Influence of Temperature and Penetration Depth on Photopolymerization of *n*-Butyl Acrylate Using a Narrow Channel Reactor

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ABSTRACT: The influence of temperature and reactor size on photopolymerization kinetics of n-butyl acrylate (n-BA) using narrow channel reactors has been investigated. Experimental results have shown that increase in temperature and decrease in size of the reactor increases the monomer conversion. The effect of temperature was studied by immersing the reactor in a water bath maintained at different temperatures. A narrow channel glass reactor, 900 mm long, with diameters 1.5 mm, 1.0 mm, and 0.5 mm respectively were used to study the effect of light penetration depth on the rate of polymerization and molecular weights of the polymer produced. The degree of branching in the polymer produced was also estimated and compared with published data. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1940–1947, 2010

Key words: branched; photopolymerization; thermal properties; NMR; gel permeation chromatography (GPC)

INTRODUCTION

Photopolymerization is a process, in which light is used as a means of making polymers. The interest in photopolymerization has increased with demand for energy efficiency and solventless processes. However, attenuation of light in the sample limits its use to thin films only. This has also been limited to static films, owing to the difficulty in generating thin films in a flow system. This work explores the use of a narrow channel reactor as a means of making polymer resins using UV as the mode of initiation. The design of the reactor developed is in accordance to the benefits of process intensification, which promotes continuous processing using thin films for enhancement in the transport properties.[1] The flow system gives precise control of the exposure time by controlling the flow rate through the reactor.

In photopolymerization reactions with flood lamps, there is a significant amount of radiative heat from the lamp. In addition, there is heat of polymerization that becomes significant at high rates of propagation. The effect becomes mutual in the absence of a heat sink to control the temperature. The effect of temperature is different in photopolymerization as compared to thermal polymerization where in the later case, the rate of initiation is also dependant on temperature. Iwasaki and Yoshida[2] reported thermal polymerization of *n*-BA using a microreactor to obtain low pdi of the polymer. It was attributed to efficient heat transfer in the reactor causing uniform rates of initiation. In thermal polymerization, the rate of initiation and the rate of polymerization increase with temperature. The temperature gradient in a reactor will have a direct influence on the rate of polymerization. This effect becomes even more evident with formulations that have faster kinetics.

Extensive studies on the effect of temperature in photopolymerization have been carried out in static films.[3–5] Tryson and Shultz[6] used photo-DSC to investigate the extent of monomer conversions by monitoring the heat of polymerization. Scherzer and Decker[4] investigated the variation in maximum rate of polymerization of Tripropylene glycol diacrylate (TPGDA) and Bisphenol A Epoxy diacrylate oligomer (BA-EpAc) with temperature using different photoinitiators. It was found that the maximum rate of polymerization increased with temperature with low extinction coefficient photoinitiators and decreased with increase in temperature when high extinction coefficient photoinitiators were used. The high rate of termination was found to be the cause for this behavior with high extinction coefficient photoinitiators. As reported by

TABLE I
Rate Constants for Backbiting in *n*-BA Polymerization from Various Researchers

Backbiting rate constant (s^{-1})	Notes	Reference
924	75°C	Plessis et al.[15]
9310, 13200, 18200	140, 160, 180°C	Quan[10]
$3.5 \times 10^7 \exp\left(\frac{-29,300}{RT}\right)$	−16 to 60°C	Plessis et al.[12]
$4.31 \times 10^7 \exp\left(\frac{-29,800}{RT}\right)$	−41 to 40°C	Arzamendi et al.[13]
4000	138°C	Peck et al.[16]
3000	138°C	Li et al.[17]
$3.87 \times 10^6 \exp\left(\frac{-19,114}{RT}\right)$	140 to 180°C	Rantow et al.[11]
$4.84 \times 10^7 \exp\left(\frac{-31,700}{RT}\right)$	−10 to +30°C	Niktin et al.[14]

Goodner and Bowman,[7] this behavior is due to the primary radical termination behavior that is known to occur at high concentrations of initiator. Jachuck and Nekkanti[8] have reported that primary radical termination is found to be significant for photoinitiator (2,2-dimethoxy-2-phenyl-acetophenone) concentration above 2.5% w/w of *n*-BA. Therefore, in the current investigation, a photoinitiator concentration of 2.0% w/w of *n*-BA has been maintained in all experiments to minimize any effects by primary radical termination. Scherzer and Decker[4] studied the effect of temperature on polymerization by varying the viscosity of the reaction system and has found that the increase in the polymerization rate is mostly due to reduction in viscosity.

In a photopolymerization process, the rate of initiation is affected by the local intensity of light. The local light intensity in the sample is dependant on the concentration of light absorbing species and the thickness of the sample. The light intensity varies along the sample thickness according to the Beer's law of absorption. As reported by Terrones and Pearlstein[9] the light attenuation leads to nonuniform rate of initiation along the depth of the sample. This leads to variable degree of polymerization at different depths of sample. To understand this behavior, reactors with different diameters were used in this study to investigate the influence of penetration depth on the kinetics of photopolymerization.

The level of branching from NMR analysis along with the monomer conversion values from Gas chromatograph (GC) analysis can be used to estimate the backbiting rate constant. Quan[10] and Rantow et al.,[11] have estimated the rate constant from high temperature solution polymerization of BA in the absence of thermal initiators. Plessis et al.,[12] have obtained branched poly(BA) from PLP carried out in bulk and solution polymerization between −16°C and 60°C. Similar expression has been derived by Arzamendi et al.,[13] from Monte Carlo simulations for PLP experiments for BA. It was shown that the intramolecular chain transfer event dominates other chain transfer events such as chain transfer to monomer and intermolecular chain transfer to polymer reactions. Niktin et al.,[14] have reported a rate constant based on dispersion parameter of size exclusion chromatogram (SEC) broadening in PLP experiments. Table I summarizes the available literature on backbiting rate constant in BA polymerization along with the window of temperature used.

Plessis et al.,[18,19] have reported that the level of branching in the polymer increases with temperature and decreasing monomer concentration. The effect of temperature on branching in the flow reactors is estimated in this work. The obtained Arrhenius dependant expression will be compared to those reported so far.

EXPERIMENTAL SECTION

Description of the experimental setup

The experimental setup consisted of a narrow channel reactor made of borosilicate. The reactor that can be seen in Figure 1 and Figure 2 has a length of 900 mm and an internal diameter of 1.5 mm. The reactor
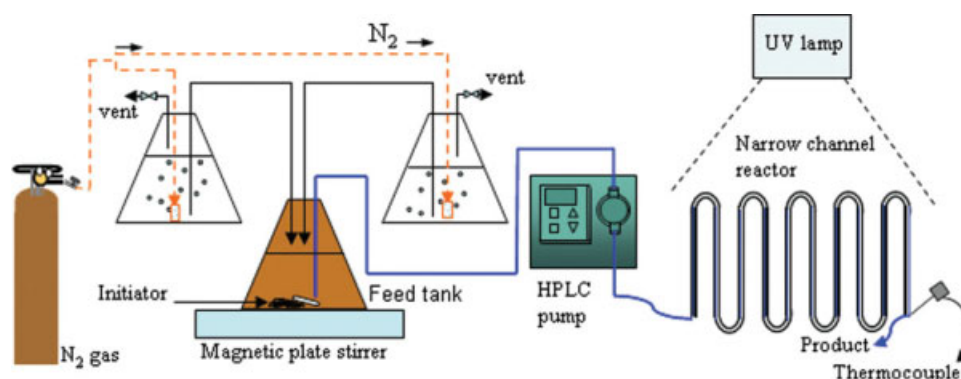

Figure 1 Detailed schematic of the experimental setup. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
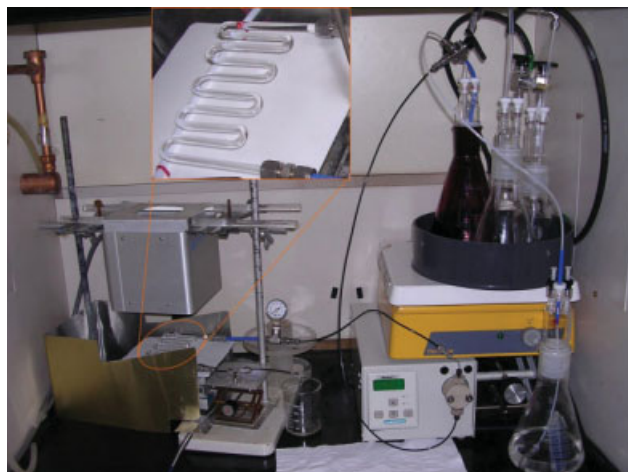
Figure 2 Photograph of the experimental setup. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

has 10 linear sections each of 70 mm length and nine semicircular bends with a radius of 7 mm. To investigate the influence of penetration depth of light, reactors of same length and shape but different internal diameters of 1.0 mm and 0.5 mm were used. Ultraviolet radiation was generated by using a 400 W metal halide flood lamp supplied by Dymax Corp. The UV flood lamp has a maximum intensity at 365 nm, which is also the excitation wavelength of the initiator.[20] The lamp was supported by clamp stands in a manner such that the distance between the lamp and the reactor surface could be altered to study the influence of UV intensity on the reaction kinetics. The intensity of the UV radiation received on the reactor was measured by using a UV-A radiometer (Model: Accucal 20 series) from Dymax with ± 2% accuracy. The exposure times have been varied by changing the flow rate through the reactor. A HPLC pump (model C-74930-00, Cole Parmer) was used to deliver the desired flow rate (1–10 mL/min). A thermocouple was used to measure temperature at the outlet of the reactor. The outlet temperature profiles against experimental time were recorded using a thermocouple-computer interface (Pico Technology). Polymerization of n-butyl acrylate is an exothermic reaction and the UV flood lamp used generates heat; hence time–temperature profile was used to identify the steady state condition in an experiment, in which exposure time (or flow rate), light intensity, and initiator concentration in feed were all constant. Samples were collected for each experiment after steady state conditions were achieved.

To study the effect of temperature, the (thermal) conditions outside the reactor have been altered. Experiments carried out in ambient air without any provisions for forced cooling except by natural convection (by ambient air) have been termed as 'no

water bath' condition. Experiments with the reactor immersed in an isothermal water bath have been termed as 'water bath' condition. Water is used as medium to maintain the desired temperature due to its transparency in the UV-region.[21–23] It is cautioned that the glass reactor used is a bad conductor of heat and hence, the temperatures monitored at the exit of the reactor are again used to identify the steady state condition.

An extensive arrangement was made to ensure the feedstock was free of oxygen. It was found that about 20 min was sufficient to effectively purge the system free of oxygen. As shown in Figure 2, the monomer and solvent were purged separately in Erlenmeyer flasks for 20 min and then fed to another Erlenmeyer flask, which contains a premeasured amount of initiator. The transfer of the monomer and solvent was done by controlling/closing the exit valve of nitrogen to develop a positive pressure on the liquid. This approach was employed to ensure that the composition in the feed does not change due to loss of solvent and monomer by vaporization during the purging process. The preloaded initiator, monomer, and solvent were mixed for about 20 min using a magnetic stirrer. All the experiments were carried out with 20% of toluene by volume.

Chemicals used

The monomer, n-butyl acrylate (Aldrich) was passed through an inhibitor remover column (Aldrich packed columns, 306312). Toluene, 2,2-dimethoxy-2-phenyl-acetophenone, and hydroquinone were obtained from Aldrich. Tetrahydrofuran (THF) obtained from J. T. Baker was used to dissolve the hydroquinone and the solution was added to the product collected from the experiments to quench any unreacted radicals. Oxygen-free grade nitrogen was used for purging the feed mixture.

Characterization

GC was used for detection of monomer in the sample. Conversion is obtained by measuring the monomer peak area in the feed and product. A Thermo Electron Focus GC equipped with an auto sampler, split type injector, and flame ionization detector (FID) has been used. Helium was used as a carrier gas; and hydrogen and air were used as FID gases. The following was the method used: (1) initial temperature of 50°C, followed by a heating rate of 30°C/min to a final temperature of 100°C and (2) heating rate of 40°C/min to a final temperature of 250°C and hold for 1 min at the final temperature. A J and W scientific DB-5 column with 0.53 mm × 1.5 μm × 15 m dimensions and (5%-phenyl)-methylpolysiloxane as stationary phase was used in the GC.
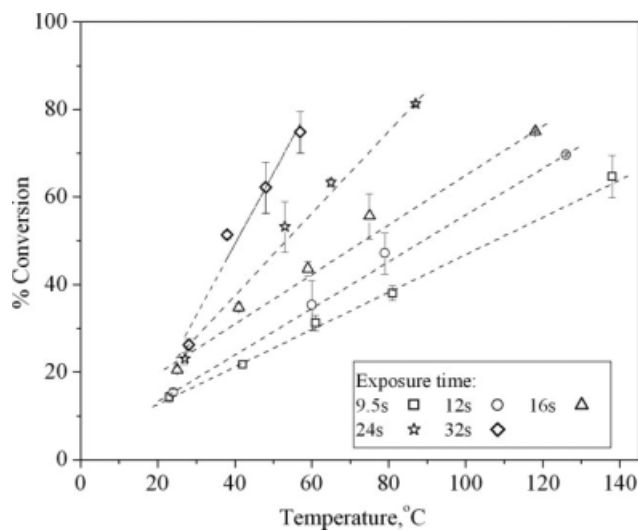
Figure 3 Influence of temperature on monomer conversion in 1.5 mm diameter reactor.

Gel permeation chromatography (GPC) system (PL-GPC 50; 2 x PL ResiPore (300 × 7.5 mm) columns; refractive index (RI) detector) from Polymer Laboratories (PL) was used for obtaining the molecular weight distribution of the product. The oven was maintained at a constant temperature of 30°C. THF was used as a solvent at a flow rate of 1 mL/min. The molecular weights of the polymer were obtained by comparing against a calibration curve generated using polymethylmethacrylate (PMMA) narrow standards. Samples for GPC were made by dissolving 200 μL of sample in 5 mL of THF. About 500 μL of the diluted sample was then injected and the chromatogram obtained was analyzed for the molecular weight distribution. Mark–Houwink parameters ($K = 12.2 \times 10^{-5}$ dL/g and $a = 0.70$) for poly(butyl acrylate) reported by Beuermann et al.[24] were used to estimate the absolute average molecular weights from the SEC curve.

The degree of branching in polymer has been characterized by using nuclear magnetic resonance (NMR) spectroscopy. The quenched samples from selected experiments were dissolved in chilled hexane to remove the nonpolymer fraction. Samples were centrifuged and the supernatant was removed to separate the polymer fraction. The residue was vacuum dried at room temperature for about 48 h. The dried polymer was dissolved in deuterated chloroform ($CDCl_3$) to give a concentration of 100 mg/mL. ^{13}C-NMR spectra were obtained at 40°C using Bruker Avance DMX-400 NMR spectrometer operating at 400 MHz. Chemical shifts were referenced to tetramethylsilane (TMS) peak at 0 ppm. To maximize the signal to noise ratio during analysis, ^{13}C spectra were run with continuous proton decoupling using a pulse interval of 5.25 μs. The number of scans varied from 32,000 to 49,000 with an acquisi-

tion time of 0.65 s. The degree of branching has been estimated from the ratio of the sum of the branched CH and CH_2 integrals to the total integral for backbone carbon atoms.[16,25]

RESULTS AND DISCUSSION

Effect of temperature on the kinetics

Figure 3 shows the effect of temperature on monomer conversions for different exposure times. The data with same exposure time was represented with same symbols. Experiments were performed using a constant light intensity of 86 mW/cm^2 and an initial photoinitiator concentration, $[P]_0$, of 2.0% w/w of BA. The temperatures monitored depend on the temperature of the water bath outside the glass reactor and the exposure time. The monomer conversion increases with increase in temperature for the same exposure time. In a typical thermal polymerization, the effect of temperature is directly dependant on the rate of initiation. But, in photopolymerization, the effect of temperature on the initiation can be neglected as it is known that DMPA is thermally stable up to 300°C[26] and self-initiation of n-BA occurs only above 140°C.[10,11] Therefore, the increase in monomer conversion is only due to the Arrhenius dependant behavior of the rate constants.

Scherzer[4,26] has successfully identified viscosity as the major contributing factor for the increase in the rate of polymerization with temperature. The monomer conversions are plotted as a function of exposure time and a curve fit was generated to obtain an expression. The obtained expression was differentiated with time to obtain the rate of polymerization for the corresponding exposure time. Figure 4 shows the effect of temperature on rate of polymerization
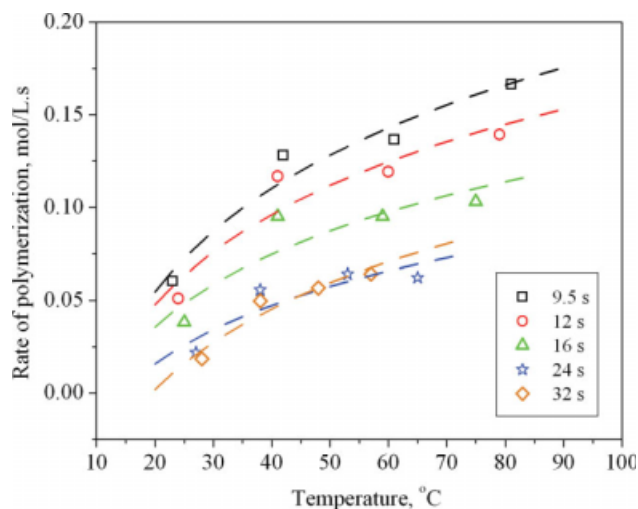

Figure 4 Effect of temperature on rate of polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
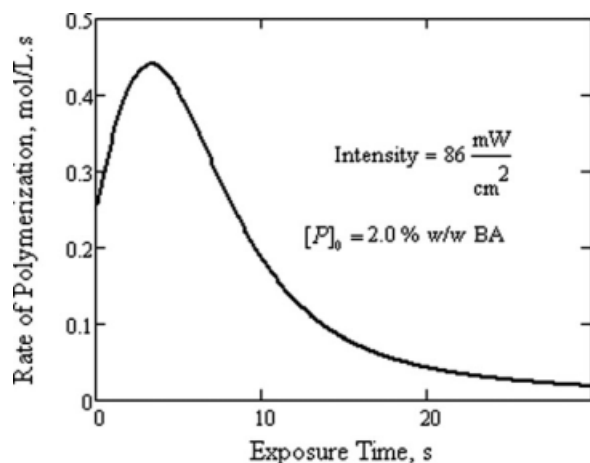
Figure 5 Influence of exposure time on rate of polymerization.

for different exposure times. As expected, the rate of polymerization increases with increase in temperature. In a typical photopolymerization process, the rate of polymerization increases initially reaching a maximum followed by a gradual decrease.[3,4] The trend in the rate of polymerization is similar to that of thermal polymerization, except that the time scale is usually smaller due to high rates of initiation in photopolymerization. The rate of polymerization decreases gradually as exposure time increases after the maximum has been attained. The rate of polymerization as a function of exposure time obtained from photopolymerization of n-BA using a 1.5 mm diameter channel reactor, which was exposed to the surrounding environment (reactor was not placed in the water bath), is shown in Figure 5. A constant photoinitiator concentration of 2.0% w/w and intensity of 86 mW/cm^2 were maintained while increasing the exposure time from 9.5 to 24 s. It must be noted that as the exposure time was increased from 9.5 to 24 s the reaction temperature, which strongly influenced the rate of polymerization, increased from 90 to 140°C.

Therefore, as shown in Figure 4, for a constant temperature, the rate of polymerization values decrease as the exposure times increase from 9.5 to 32 s.

Influence of penetration depth on conversion

Figure 6 (a) shows the effect of exposure time on the monomer conversions for different channel diameters used. The reactors were immersed in a constant temperature water bath. The temperatures recorded using different channel diameters are shown in Figure 6 (b). As can be seen in Figure 6 (a), for the same exposure times, the monomer conversions increase with decrease in the size of the reactor. Smaller channels will have reduced light attenuation

and therefore yield higher rates of initiation. The rate of initiation is directly proportional to the rate of polymerization and hence the increase in the monomer conversions.

Effect of temperature on the molecular weight of polymer

Figure 7 shows the effect of monomer conversion on molecular weight of polymer at different temperatures using 1.5 mm diameter reactor. The molecular weight decreases with increase in monomer conversions. For the same conversion values the molecular weight increases with increase in sample temperature. It is known that the number average molecular weight of a polymer, $\bar{M}_n$, is proportional to rate of polymerization, R_p, and inversely proportional to rate of initiation, R_i. $\bar{M}_n \propto \frac{R_p}{R_i}$. The rate of initiation in photopolymerization is independent of temperature and the rate of polymerization increases with
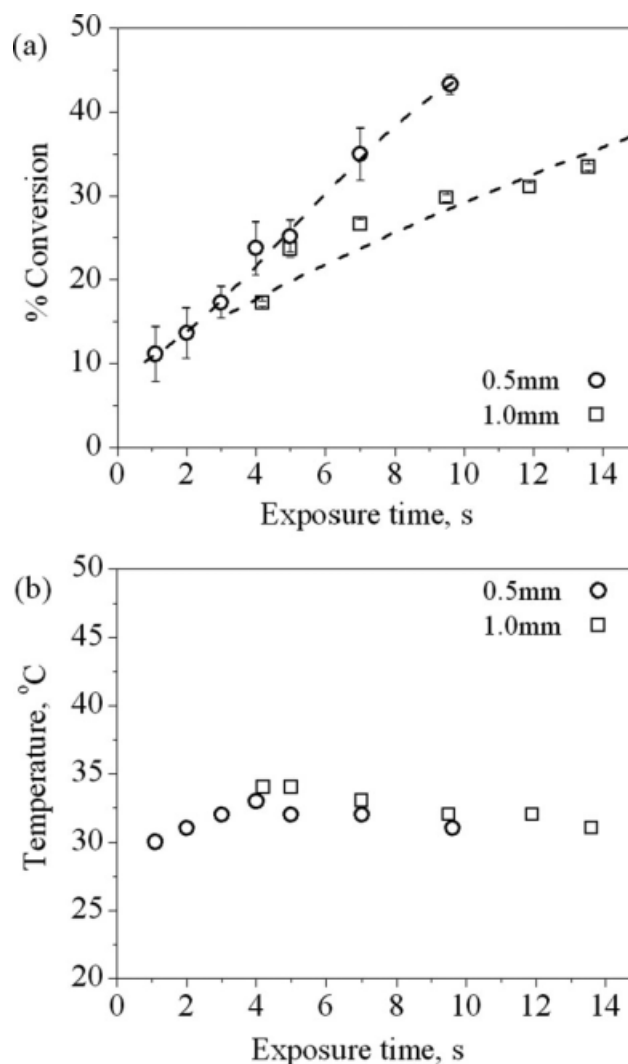

Figure 6 Influence of penetration depth on conversion when immersed in a water bath.
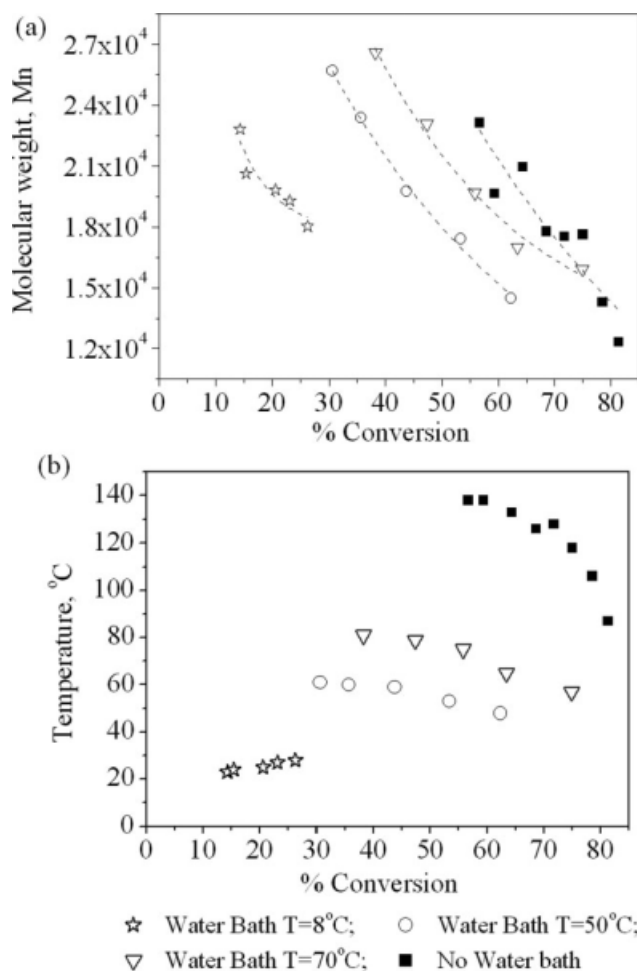
Figure 7 Influence of temperature on molecular weight using 1.5mm diameter reactor

temperature and therefore the molecular weight also increases with temperature. The effect of increase in molecular weight with temperature was found to be less in the high conversion region. This could be due to secondary reactions that become significant in polymerization of *n*-butyl acrylate at high temperatures. The secondary propagating radicals are known to undergo a backbiting effect and convert to tertiary radicals. The newly formed tertiary radicals reduce the overall rate of polymerization.[16,18,27,28]

Effect of penetration depth on the molecular weight of polymer

Figure 8(a) shows the influence of monomer conversions on the molecular weight of the polymer formed using reactors of 0.5 mm and 1.0 mm channel diameter. As can be seen in the experiments with water bath, the molecular weight of polymers formed using 1.0 mm diameter reactor yielded higher values than those obtained using 0.5 mm diameter reactor. The exit temperatures for the respective conversion values are given in Figure 8(b). The

temperature values indicate that the Arrhenius rate constants assume a constant value and the variation in the molecular weights is only due to the variation in the rate of initiation.

Assuming the majority of the propagating chains terminate by coupling mechanism, the number average degree of polymerization, $\bar{X}_n$, is given by the following:

$$\bar{X}_n = 2 \cdot \upsilon \tag{3.1}$$

Neglecting the chain transfer reactions, the kinetic chain length, υ, can be expressed as:

$$\upsilon = \frac{R_p}{R_i} \tag{3.2}$$

R_p is the rate of propagation and R_i is the rate of initiation.

The number average molecular weight of the polymer is defined as:

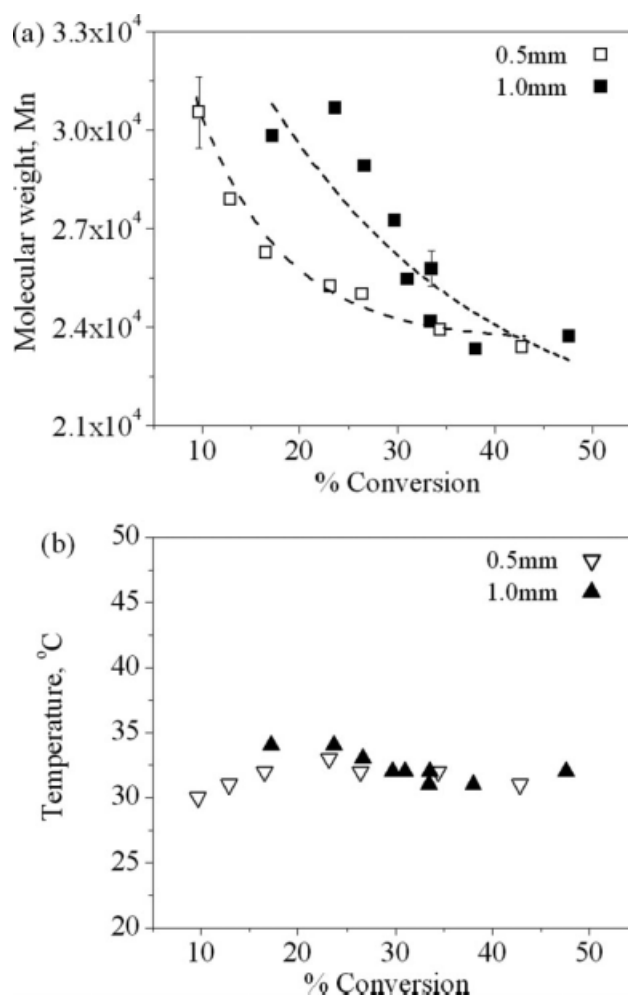$$\bar{M}_n = M_{BA}\bar{X}_n \tag{3.3}$$

Figure 8 Influence of reactor size on molecular weight when immersed in a water bath.
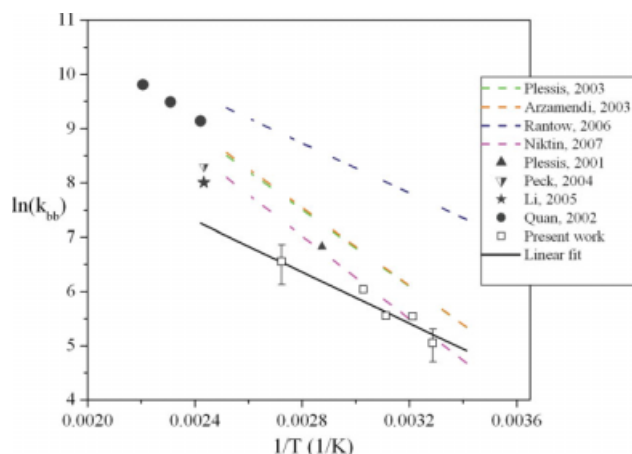
Figure 9 Arrhenius plot of backbiting rate constant. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

M_{BA} is the molecular weight of the monomer.

$$\bar{M}_n = \frac{\sqrt{2} \cdot M_{BA} \cdot [M]_0 \cdot k_{p,eff}(T) \cdot (1 - X)}{\sqrt{k_t(T)} \cdot \sqrt{R_i}} \quad (3.4)$$

where, $[M]_0$ is the monomer concentration in the feed, $k_{p,eff}$ is the effective propagation rate constant of butyl acrylate, T is the temperature, X is the monomer conversion, and k_t is the termination rate constant. Equation 3.4 can be modified to expression 3.5 under constant monomer conversion and temperature values.

$$\bar{M}_n \propto \frac{1}{\sqrt{R_i}} \quad (3.5)$$

According to Beer's law, optical attenuation varies with the channel diameter. Smaller dimensions have higher rate of initiation and this leads to lower molecular weights for the same monomer conversion values. As explained by Terrones and Pearlstein,[9] with increase in reaction time, the effect of optical attenuation becomes less significant at higher conversions. Therefore, at higher conversion values the effect of channel diameter or optical attenuation on the molecular weight becomes less significant. This effect can be seen in Figure 8(a) for conversion values above 35%.

Rate constant for backbiting

Any mathematical model developed to predict the monomer conversion values should use appropriate Arrhenius dependant rate constants. With newer techniques the rate constant for propagation, termination, and chain transfer to monomer reported in the literature are well validated.[29] The estimation of rate constant for backbiting in n-BA polymerization is a topic currently being explored. Figure 9 shows the Arrhenius dependant rate constants at various temperatures obtained from various sources to highlight the variation among these values. The dashed lines in the plot are generated based on the Arrhenius expressions listed in Table I.

The scatter in the published data prompted us to perform NMR analysis for obtaining backbiting rate constant for the current system. Selected samples, preferably samples with sufficient polymer content, were analyzed for branching and the rate constant for backbiting is estimated based on the local concentration of monomer and temperature of the sample as given by the eq (3.6).

$$k_{bb} = \frac{branching \cdot k_{p1} \cdot [M]_0[1 - X]}{1 - branching} \quad (3.6)$$

In the above expression, k_{p1} was obtained based on the measured temperature and the monomer conversion, X, was obtained by GC analysis.

The experimentally estimated branching data, temperature, and monomer conversions are given in Table II. The obtained k_{bb} values are plotted against the temperature and the linear fit through these points is shown as a solid line in Figure 9. The obtained Arrhenius dependant rate constant for backbiting is given in eq (3.7).

$$k_{bb} = 4.3 \cdot 10^5 \exp\left(\frac{-19600}{RT}\right) \quad (3.7)$$

The expression derived is applicable for the current reactor configuration, where the flow conditions

TABLE II
Mole Percent Branches in the Polymer Prepared by Photopolymerization with 2.0% w/w of DMPA and 86 mW/cm² Intensity Under Different Thermal Conditions

Conditions outside the reactor	Steady state exit Temperature (°C)	Exposure time (s)	(%) Conversion	(%) Molar branching
NWB	94	24	81.33 ± 0.33	1.334 ± 0.443
WB ($T = 70°C$)	57	32	74.9	0.93
WB ($T = 50°C$)	48	32	62.2	0.47
WB ($T = 30°C$)	38	32	51.2	0.42
WB ($T = 25°C$)	33	16	37.97 ± 0.99	0.276 ± 0.077

WB, constant temperature water bath; NWB, no water bath.

cannot be assumed to be the same as in an ideal reactor with minimal mass transport limitations. Any reaction rate constant is a thermodynamic property and should be independent of heat and mass transfer capabilities of the reactor system. However, the reported values from the literature as shown in Figure 9, indicate that the rate constant can be used only when the exact operating conditions are maintained and it ignores the influence of flow conditions on kinetics.

CONCLUSIONS

Photopolymerization of n-BA was performed in a flow system using narrow channel glass reactors for a UV intensity of 86 mW/cm^2 and $[P]_0$: 2% w/w. The effect of temperature and penetration depth on the kinetics has been investigated. It may be concluded that the monomer conversion increases with increase in the temperature and with decrease in diameter of the reactor. Higher temperatures increase the segmental mobility of the chains thus increasing the monomer conversions. The rate of polymerization increases rapidly, attains a maximum and then decreases steadily with increase in exposure time. The molecular weight of the polymer decreases as monomer conversion increases. For the same monomer conversion values, the molecular weights increase with increase in temperature. For constant temperature and constant monomer concentration values, the molecular weight decreases with increase in rate of initiation. The branching studies have indicated that the amount of branching in polymer obtained from narrow channel reactor yielded lower values in comparison to the values reported from traditional reactors. It is believed that the shear in the flow conditions might be contributing to this effect.

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