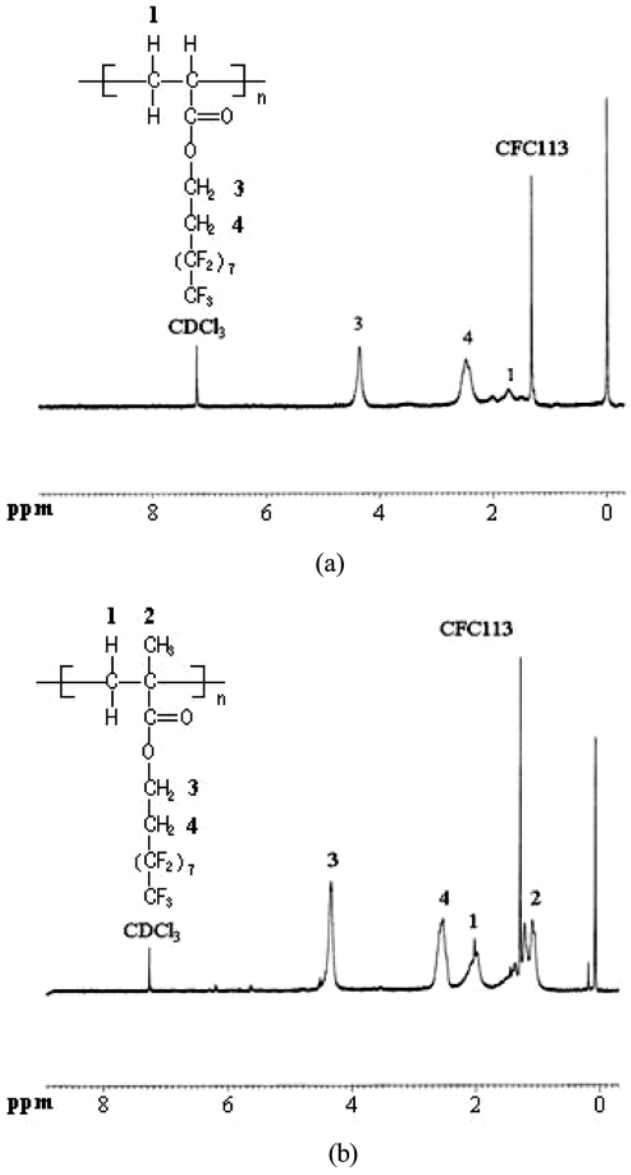

Fig. 3. ^{1}H-NMR spectroscopy of fluorinated acrylic polymers (a) poly(HDFDA), (b) poly(HDFDMA).

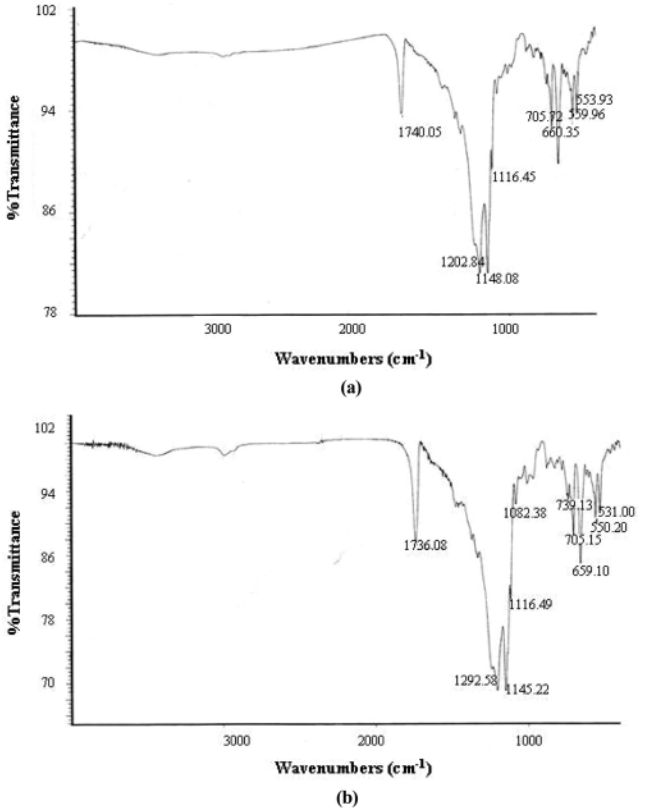

Fig. 4. FT-IR spectroscopy fluorinated acrylic polymers of (a) poly (HDFDA), (b) poly(HDFDMA).

to determine a molecular weight using GPC, etc. because of strong interaction between fluorines. Moreover, this polymer has very low solubility in typical solvents except CFCs and there is not much difference in refractive index between polymer and solvent. So we measured inherent viscosity of polymer to determine relative order of molecular weight on polymer. Viscosity of polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity we should be able to get an idea about molecular weight. Viscosity techniques are very popular because they are experimentally simple. They are, however, less accurate and the determined molecular weight, the viscosity average molecular weight, is less precise. Despite these defects, viscosity techniques are very valuable. The inherent viscosities of poly(HDFDA) and poly(HDFDMA) were measured at a concentration of 0.5 g/dL in 1,1,1,3,3,3-hexafluoro isopropanol (HFIP, CAS No. 920-66-1) at 31 °C and 34 °C with Ubbelohde viscometer with suspending ball-level. Samples were used immediately after prepa-

ration.

RESULTS AND DISCUSSIONS

1. Initiator Concentration Effect

Table 1 shows the inherent viscosity of poly(HDFDA) and poly (HDFDMA) polymerized at different conditions. It is known that the viscosity of a polymer solution increases with increasing molecular weight of polymer. Therefore, we can confirm relative order on molecular weight of polymer from Table 1.

Table 2 shows experimental results for solution polymerization of poly(perfluoro alkyl (meth)acrylate) at temperature of 72.5 °C and pressure 300 bar for 24 h. Recovery ratio was determined as the ratio of residual mass in the reactor after CO_2 separation to initially charged monomer mass. And the ratio is over 96%; thus we could know that the loss during the polymerization step is negligible. In free radical polymerization, generally, it is known that the conversion is improved with increasing concentration of initiator. We obtained that the conversion of acrylate monomer is higher than that of methacrylate monomer. Figs. 3 and 4 show the results of ^{1}H-NMR, FT-IR analysis after removal of monomer, respectively. In Fig. 4, the peak near 1740 cm^{-1} is associated with C=O stretching and the 1300-1000 cm^{-1} region corresponds with strong C-F stretching. Also, C-H stretching is observed in the 3100-2800 cm^{-1} region. The C=C peak is not observed near 1680-1600 cm^{-1} region. Therefore, from the results of ^{1}H-NMR and FT-IR analysis, it could be known that monomer was synthesized to polymer and monomer was completely removed in perfluoro alkyl acrylate polymer after recrystallization from methanol. The melting points (T_m) for poly(HDFDA) and poly(HDFDMA) were obtained around 70 °C with DSC analysis (Fig. 5).

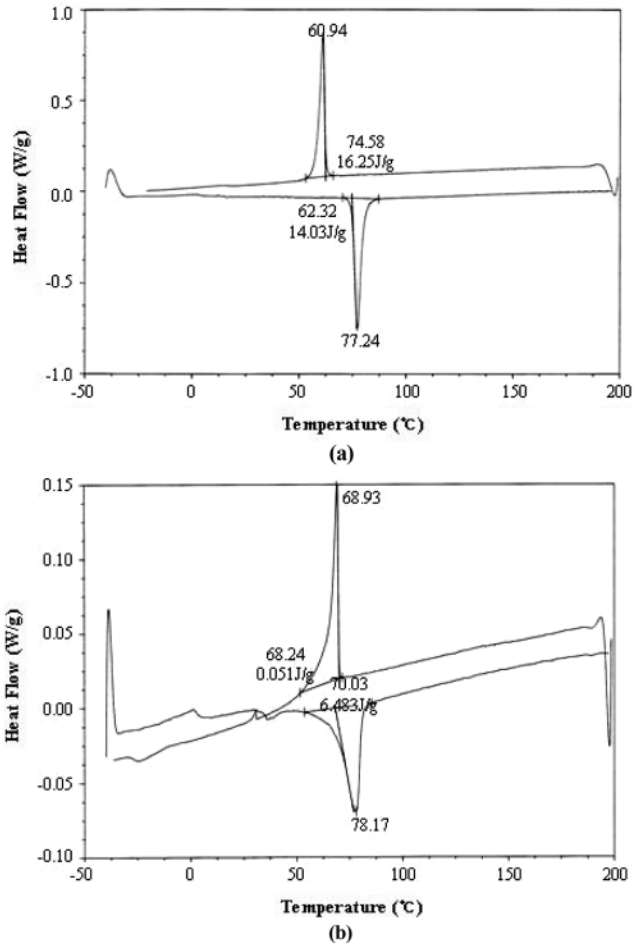

Fig. 5. DSC chart of fluorinated acrylic polymers (a) poly(HDFDA), (b) poly(HDFDMA).

2. Polymerization Time Effect

We measured conversion (%) of monomer to polymer with chang-

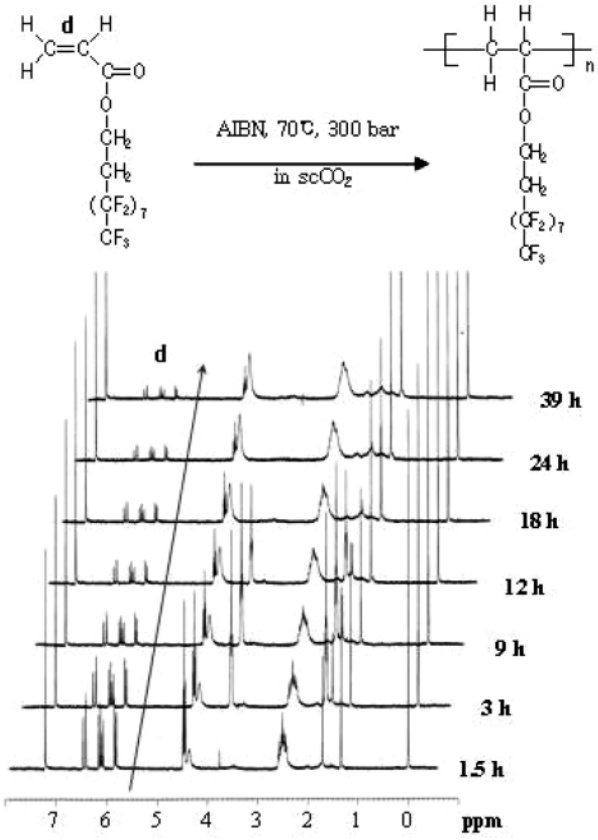

Fig. 6. Effect of polymerization time on conversion of poly(HDFDA) at T=72.8 °C.

Table 3. K value and decomposition rate constant (k_d) of AIBN for poly(HDFDA) and poly(HDFDMA) by a nonlinear least square method ($[I]_0=8.12\times10^{-3}$ mol/L) and dead-end theory

	Nonlinear least square method		Dead-end theory
	K $(L/mol)^{1/2}$	$k_d\times10^5$ (s^{-1})	$k_d\times10^5$ (s^{-1})
Poly(HDFDA)			
52.3 °C	5.94	2.71	1.91
62.7 °C	10.06	3.77	3.84
72.8 °C	11.77	7.41	5.54
Poly(HDFDMA)			
52.3 °C	6.87	1.44	1.68
62.5 °C	10.83	2.71	3.04
72.5 °C	11.62	4.90	4.28

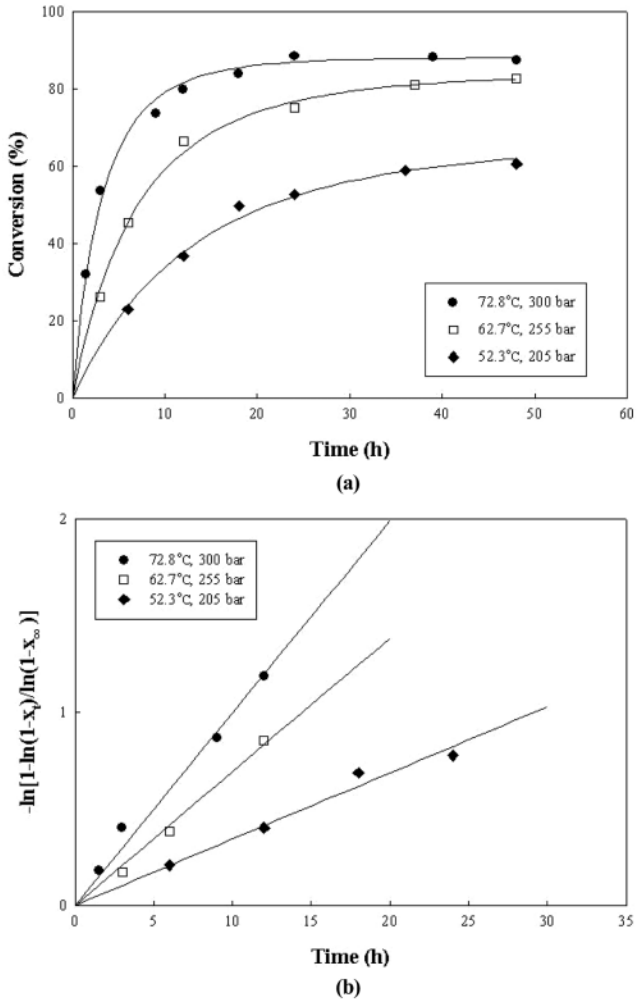

Fig. 7. Kinetics study of poly(HDFDA) (a) nonlinear least square method, (b) dead-end theory.

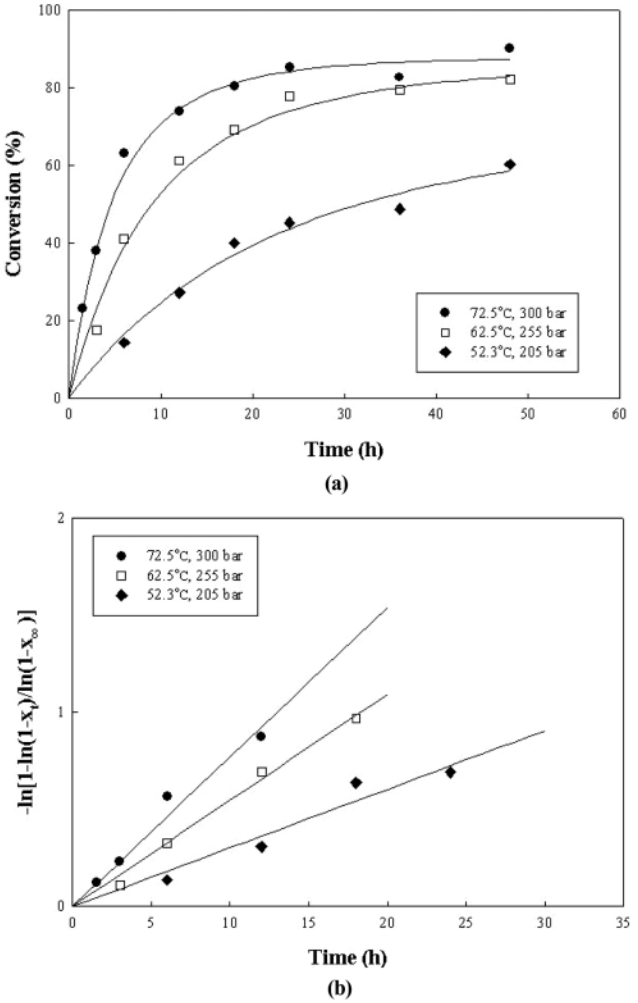

Fig. 8. Kinetics study of poly(HDFDMA) (a) nonlinear least square method, (b) dead-end theory.

ing polymerization time. Polymerizations were performed at 52.5 °C (P=205 bar), 62.5 °C (P=255 bar) and 72.5 °C (P=300 bar) under the same condition for the others (Monomer (4.00 g) and AIBN (1.0 wt% of monomer)). To get k_d with nonlinear least square method, we measured conversion by polymerization for 48 h. Moreover, conversion X_∞ was obtained from polymerization for arbitrary time 168 h to use dead-end theory. Fig. 6 shows analysis of ^{1}H-NMR for effect of polymerization time on conversion of poly(HDFDA) at a temperature of 72.8 °C and pressure of 300 bar before removal of monomer. The peak **d** represents the C=C double bond of monomer and means monomer concentration. It shows that monomer concentration decreases as the polymerization proceeds. Table 3 represents k_d for different temperatures that were obtained by nonlinear least square method and dead-end theory, respectively. Both nonlinear least square method and dead-end theory show similar k_d. Figs. 7 and 8 show modeling results with nonlinear least square method and dead-end theory, respectively. The conversion could be represented on both monomers with Eqs. (1)-(5).

3. Polymerization Condition Effect

Fig. 9 shows the decomposition rate of AIBN obtained from our group in comparison with that of other groups [11]. k_d obtained by using HDFDA and HDFDMA as monomer is higher than that of other groups. The difference is predicted results by pressure as well as

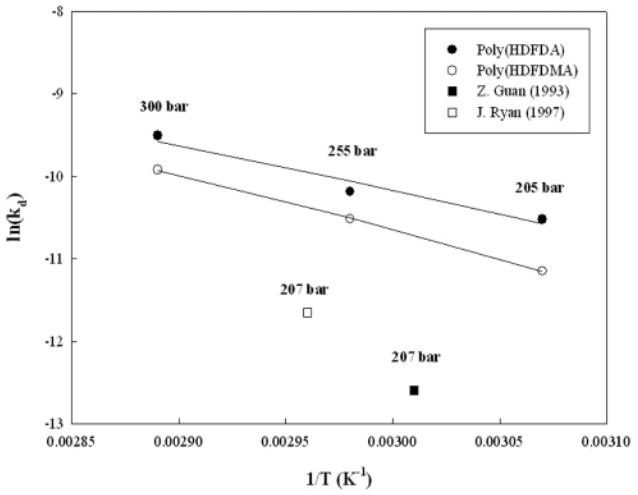

Fig. 9. Effect of polymerization temperature on the decomposition rate constants.

Table 4. Activation energy (E_d) and frequency factor (A_d)

	Poly(HDFDA)	Poly(HDFDMA)
E_d (kJ/mol)	45.64	56.68
A_d (s^{-1})	5.39×10^{2}	1.79×10^{4}

types of monomer. As Guan et al. [11] point out, the polarity of $scCO_2$ changes by pressure and k_d also changes. According to the study results of Guan et al. [11], for AIBN at 60 °C, it is known that the decomposition rate is a maximum at about 250 bar. In the other groups, k_d was measured at 207 bar, but we measured k_d at 255 bar; thus, it is inferred that k_d increased as the pressure increased. k_d was 3.77×10^{-5} s^{-1} and 2.71×10^{-5} s^{-1} at 62.7 °C and 62.5 °C for poly(HDFDA) and poly(HDFDMA), respectively, in $scCO_2$. Table 4 shows activation energy (E_d) and frequency factor (A_d) obtained without considering pressure effect.

In the case of $scCO_2$, various physicochemical properties such as density, viscosity, diffusivity and dielectric constant change with pressure and temperature. However, pressure effect on $scCO_2$ was very complex and not fully understood yet. Further research is required to analyze the pressure effect for polymerization in SCFs.

CONCLUSION

We carried out free radical solution polymerization of HDFDA and HDFDMA using AIBN as initiator in $scCO_2$ with changing the initiator concentration, temperature and polymerization time to study polymerization kinetics. Experiments with various polymerization times were performed and k_d was obtained by modeling with nonlinear least square method and dead-end theory. In case of poly (HDFDA), k_d were obtained as 2.71×10^{-5} s^{-1} at 52.3 °C, 3.77×10^{-5} s^{-1} at 62.7 °C and 7.41×10^{-5} s^{-1} at 72.8 °C by nonlinear least square method. For poly(HDFDMA), k_d were 1.44×10^{-5} s^{-1} at 52.3 °C, 2.71×10^{-5} s^{-1} at 62.5 °C and 4.91×10^{-5} s^{-1} at 72.5 °C. Conversion of poly (HDFDA) was higher than that of poly(HDFDMA) under the same conditions. Similar values and trends were also obtained with the dead-end theory.

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NOMENCLATURE

A_d : frequency factor [s^{-1}]
E_d : activation energy [kJ/mol]
f : initiator efficiency
I : initiator [mol/L]
K : $K = \frac{k_p\sqrt{f}}{\sqrt{k_d k_t}}$ [L/mol]$^{1/2}$
k_d : decomposition rate constant of initiator [s^{-1}]
k_p : rate constant of propagation [L/mol-s]
k_t : rate constant of termination [L/mol-s]
t : time [h]
X : conversion [%]

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