

Effect of alkyl group substituents on the degradation of poly (alkyl methacrylates) in supercritical fluids

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Abstract

The effect of alkyl group substituents on the degradation kinetics of poly(alkyl methacrylates) namely poly (n-butyl methacrylate) (PBMA), poly (iso-propyl methacrylate) (PPMA), poly (ethyl methacrylate) (PEMA), and poly (methyl methacrylate) (PMMA) in supercritical and subcritical conditions was studied at various temperatures (250 – 375 °C). The molecular weight distributions were measured by gel permeation chromatography and continuous distribution kinetic models were used to determine the degradation rate coefficients. The degradation rate coefficients in the supercritical condition were found to be significantly higher than that in the subcritical condition. The degradation rate of poly(alkyl methacrylates) increased with increase in the number of carbon atom of the alkyl substituents and thus followed the order PBMA>PPMA>PEMA>PMMA. The activation energy decreased with chain length in both subcritical and supercritical conditions. The degradation of PBMA was investigated at various pressures (20 – 85 bar) at 325 °C and the effect of pressure on the degradation rate coefficient was modeled using transition state theory. The degradation of PBMA was also investigated in different solvents at 325 °C and 60 bar. The supercritical state and the density of the solvent were found to be important factors that influences the degradation kinetics.

Keywords: Poly(alkyl methacrylate), Molecular weight distribution, Transition state theory, supercritical and subcritical conditions

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Introduction

The study of degradation of polymers is important for understanding its stability and recycling. The production and consumption of plastics have increased significantly in recent years and wastes are commonly disposed by pyrolysis. This technique has some disadvantages like poor heat transfer rate and undesirable gum formation. The degradation of polymer in solution can overcome some of these limitations. A number of studies have investigated the degradation of poly(methyl methacrylate) in solution.^{1,2,3} The use of supercritical fluid as a solvent in the polymer synthesis⁴ and degradation⁵ has attracted attention in recent years. The enhanced solubilities and diffusivities in supercritical fluids make it an attractive media for chemical reactions. The enhancement in degradation of polystyrene⁶ and polycarbonate⁷ in supercritical benzene has been observed. The degradation of styrene-butadiene copolymer in supercritical toluene-tetralin mixture resulted in low molecular weight aromatics consisting mainly of xylene, alkyl benzene and diphenylalkanes.⁸ The methanolysis depolymerization of poly(trimethylene terephthalate) in supercritical methanol⁹ confirm the large density and high kinetic energy effect of supercritical fluids. The degradation of polyethylene terephthalate^{10,11} in supercritical methanol showed high yields to its monomers. The recovery of styrene from waste polystyrene in different supercritical solvents has been investigated⁵ with higher yield of styrene recovery in supercritical toluene than in other solvents like benzene, ethyl benzene and p-xylene. Thus the study of degradation of polymers in supercritical fluids is of immense interest.

Recent studies^{12,13} have investigated the effect of alkyl substituents on the thermal, ultrasonic and enzymatic degradation of poly(alkyl acrylates), where it was reported that

the degradation decreases with increase in alkyl group chain length. The effect of alkyl substituents on the thermal degradation of poly(alkyl methacrylates) showed¹⁴ that the smallest energy was required for the degradation of poly (n-butyl methacrylate) (PBMA) compared to poly (propyl methacrylate) (PPMA), poly (ethyl methacrylate) (PEMA), and poly (methyl methacrylate) (PMMA). The degradation of poly(acrylates) and poly(*n*-alkyl methacrylates) under SF₅⁺ primary ion bombardment using time-of-flight secondary ion mass spectrometry (SIMS) has been investigated.¹⁵ The stability of the characteristic secondary ion intensities of these polymers decreased linearly with alkyl pendant group length, suggesting that lengthening the *n*-alkyl pendant group resulted in increased loss of the alkyl pendant groups. Unlike thermal degradation where these polymers degrade primarily via depolymerization, the polymers degraded by intra- or intermolecular cross-linking under SF₅⁺ bombardment.

In the present study, the effect of alkyl group on the degradation kinetics of poly(alkyl methacrylates) was investigated in both subcritical and supercritical states. The effects of solvents and pressure on the degradation rate were also investigated. A continuous distribution model was used to determine the kinetic parameters and activation energies were determined from the temperature dependence of the rate coefficients.

Experimental Section

Materials. Methyl methacrylate, poly (ethyl methacrylate) (number average molecular weight, $M_{n0} = 114000$ and polydispersity, $PD = 1.2$), poly (isopropyl methacrylate) ($M_{n0} = 94000$ and $PD = 1.2$) and poly (butyl methacrylate) ($M_{n0} = 101000$ and $PD = 1.2$) were obtained from Sigma Aldrich. Poly(methyl methacrylate) ($M_{n0} = 340000$ and $PD = 1.2$)

was synthesized by bulk polymerization technique with benzoyl peroxide as the initiator. The solvents tetrahydrofuran, chlorobenzene, dichlorobenzene, toluene, benzene, ethyl benzene and cyclohexane were procured from S.D. Fine Chemicals (India) and filtered through 0.2 μm nylon filter paper prior to use.

Degradation in solution. The experiments were conducted at a constant polymer concentration of 1 kg/m^3 in 11 ml stainless steel reactor. A predetermined volume (calculated by the Peng Robinson equation of state) of polymer solution was initially fed to the reactor so that the system reaches the desired pressure at the particular temperature. The reactors were kept in the furnace in which the desired temperature was maintained within ± 1 $^{\circ}\text{C}$. The degradation of PMMA, PEMA, PPMA and PBMA was studied in toluene at various temperatures from 250 to 375 $^{\circ}\text{C}$. The degradation of PBMA was also investigated in five other solvents (benzene, chlorobenzene, dichlorobenzene, ethylbenzene and cyclohexane) and at various pressures at 325 $^{\circ}\text{C}$. Each reactor was taken out of the furnace after the desired time interval and immersed in ice cold bath. Samples of 1 ml was collected from the reactor and analyzed in GPC. Several experiments were conducted in triplicate and the variation in the rate coefficients was less than 3%.

Sample analysis. The molecular weight distribution of the polymer samples was determined by gel permeation chromatography (GPC, Waters, USA). The GPC system consists of an isocratic pump, a sample loop (50 μl), three size exclusion columns of varying pore size (HR 5E, HR 3 and HR 0.5; 300 mm x 7.5mm) and differential refractive index detector. Tetrahydrofuran (THF) was used as eluent with constant flow rate of 1 ml/min through the system and the columns were maintained at 50 $^{\circ}\text{C}$. The

refractive index was continuously monitored and stored digitally using data acquisition system. The chromatograph was converted to molecular weight distribution using a universal calibration curve determined using polystyrene standards (Polymer Lab, UK).

Degradation by pyrolysis. 10-15 mg of the polymer was pyrolysed in a thermogravimetric analyzer (TGA) (Perkin-Elmer, Pyris, USA) under a nitrogen flow of 150 cc min⁻¹ at four different heating rates (5 – 20 °C/min). Experiments were repeated twice to ensure that the same profile was obtained.

Theoretical Model

Degradation in solution. A polymer can be considered as a mixture of large number of molecules of different sizes with the molecular weight x as a continuous variable. For a polymer of molecular weight x' , $P(x')$, the random degradation of the polymer chain can be represented as



where k represents the degradation rate coefficient. The absence of specific products in the GPC chromatograph and the increase of polydispersity (due to the broadening of molecular weight distribution) approaching two at long times¹⁶ confirms the random scission of the polymer in both the subcritical and supercritical solvents. The degradation mechanism is the formation of free radicals by random scission followed by conversion of free radicals into end products by unimolecular decomposition or disproportionation. The rate coefficient, k , in Eq 1, is the overall degradation rate coefficient that includes the rate coefficients for the detailed degradation mechanism that includes initiation, termination, propagation, intermolecular and intramolecular hydrogen abstraction¹⁷.

The population balance equation for the polymer undergoing reaction (1) in a batch reactor can be written as

$$\frac{\partial p(x,t)}{\partial t} = -k(x)p(x,t) + 2 \int_x^{\infty} k(x')p(x',t)\Omega(x,x')dx' \quad (2)$$

The stoichiometric kernel $\Omega(x,x')$ in equation (2) determines the distribution of scission products and is $1/x'$ for random chain scission¹⁷. The degradation rate coefficient is assumed to be linearly dependent¹⁸ on the molecular weight x ($k(x) = k_d x$).

$$\frac{\partial p(x,t)}{\partial t} = -k_d x p(x,t) + 2 \int_x^{\infty} k_d p(x',t) dx' \quad (3)$$

Applying the moment operation to equation (3) yields

$$dp^{(j)}/dt = -(j-1)/(j+1)k_d p^{(j+1)}(t) \quad (4)$$

For $j = 0$ and 1 corresponding to the zeroth, and first moments, respectively,

$$dp^{(0)}/dt = k_d p^{(1)}(t) \quad (5)$$

$$dp^{(1)}/dt = 0 \quad (6)$$

where $p^{(0)}$ and $p^{(1)}$ represent the molar concentration and mass concentration of the polymer. According to the first moment (equation 6), the mass concentration of the polymer is constant throughout the reaction. Solving equation (5) with initial condition, $p^{(0)}(t=0) = p_0^{(0)}$,

$$p^{(0)}(t) - p_0^{(0)} = k_d p_0^{(1)} t \quad (7)$$

By defining the number average molecular weight M_n , as $p^{(1)}/p^{(0)}$, equation 7 can be rearranged as

$$(M_{n0}/M_n) - 1 = k_d M_{n0} t \quad (8)$$

Thus the variation of M_n with time is essentially the same as the variation of the inverse of molar concentration with time. Equation (8) indicates that the variation of $M_{n0}/M_n - 1$ with time is linear with the slope of $k_d M_{n0}$, where k_d is the degradation rate coefficient that is independent of initial molecular weight.

Degradation by pyrolysis. The degradation rate¹⁹ of the polymer by pyrolysis is

$$-\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(\frac{-E}{RT}\right) \quad (9)$$

where α is the degree of conversion at any time t , A is the preexponential factor, n is order of degradation, E is the activation energy, R is the universal gas constant and T is the temperature of the sample. According to the Kissinger method, the maximum temperature, T_m , can be obtained at the maxima of the first derivative weight loss curve.¹²

Assuming a linear heating rate, β , and differentiating equation (9) with respect to time and setting the resulting expression to zero gives

$$\frac{E\beta}{RT_m^2} = An(1-\alpha)_m^{n-1} \exp\left(\frac{-E}{RT_m}\right) \quad (10)$$

For first-order degradation, $n(1-\alpha)_m^{n-1}$ is equal to unity, and differentiating both sides of equation (10) with respect to $(1/T_m)$

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = \frac{-E}{R} \quad (11)$$

Equation (11) indicates that a plot of $\ln(\beta/T_m^2)$ versus $(1/T_m)$ would be linear.

Results and discussion

The degradation of poly(methyl methacrylate) was investigated in toluene ($T_c = 318.8\text{ }^\circ\text{C}$, $P_c = 41\text{ bar}$) at different temperatures ranging from subcritical ($250\text{ }^\circ\text{C}$, $275\text{ }^\circ\text{C}$, $300\text{ }^\circ\text{C}$) to supercritical ($325\text{ }^\circ\text{C}$, $350\text{ }^\circ\text{C}$, $375\text{ }^\circ\text{C}$) conditions at 60 bar. Figure 1a shows the variation of number average molecular weight of PMMA with time. The degradation rate coefficient, k_d , which is independent of initial molecular weight, is determined from the slope of the regressed line (Eq. 8) for all temperatures (Table 1). The rate coefficient, k_d ($\times 10^{-9}\text{ mol g}^{-1}\text{ min}^{-1}$) increases from 1.44 to 867 when the temperature increases from $250\text{ }^\circ\text{C}$ to $375\text{ }^\circ\text{C}$ indicating that the degradation rates in the supercritical condition are two orders of magnitude higher than that in the subcritical condition. The effect of alkyl substituents was investigated by studying the degradation of PEMA, PPMA and PBMA in toluene at different temperatures ($250 - 375\text{ }^\circ\text{C}$) and at 60 bar. Figures 1b, 1c, 1d show the variation of number average molecular weights of PEMA, PPMA and PBMA, respectively, with time for different temperatures. Table 1 shows that the rate coefficients increases with increase in alkyl group and the degradation rate follows the order, $\text{PBMA} > \text{PPMA} > \text{PEMA} > \text{PMMA}$.

A similar trend has been reported¹⁵ for the degradation of poly(alkyl methacrylates) degradation by ion bombardment and it was suggested lengthening the alkyl group resulted in increased loss of alkyl pendant groups. The trend is also predicted theoretically by the electron delocalization molecular orbital theory.¹⁴ According to this theory, the energy separation can be defined as difference in energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

(LUMO) of the monomers suggesting that the lower the energy separation, the higher the reactivity of the monomer and instability of the polymer. The energy of separation is 3.368, 3.379, 3.350, and 3.433 eV for MMA, EMA, PMA and BMA monomers, respectively, and, therefore, the polymer stability follows the same order. Thus the increase in degradation rate with chain length can be attributed to the steric factor of the larger alkyl chain in the methacrylates.¹⁴

Figure 2 shows the Arrhenius plots for the degradation rate coefficients of PMMA, PEMA, PPMA and PBMA in toluene. The activation energies for PMMA, PEMA, PPMA and PBMA were determined to be 26.6, 25.5, 23.6 and 16.3 kcal/mol, respectively in subcritical condition and 33.9, 32.9, 30.5, 27.2 kcal/mol in supercritical condition. This indicates the decrease in activation energy with length of alkyl group in both subcritical and supercritical conditions. The activation energy is basically the energy required to overcome the electron cloud. As the length of the side chain increases, higher will be the delocalisation of electrons and lower the electron density. Therefore, the activation energy decreases with an increase in the length of the side chain. Earlier studies^{14, 20, 21} also show a decrease in electron mobility and increase in electron cloud for reactions in supercritical fluids. The figure also shows a break and indicates a transition near the supercritical point. The activation energies obtained for the polymers are similar to that obtained for the degradation of polycarbonate⁶ (= 13.8 kcal/mol) and polystyrene⁷ (= 20.4 kcal/mol) in supercritical benzene.

In order to compare the activation energies obtained for the degradation of these polymers in solution with that of the polymers in pyrolysis, the thermal degradation of PMMA, PEMA, PPMA and PBMA was investigated in nitrogen environment at four

different heating rates of 5, 10, 15 and 20 °C/min. Figures 3a–3d show the normalized weight loss profiles for the pyrolysis of poly (alkyl methacrylates). Based on the differential thermogravimetry plots, the temperature (T_m) at which maximum degradation rate occurs is obtained and plotted against the heating rate (Figure 4). The activation energies determined from the slopes of the plot are 37.9, 36.1, 31.1 and 29.9 kcal/mol for PMMA, PEMA, PPMA and PBMA, respectively. These values of activation energies are similar to that obtained previously²² (37.2 and 27.5 kcal/mol for PMMA and PBMA, respectively). The activation energies for the degradation of polymers in both pyrolysis and solution decrease with increase in alkyl group. Though they follow a similar trend to that of the degradation in solution, the values of the activation energies for the degradation of the polymers are much lower in solution indicating that a faster mechanism is rate controlling in supercritical conditions.

The degradation of the polymer in subcritical and supercritical solvents is through the random chain scission, which could be primarily due to the collision of the solvent molecule to the polymer main chain. The degradation of the polymer in pyrolysis occurs by both random chain scission^{22, 23, 24} and by chain end scission²⁵, though it is primarily by the latter¹⁹. The longer the side chain, the easier is the main chain movement leading to molecular chain scission in the main chain. Thus, with an increase in the length of the side chain, the degradation rate of the polymer increases.

To investigate the effect of pressure, the degradation of PBMA was investigated in toluene at a constant temperature of 325 °C and at different pressures to cover both subcritical (20, 30 and 40 bar) and supercritical (60, 70, 85 bar) regions. Figure 5 shows the time variation of number average molecular weight at various pressures in subcritical

and supercritical conditions. The degradation rate coefficient, k_d ($\times 10^{-7}$ mol g⁻¹ min⁻¹), determined from the slope of the lines, decreases from 4.71 at 20 bar to 0.153 at 85 bar. The effect of pressure on the rate coefficient can be possibly be explained thermodynamically by transition state theory which assumes thermodynamic equilibrium between the reactants and a transition state. For unimolecular reaction, the effect of pressure on the reaction rate coefficient, k , can be written as²⁶

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta \bar{v}}{RT} \quad (12)$$

where $\Delta \bar{v}$ is the reaction activation volume, which is dependent on the difference in the partial molar volume of the transition state complex and the reactant. This indicates that a semilog plot of the degradation rate coefficient with pressure at constant temperature would be linear. Figure 6 shows that the variation of degradation rate coefficient with pressure is indeed linear. At the same temperature, as the pressure increases, the molecular motion of the solvent and the polymer main chain is restricted leading to a decrease of energy of collision between the solvent and the polymer. This results in a decrease of the degradation rate with increase of pressure. A significant variation of the rate coefficients is observed in the supercritical region while only a small variation is apparent in the subcritical region. It is well known that the partial molar volume of a dilute solute is proportional to the isothermal compressibility. Thus the activation volumes are the largest near the critical point of the mixture. The variation of rate coefficient with pressure is more significant in the supercritical condition than in subcritical condition due to the long-range density fluctuations that result in a large isothermal compressibility of the solvent and large partial molar volume of the dilute solute.²⁶ The activation volumes are 2-3 orders of magnitude larger in supercritical fluids

compared to that in liquids indicating that a small change in pressure can result in a large change in the reaction rate in supercritical fluids while a similar change in pressure would only result in a minimal change in the reaction rate of liquids.

To investigate whether the degradation is dependent on temperature and pressure rather than on the supercritical state of the solvent, the degradation of PBMA was investigated at 325 °C and 60 bar with different solvents such that benzene, toluene and cyclohexane are in supercritical condition and ethylbenzene, chlorobenzene and dichlorobenzene are in subcritical condition. Figure 7 shows the variation of number average molecular weight of PBMA with time for different solvents at 325 °C and 60 bar. Despite the same temperature and pressure, the degradation rate coefficient of PBMA is significantly higher when the solvent is supercritical compared to that when the solvent is subcritical. This indicates that the supercritical state of the solvent is the controlling factor in determining the degradation rate.

One important factor in the characterization of the rates in supercritical fluids is to understand to what degree the rate constants are influenced by the thermodynamic variables such as temperature and pressure compared to the changes in bulk physical properties of the solvent like density.²⁶ Therefore, the variation of rate constants with density has been extensively investigated. The dependence of the reaction rate with the solvent density has been investigated in various studies: dimethoxybenzhydryl cation with triethylamine in supercritical fluoroform²⁷, maleic anhydride and 2,3-dimethylbutadiene in supercritical propane²⁸, naphthalene fluorescence quenched by bromoethane in supercritical ethane²⁹ and cyclohexane oxidation²¹. Although pressure is usually the experimentally controlled variable, thus examining the variation of the rate

coefficient with density can facilitate the analysis of experimental data. Equation 12 can be rewritten in terms of density as

$$\left(\frac{\partial \ln k}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial P}\right)_T = -\frac{\Delta \bar{v}}{RT} \quad (13)$$

The equation indicates that the variation of the rate coefficient with density is also expected to be linear. To investigate the effect of density, the degradation rate coefficients obtained from the experimental data for the degradation of PBMA at various temperatures in toluene at 60 bar (Figure 1d), in toluene at various pressures at 325 °C (Figure 5) and for different solvents (Figure 7) are plotted against density in Figures 8a, b, and c, respectively. In case of degradation at 60 bar at various temperatures from 250 °C to 375 °C, toluene is initially liquid and becomes supercritical at higher temperatures. In this case, the density of supercritical toluene is lower than that of liquid toluene. However, in the case of degradation in toluene at 325 °C with pressure varying from 20 bar to 85 bar, toluene is initially a gas at lower pressures and becomes supercritical at higher pressures. In this case, the density of supercritical toluene is higher than that of gaseous toluene. The increase of reaction rates in supercritical fluids is consistent with our earlier study on the degradation of polycarbonate in supercritical benzene⁶. However, in our previous study⁶, the variation of the reaction rate coefficient decreased linearly with increase in density. However, as shown in Figure 8, there is break in the variation of the reaction rate coefficient with density in this study. This is because the dependence of the degradation rate coefficient on density is dependent on the system. The observed rate enhancement in the critical region is caused by a combination of solute-solute and solvent-solute clustering.²⁶ At higher densities, solvent-solute clusters dominate and a large excess of solvent molecules may orient about a solute molecule retarding the

degradation rate of the solute. In case of different solvents at 325 °C and 60 bar, three of the solvents (benzene, cyclohexane and toluene) are in the supercritical state while three (ethylbenzene, chlorobenzene and dichlorobenzene) are in subcritical state. The degradation rate coefficient follows the order, benzene > cyclohexane > toluene > ethylbenzene > chlorobenzene > dichlorobenzene and also decreases with increasing density. Clearly, the rate coefficients of PBMA in supercritical solvents is much higher than that in subcritical solvents indicating that the supercritical state of the system plays a major role in determining the degradation rate.

Conclusions

The degradation of four poly(alkyl methacrylates) was carried out in subcritical and supercritical conditions. The effects of alkyl substituents, pressure and solvent were investigated. The time evolution of molecular weight distributions, determined from the experiments, were modeled by continuous distribution kinetics. The degradation rate of poly(alkyl methacrylates) increased with increase in the number of carbon atom of the alkyl substituents with the degradation rate following the order, PBMA > PPMA > PEMA > PMMA in both subcritical and supercritical conditions. The degradation rate coefficients in the supercritical condition were one to two orders of magnitude higher than that in the subcritical condition. The degradation of the polymers was also investigated by pyrolysis in nitrogen environment and the activation energies were obtained by the Kissinger method. The activation energies for the degradation of the polymers in solution were lesser than that observed for degradation by pyrolysis. The degradation of PBMA was also investigated in different solvents and at different pressures. The rate of degradation decreased exponentially with increase in density of the solvents. Further, the degradation rate coefficients in subcritical solvents were much lower than that in supercritical solvents indicating that the supercritical state of the system plays a major role in determining the reaction rates.

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Table 1: Degradation rate coefficients, $k_d \times 10^9$ ($\text{mol g}^{-1} \text{min}^{-1}$), of various poly(alkyl methacrylates) in toluene at different temperatures and at 60 bar.

Temperature(°C)	PMMA	PEMA	PPMA	PBMA
250	1.44	2.27	4.54	12.85
275	3.81	7.87	15.5	24.7
300	13.5	21.8	32.7	50.4
325	96.7	153	208	250
350	320	478	508	611
375	867	1290	1520	1448

Figure Captions

Figure 1. Variation of number average molecular weight of (a) PMMA (b) PEMA (c) PPMA (d) PBMA with reaction time at different temperatures in toluene.

Legend: (■) 250 °C; (●) 275 °C; (▲) 300 °C; (○) 325 °C ; (Δ) 350 °C ; (▽) 375 °C; — Model fit to data.

Figure 2. Arrhenius plot for the degradation of poly(alkyl methacrylates) in toluene.

Legend: (■) PMMA(subcritical); (●) PEMA(subcritical); (▽) PPMA(subcritical); (▲) PBMA(subcritical); () PMMA(supercritical); (O) PEMA(supercritical); (▽) PPMA(supercritical); (Δ) PBMA (supercritical).

Figure 3. Variation of weight fraction for the pyrolysis of (a) PMMA (b) PEMA (c) PPMA (d) PBMA with temperature. The arrow showing increasing heating rates from 5 to 20 °C/min.

Figure 4. Kissinger plot for the pyrolysis of (■) PMMA; (●) PEMA; (▲) PPMA; (▽) PBMA.

Figure 5. Variation of number average molecular weight of poly(butyl methacrylate) with reaction time at different pressures in toluene at 325 °C.

Legends: (■) 85 bar; (●) 70 bar; (▲) 60 bar; (○) 40 bar; (Δ) 30 bar; (▽) 20 bar; — Model fit to data.

Figure 6. Variation of rate coefficients with pressure for degradation of poly(butyl methacrylate) in toluene at 325 °C in (●) subcritical (■) supercritical conditions.

Figure 7. Variation of number average molecular weight of poly(butyl methacrylates) with reaction time at 60 bar and 325 °C in (◆) dichlorobenzene; (▼) chlorobenzene; (▲) ethyl benzene; (○) toluene; (Δ) cyclohexane; (▽) benzene; — Model fit to data

Figure 8. Variation of degradation rate coefficient with density in (a) toluene at different temperatures in (●) subcritical (■) supercritical conditions (b) toluene at different pressures at 325 °C in (●) subcritical (■) supercritical conditions. (c) various solvents at 60 bar and 325 °C in (◆) dichlorobenzene; (▼) chlorobenzene; (▲) ethyl benzene; (○) toluene; (Δ) cyclohexane; (▽) benzene

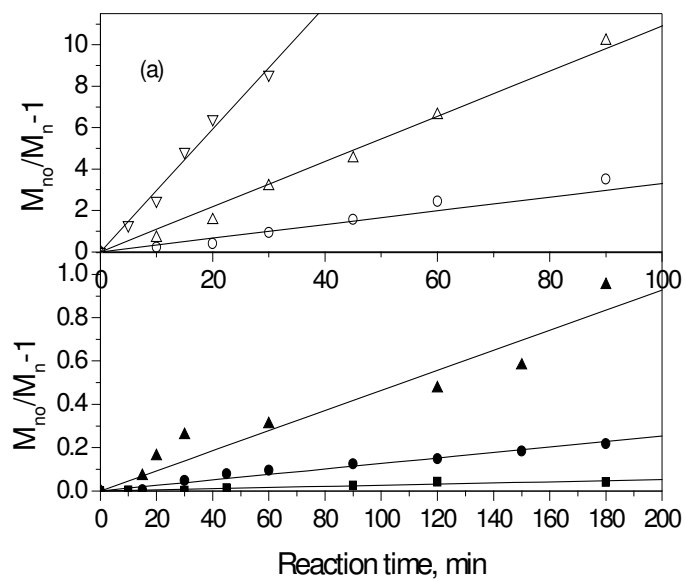


Figure 1a

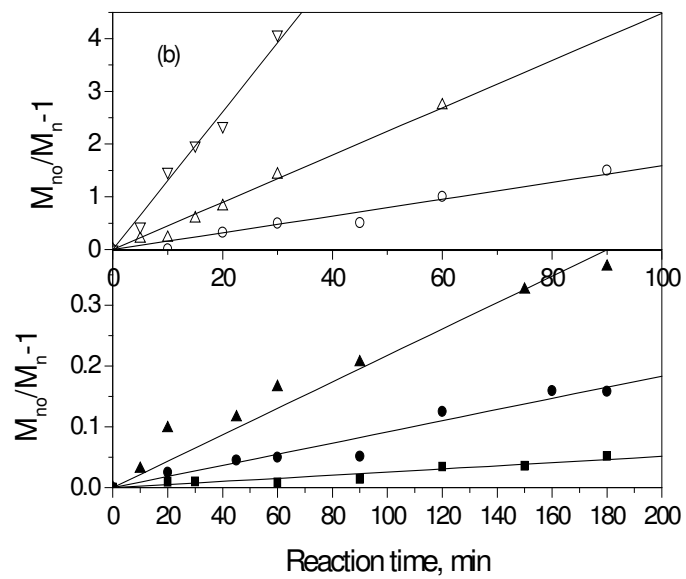


Figure 1b

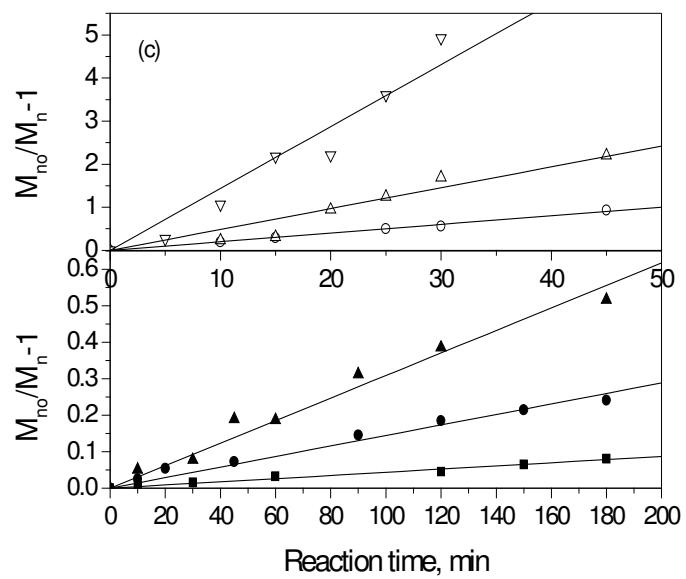


Figure 1c

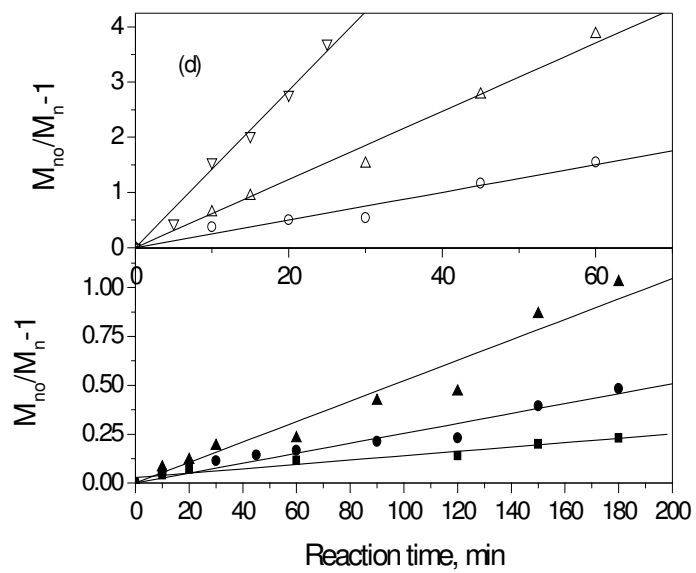


Figure 1d

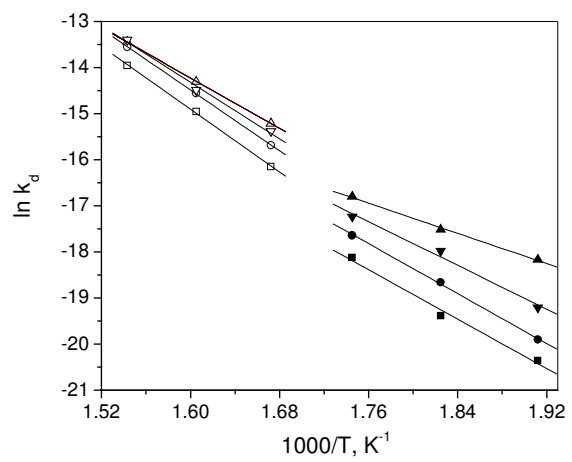


Figure 2

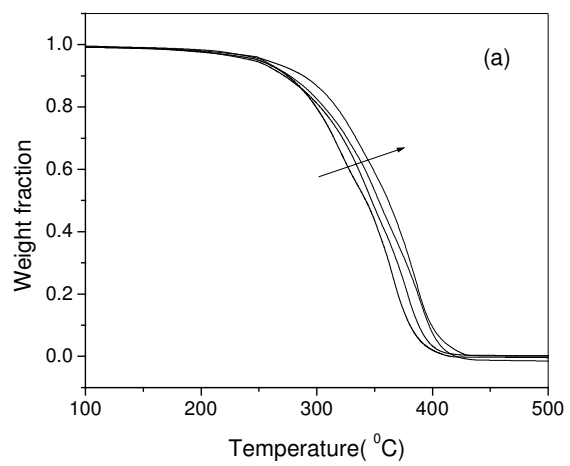


Figure 3a

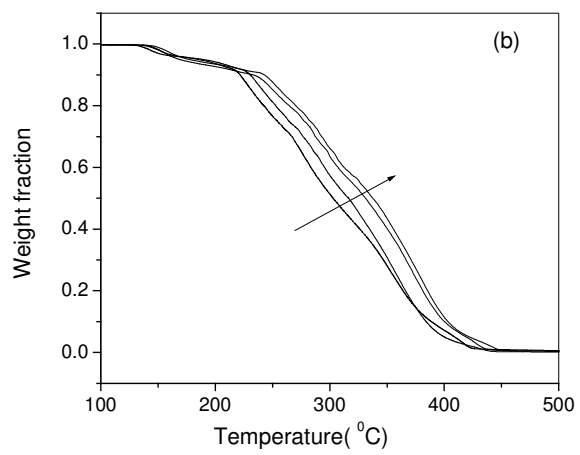


Figure 3b

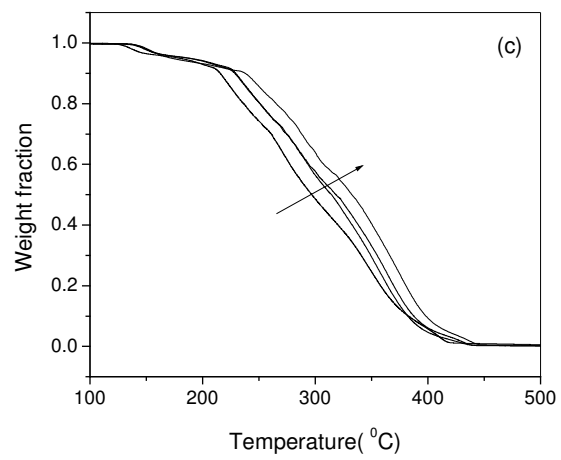


Figure 3c

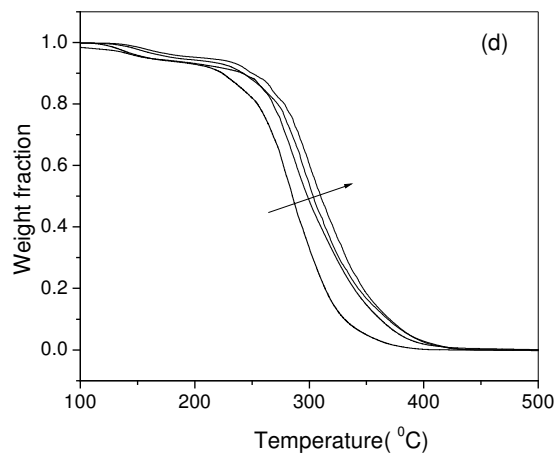


Figure 3d

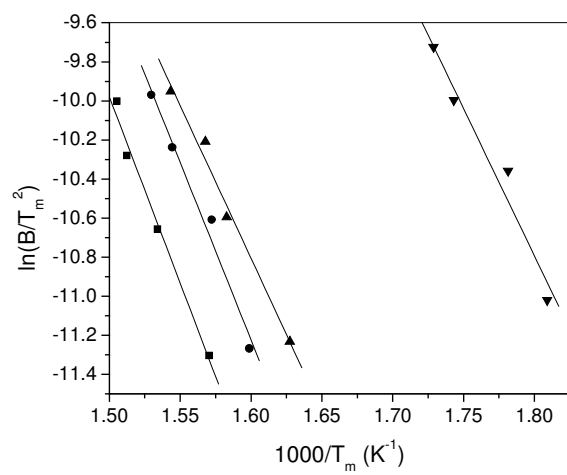


Figure 4

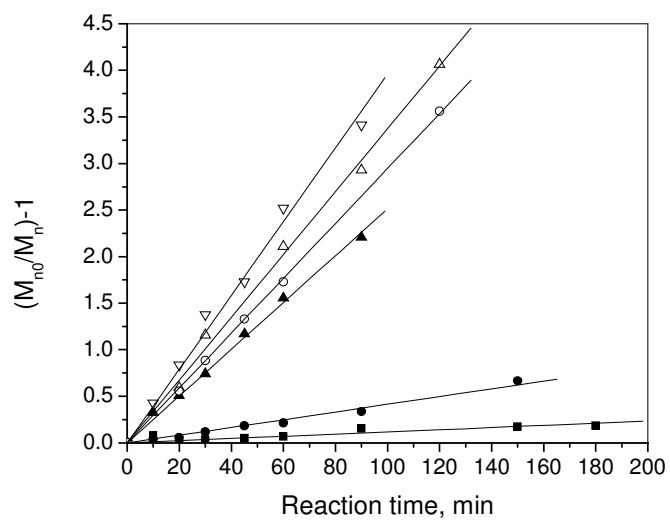


Figure 5

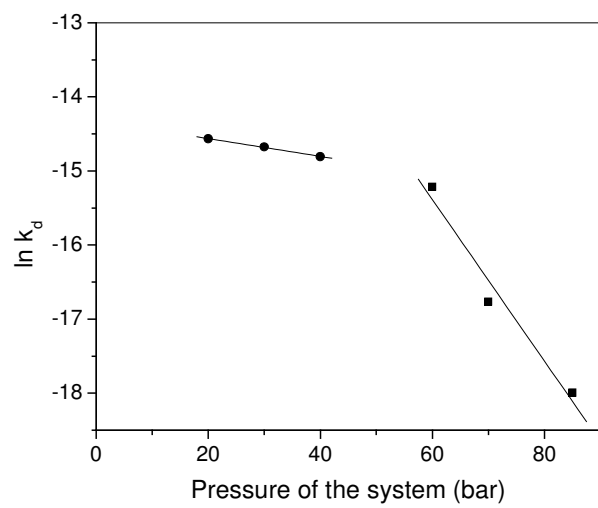


Figure 6

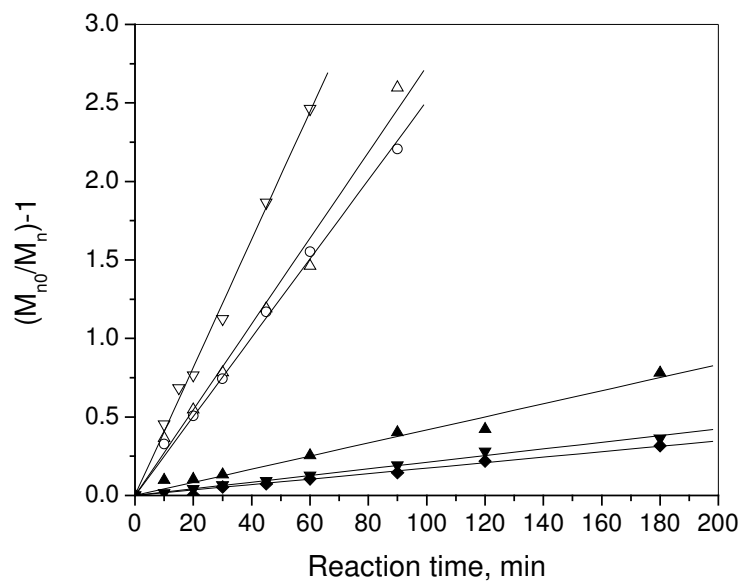


Figure 7

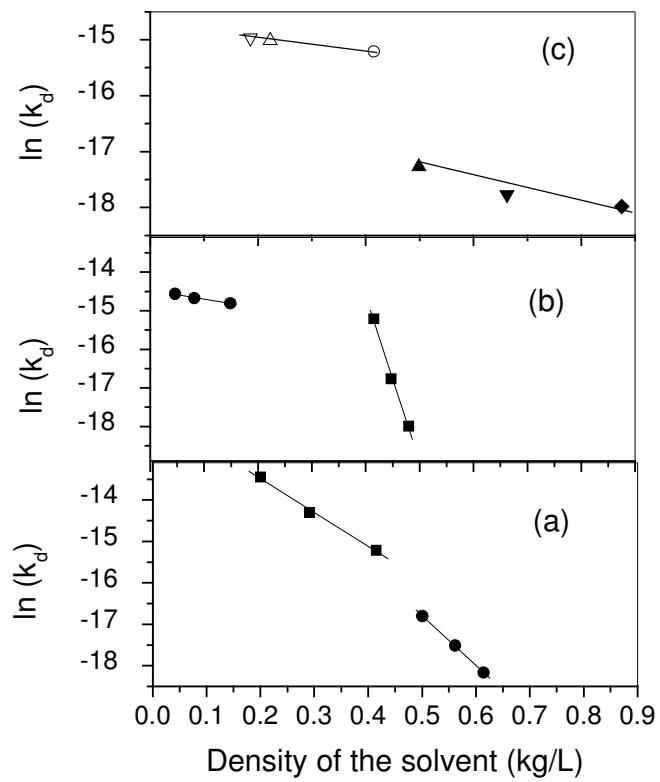


Figure 8