

Kinetics of Butylacrylate Polymerization in a Starved Feed Reactor

Gui-Ping Cao, Zhong-Nan Zhu, Ming-Hua Zhang, Wei-Kang Yuan

State Key Lab of Chemical Engineering, UNILAB Research Center of Chemical Reaction Engineering, East China University of Science and Technology, Shanghai 200237, China

Received 28 May 2003; accepted 1 March 2004

DOI 10.1002/app.20622

Published 2004 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A starved feed reactor (SFR) is a semibatch polymerization reactor where initiator and monomer are fed slowly into a fixed amount of solvent. The polymerization is carried out isothermally at elevated temperatures. The added initiator decomposes instantaneously and the added monomer polymerizes immediately. The molecular weight of the product polymer can be effectively controlled by the feed ratio of monomer to initiator. This article presents a study on the kinetics of butylacrylate polymerization in an SFR. The model parameters are regressed with experimental

data. Although the solids fraction in the SFR is high (>50%), viscosity is not high and the "gel effect" is weak because of the low molecular weight of the products. It is found that the termination rate constant is a power function of molecular weight, and the lumped rate constant $k_p/(k_t)^{1/2}$ can be modeled through an Arrhenius equation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1519–1525, 2004

Key words: starved feed reactor; radical polymerization; kinetics (polym.); *n*-butylacrylate; initiators

INTRODUCTION

A starved feed reactor (SFR) is a semibatch polymerization reactor into which initiator and monomer are fed continuously. The molecular weights of the products in the reactor can be controlled effectively by the ratio of the flow rates of monomer and initiator. The low molecular weight polymer can thus be directly used in high solids fraction coatings. In one such type of a reactor, the flow rates of the reactants are very low, and the amount of initiator used is greater than that normally practiced. The reaction temperature is so high that the initiator fed into the reactor decomposes instantaneously and the monomer also reacts immediately. In an ideal case, the concentrations of the initiator and the monomer in the reactor should be very low, ideally approaching zero. Moreover, the reactor is in a "starved" status for reactants, and molecular weight is very low (usually the degree of polymerization is 30–70).

The kinetics behavior of butylacrylate (BA) polymerization in an SFR is not the same as that in a normal reactor. Literature on polymerization kinetics is abundant, but few reports are concerned with SFR performances.^{1–3} The kinetics of BA polymerization in SFR has not been seen, and thus the aim of this article

was to present a kinetics model of BA polymerization in SFR.

KINETICS MODEL FOR BA POLYMERIZATION IN AN SFR

In a radical polymerization, the initiator decomposes into primary radicals.

Initiator initiation



At the same time, the monomer may also form a primary radical at high temperatures. Hui and Hamielec,⁴ who studied the kinetics of styrene thermal polymerization, proposed the following thermal initiation mechanism.

Thermal initiation



Correspondence to: G.-P. Cao (gpcao@ecust.edu.cn).
Development project of Shanghai Priority Academic Discipline.

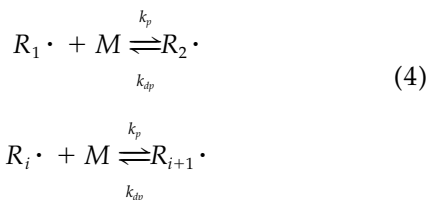
No references to BA thermal polymerization were seen, but from the perspective of chemical engineering, the order of the reaction is not higher than 3; here we assume the thermal initiation is followed by eq. (2).

The primary radical $R_0\cdot$ reacts with the monomer to form initiated monomer radicals:



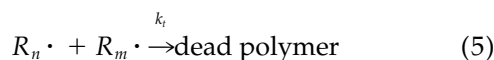
The radical species then attack the monomer to form a growing macroradical chain; meanwhile, the growing macroradicals may depropagate at elevated temperatures.

Propagation and depropagation



Two propagating radicals can terminate, thus forming dead polymer chains.

Termination



For a typical polymerization in this reactor, the relative contribution of chain-transfer reaction to the initiator, solvent, monomer, as well as to the polymers is negligible. If thermal initiation occurs at high temperatures, the initiation rate may be written in the form

$$r_i = r_{i,T} + r_{i,T} = 2fk_d[I] + 2\bar{k}_i[M]^3 \quad (6a)$$

where \bar{k}_i is the thermal initiating rate constant and k_d is the decomposition rate constant of initiator, which for 2,2'-azobisisobutyronitrile (AIBN) is

$$k_d = 1.6248 \times 10^{15} \exp(-1.551 \times 10^4/RT) \quad (T/K)$$

Cao et al.² calculated the fraction thermal initiation in the total initiation for styrene polymerization in an SFR. The value is $r_{i,T}/r_i = 5-8 \times 10^{-6}$. For BA polymerization, the rate of thermal initiation is generally lower than that of styrene thermal polymerization; thus, thermal initiation is negligible. The initiation rate may be written in the form

$$r_i = r_{i,T} + r_{i,T} \approx r_{i,T} = 2fk_d[I] \quad (6b)$$

Figure 1 is a chart of SFR. The initial solvent charged into the reactor is V_0 ; the initiator solution and monomer are fed into the reactor at a constant flow rate of

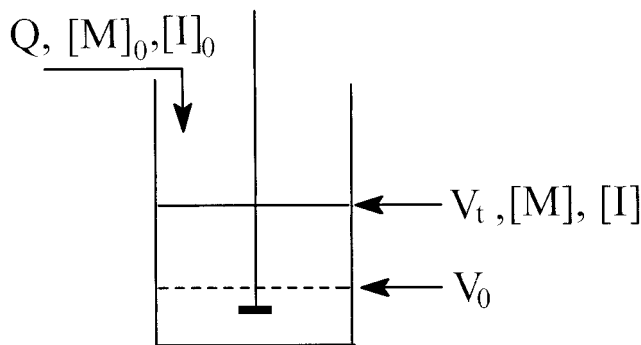


Figure 1 Chart of a starved feed reactor.

Q ; and their concentrations in the feed stream are $[I]_0$ and $[M]_0$, respectively.

The material balance for the initiator is

$$\frac{d\{V_t[I]\}}{dt} = [I]_0Q - k_d[I]V_t \quad (7)$$

Integration of eq. (7) yields

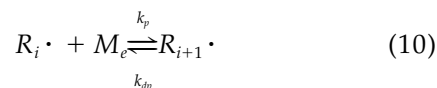
$$[I] = \frac{Q[I]_0}{V_t} \frac{1}{k_d} [1 - \exp(-k_d t)] \quad (8)$$

By assuming that the number of radicals in the reactor is constant, one obtains

$$\frac{d\{V_t[R_1\cdot]\}}{dt} = \left\{ r_i + k_{dp}[R_2\cdot] - k_p[M][R_1\cdot] - k_t[R_1\cdot] \left(\frac{r_i}{k_t} \right)^{1/2} \right\} V_t = 0 \quad (9a)$$

$$\frac{d\{V_t[R_i\cdot]\}}{dt} = \left\{ k_p[M][R_{i-1}\cdot] + k_{dp}[R_{i+1}\cdot] - k_p[M][R_i\cdot] - k_t[R_i\cdot] \left(\frac{r_i}{k_t} \right)^{1/2} \right\} V_t = 0 \quad (9b)$$

When propagation and depropagation reach equilibrium



The equilibrium equation can be written as

$$k_p[R_i\cdot][M]_e = k_{dp}[R_{i+1}\cdot] \quad (11)$$

Noting that $J = [R_{i+1}\cdot]/[R_i\cdot]$, eq. (11) can be rewritten as

$$k_{dp} = k_p[M]_e/J \quad (12)$$

By substituting eq. (12) into eqs. (9a) and (9b), one obtains

$$J = \frac{(k_p/\sqrt{k_t})([M] - [M]_e)}{(k_p/\sqrt{k_t})([M] - [M]_e) + \sqrt{r_1}} \quad (13)$$

$$[R_1 \cdot] = \left(\frac{r_1}{k_t}\right)^{1/2} (1 - J) \quad (14a)$$

$$[R_i \cdot] = \left(\frac{r_1}{k_t}\right)^{1/2} (1 - J)^{i-1} \quad (14b)$$

The monomer balance in the system is

$$\frac{d\{V_t[M]\}}{dt} = Q[M]_0 - r_{POL}V_t \quad (15)$$

where r_{POL} represents the rate of monomer consumption in the reaction with the primary radicals in the initiation step and with macroradicals in the propagation step.⁵ If the macroradicals undergo depropagation in the process, r_{POL} may include the rate of monomer production in the depropagation step. Then r_{POL} can be written as

$$r_{POL} = r_i + r_p - r_{dp} \quad (16)$$

In eq. (16) r_p represents the propagation rate:

$$r_p = k_p[M] \sum_{i=1}^{\infty} [R_i \cdot] = k_p[M] \left(\frac{r_1}{k_t}\right)^{1/2} \quad (17)$$

and r_{dp} represents the depropagation rate:

$$r_{dp} = k_{dp} \sum_{i=2}^{\infty} [R_i \cdot] = Jk_{dp} \sum_{i=1}^{\infty} [R_i \cdot] \quad (18)$$

Substituting eq. (12) into eq. (18) yields

$$r_{dp} = k_p[M]_e \left(\frac{r_1}{k_t}\right)^{1/2} \quad (19)$$

Substituting eq. (17) and eq. (19) into eq. (16) yields

$$r_{POL} = \sqrt{r_1} \left\{ \sqrt{r_1} + (k_p/\sqrt{k_t})([M] - [M]_e) \right\} \quad (20)$$

Substituting eq. (13) into eq. (20) yields

$$r_{POL} = \frac{1}{1 - J} r_1 \quad (21)$$

Thus, the material balance for the monomer is

$$\frac{d\{V_t[M]\}}{dt} = Q[M]_0 - \frac{1}{1 - J} r_1 V_t \quad (22a)$$

Equation (22a) can be rewritten as follows:

$$\frac{dn_m}{dt} = \dot{n}_m - \frac{1}{1 - J} r_1 V_t \quad (22b)$$

Equation (22a) or eq. (22b) is the kinetics model of BA polymerization in the SFR. The monomer concentration in the SFR can be calculated from the kinetics model. The model involves the following parameters:

- Initiator efficiency: f
- The lump rate constant: $k_p/\sqrt{k_t}$

Over a wide range of viscosity, the propagation rate constant k_p remains constant,⁶ but the termination rate constant k_t is influenced by the viscosity in the system and the polymer chain length. This effect was first reported by O'Dricoll et al.,⁷ and later confirmed and modeled by other researchers.⁸⁻¹¹ Models of this type take the following form:

$$\frac{k_t}{k_t^0} = (x_n)^{-\alpha} \quad (23)$$

This chain length dependency reflects the fact that the termination step in the initial stages of the reaction is controlled by the rate of segmental diffusion of the macroradical chain ends. It has been suggested that the chain length dependency of the termination rate constant can be correlated to the cumulative average degree of polymerization, such that

$$\frac{k_t}{k_t^0} = (\bar{X}_n)^{-2\alpha} \quad (24)$$

The argument supporting this conclusion is that macroradicals undergo segmental diffusion of chain ends, which is affected by the presence of the surrounding polymer, which in turn reduces the rate of termination in the system.

EXPERIMENTAL

Purification of reactants

Monomer (BA) and solvent (2-heptanone, also known as methyl amyl ketone) were washed with 5% aqueous NaOH, respectively, to remove inhibitors, antioxidants, and impurities. The organic phases were then washed with deionized water to neutral pH (=7) and dried overnight with calcium anhydride. The mono-

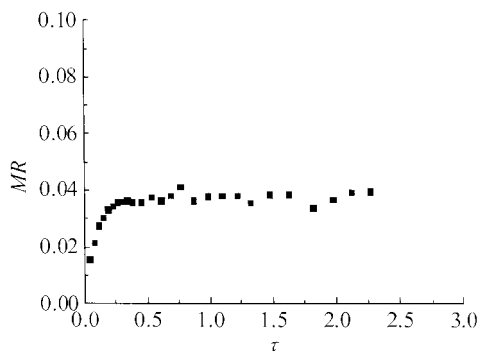


Figure 2 Mass ratio of BA to solvent versus reaction time ($T = 150^{\circ}\text{C}$, $\theta = 7934.78$ s).

mers were then distilled at reduced pressure at a reflux temperature of $<25^{\circ}\text{C}$, in which the head and tail fractions were excluded. The middle fractions were stored in sealed flasks under refrigeration (-10°C) and used within 24 h.

The initiator (AIBN) was recrystallized twice from ethanol using standard procedures, dried under high vacuum, and refrigerated (-10°C) until use.

Procedures

An initiator solution (0.3 mol L^{-1}) was made and kept at room temperature ($23\text{--}25^{\circ}\text{C}$). The monomer was stored in a bath of ice water. The initiator and the monomer were sequentially pumped into the reactor into which an aliquot of 0.2 L solvent (the mass was measured and recorded) was initially charged. The reaction temperatures were 100, 110, 120, 130, 150, and 170°C . Samples were withdrawn at intervals over the course of the run and placed in a vial where a measured quantity of inhibitor was deposited to terminate the reaction. The reaction products were then analyzed for the mass ratio of monomer to solvent (MR), solids fraction (sf), molecular weight (MW), and molecular weight distribution (MWD).

Analysis of samples

The MR in the samples was determined by a Model-1002 gas chromatography (GC), the sf in the samples was determined through gravimetry, and MW and MWD of the samples were determined by a Waters (Milford, MA) 150C ALC/GPC.

ANALYSIS OF EXPERIMENTAL DATA AND REGRESSION OF MODEL PARAMETERS

Analysis of experimental data

Figures 2–4 present the experimental results of mass ratio, solid fraction, and MW versus reaction time at

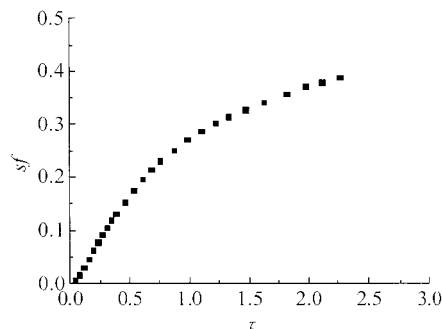


Figure 3 Solids fraction versus reaction time ($T = 150^{\circ}\text{C}$, $\theta = 7934.78$ s).

one of the reaction temperatures, where dimensionless time is used for the plots and defined as

$$\tau = t/\theta \quad \theta = V_0/Q \quad (25)$$

Because the volume of the reaction mixture was expected to change with temperature and the volume decreases with monomers polymerizing to polymers, the volume in the system at time t can be accurately calculated as follows:

$$V_i = m_s/\rho_s + m_m/\rho_m + m_p/\rho_p$$

The densities of 2-heptanone, BA, and PBA at any temperature are as follows:

- $\rho_s = A - BT - C/(D - T)$, g cm^{-3}
- $A = 1.0823$, $B = 0.68128 \times 10^{-3}$, $C = 28.077$, $D = 711.81$, T/K
- $\rho_m = (0.76995 - 2.21726 \times 10^{-3}t)^{1/3}$, g cm^{-3}
- $\rho_p = 1186.8 - 0.635(T - 273.15)$, g cm^{-3}

The mass of a sample (commonly 0.5–1.5 g) is far less than that of the contents in the reactor at any time, but the feed rates of reactants are small (commonly 1.5 g min^{-1}). If samples are taken every 5 min over the

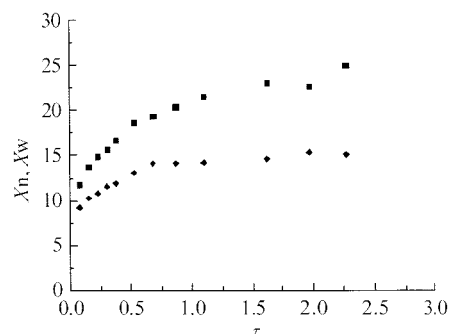


Figure 4 Average molecular weight versus reaction time ($T = 150^{\circ}\text{C}$, $\theta = 7934.78$ s). \diamond , number-average molecular weight; \blacksquare , weight-average molecular weight.

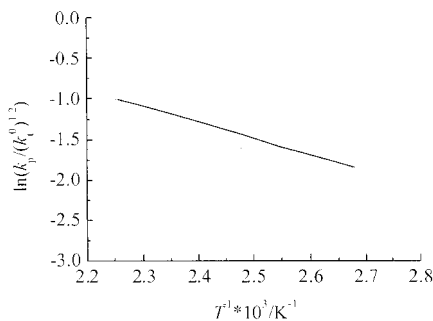


Figure 5 Rate constant $k_p/(k_t^0)^{1/2}$ versus temperature.

course of a run, the mass of material fed into the reactor is 7.5 g during the 5 min, and the mass ratio of a sample to the material fed into the reactor during the 5 min is 6.6–20%. Such an amount is comparatively large, such that corrections must be made for the contents of the reactor, taking into account the masses of the solvent, the monomer, and the polymer in the system at time t . The accurate reactor content can be calculated with the following equations:

$$(m_s)_i = (m_s^0 + \dot{m}_s t_i) - \sum_{j=1}^{i-1} \{sol\}_j$$

$$(m_m)_i = MR_i(m_s)_i$$

$$(m_p)_i = sf_i \cdot \{[m_s^0 + (\dot{m}_s + \dot{m}_m)t_i]\}$$

$$- \sum_{j=1}^{i-1} (\{sol\}_j + \{mon\}_j + \{pol\}_j) \quad (26)$$

$$(i \geq 2, j \geq 1)$$

Regression of model parameters

In the regression of model parameters, the objective function used in this article is as follows:

$$s = \ln \sum_{i=1}^{NMR} (MR_c - MR_e)_i^2 + \ln \sum_{i=1}^{NN} (sf_c - sf_e)_i^2 \quad (27)$$

where MR_e and sf_e are the experimental results and MR_c and sf_c are the model values. They are as follows:

$$MR_{c,i} = \frac{m_{m,c,i}}{m_s^0 + \dot{m}_s t_i} \quad i = 1$$

$$MR_{c,i} = \frac{m_{m,c,i} - \sum_{j=1}^{i-1} \{mon\}_j}{m_s^0 + \dot{m}_s t_i - \sum_{j=1}^{i-1} \{sol\}_j} \quad i \geq 2$$

$$sf_{c,i} = \frac{\dot{m}_m t_i - m_{m,c,i}}{m_s^0 + \dot{m}_s t_i + \dot{m}_m t_i} \quad i = 1$$

$$sf_{c,i} = \frac{\dot{m}_m t_i - m_{m,c,i} - \sum_{j=1}^{i-1} \{pol\}_j}{m_s^0 + \dot{m}_s t_i + \dot{m}_m t_i - \sum_{j=1}^{i-1} (\{sol\}_j + \{mon\}_j + \{pol\}_j)}$$

$$i \geq 2$$

where $m_{m,c,i}$ designates the results of integration of eq. (22). Equation (22) inwardly contains monomer equilibrium concentration $[M]_e$, which can be calculated from the following equation¹²:

$$[M]_e = \exp[(\Delta H_p^0 - T\Delta S_p^0)/RT]$$

where R is the gas constant and ΔH_p^0 and ΔS_p^0 are the standard enthalpy and entropy, respectively, which can be found in reference¹² ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H_p^0 = -79,838 \text{ J mol}^{-1}$, and $\Delta S_p^0 = -114.95 \text{ J mol}^{-1}$).

Discussion

Model parameters

The model parameters were calculated as discussed above. The relationship between the lump rate constant $k_p/(k_t^0)^{1/2}$ and temperature is as follows:

$$k_p/(k_t^0)^{1/2} = 35.75 \exp(-2028.6/T)$$

Figure 5 shows the relationship and Figure 6 gives parameters f and α versus reaction temperature.

Depropagation

The monomer concentration in the SFR is typically 0.5 mol L^{-1} by computation from the kinetics model. Table I shows the equilibrium concentration $[M]_e$ at various temperatures. The data in Table I show that

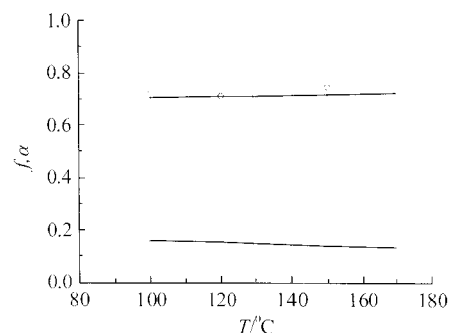


Figure 6 Relationship of f , α , and temperature: \diamond , f ; \square , α .

TABLE I
Equilibrium Concentration $[M]_e$ at Various Temperatures

	Temperature (°C)						
	60	100	120	130	150	160	170
$[M]_e \times 10^4, \text{ mol L}^{-1}$	0.0031	0.0673	0.2493	0.4570	1.4088	2.3789	3.9232

the equilibrium concentration $[M]_e$ is less than $4 \times 10^{-4} \text{ mol L}^{-1}$. Compared with the concentration in the SFR, the equilibrium concentration $[M]_e$ is very low, and the balance between $[M]$ and $[M]_e$ in eq. (13) is approximately equal to $[M]$, that is $[M] - [M]_e \approx [M]$. Thus, the macroradicals do not undergo depropagation as BA polymerization in the SFR at elevated temperatures.

CONCLUSIONS

In a starved feed reactor, the molecular weight of the resulting polymer is effectively controlled by the feed rates of the monomer and initiator. The degree of polymerization in the SFR is 30–70. In this article, a kinetics model was established, and the model parameters were regressed with experimental data. The relationship between the lump rate constant $k_p/(k_t^0)^{1/2}$ and temperature can be represented by an Arrhenius equation.

Although the solid fraction in the SFR is rather high, viscosity is not high and the “gel effect” is rather weak because of the lower molecular weight of the products. The termination rate constant was found to be a power function of the cumulative average degree of polymerization. The other parameters (initiation efficiency f and correction constant α) remain constant over the experimental range. Although the reaction temperatures were high, the macroradicals did not undergo depropagation.

NOMENCLATURE

f	initiator efficiency
I	initiator molecule
$[I]_0$	initiator concentration in the SFR feed stream, mol L^{-1}
k_d	initiator decomposition rate constant, s^{-1}
J	a constant
k_t	thermal initiation rate constant, $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$
k_p	propagation rate constant, $\text{L mol}^{-1} \text{s}^{-1}$
k_t^0	termination rate constant, $\text{L mol}^{-1} \text{s}^{-1}$
k_t^0	disproportionation, $\text{L mol}^{-1} \text{s}^{-1}$
M	monomer
\bar{M}_n	number-average molecular weight
MR	mass ratio of monomer to solvent

MW_{mon}	molecular weight of monomer
$[M]_0$	monomer concentration in the SFR feed stream, mol L^{-1}
m_m	mass of monomer in the SFR, g
m_p	mass of polymer in the SFR, g
m_s	mass of solvent in the SFR, g
m_s^0	mass of initial solvent charged to the SFR, g
\dot{m}_m	mass flow rate of monomer into the SFR, g s^{-1}
\dot{m}_s	mass flow rate of solvent into the SFR, g s^{-1}
$\{mon\}$	mass of monomer in SFR samples, g
N_i	number of samples of type i , where i represents MR, sf, \bar{M}_n
n_m	moles of monomer in the SFR, mol
\dot{n}_m	molar flow rate of monomer into the SFR, mol s^{-1}
$\{pol\}$	mass of polymer in SFR samples, g
Q	volume feed rate of the SFR feed stream, L s^{-1}
R	gas constant
R_0^{\cdot}	primary radicals
R_i^{\cdot}	a radical that has incorporated “ i ” monomer units
r_I	initiation rate, $\text{mol L}^{-1} \text{s}^{-1}$
$r_{I,I}$	initiator initiation rate, $\text{mol L}^{-1} \text{s}^{-1}$
$r_{I,T}$	thermal initiation rate, $\text{mol L}^{-1} \text{s}^{-1}$
r_p	propagation rate, $\text{mol L}^{-1} \text{s}^{-1}$
r_{POL}	rate of monomer consumption in polymerization, $\text{mol L}^{-1} \text{s}^{-1}$
s	objective function
sf	solids fraction
$\{sol\}$	mass of solvent in SFR samples, g
T	reaction temperature, K
t	time, s
V_0	volume of initial solvent charged to the reactor, L
V_t	volume of reaction mixture in the SFR at time t , L
x_n	chain length
\bar{X}_n	cumulative average degree of polymerization
α	a constant
θ	replacement time of the reactor, s
ρ	density, g L^{-1}
τ	dimensionless reaction time

Subscripts

<i>c</i>	calculated value from models
<i>e</i>	experimental value
<i>m</i>	monomer
<i>p</i>	polymer
<i>s</i>	solvent

References

1. Cao, G.-P.; Zhu, Z.-N.; et al. J Chem Eng Chin Univ 1995, 9, 52 (in Chinese).
2. Cao, G.-P.; Zhu, Z.-N.; et al. J Polym Eng 1999, 19, 135.
3. G.-P.; Cao, Zhu, Z.-N.; et al. J Chem Ind Eng 1997, 48, 208 (in Chinese).
4. Hui, A. W.; Hamielec, A. E. J Appl Polym Sci 1972, 16, 744.
5. Cao, G.-P.; Zhu, Z.-N. J Chem Ind Eng 1996, 47, 29 (in Chinese).
6. Leslie, G. L.; Maxwell, I. A.; Ballard, M. J. Aust J Chem 1988, 44, 1.
7. O'Dricoll, K. F.; Mahabadi, H. K. J Polym Sci Polym Chem Ed 1976, 14, 869.
8. Mahabadi, H. K. Makromol Chem Macromol Symp 1987, 10/11, 127.
9. Khoklov, A. R. Makromol Chem Rapid Commun 1981, 2, 633.
10. Olaj, O. F. Makromol Chem Rapid Commun 1982, 3, 549.
11. Mahabadi, H. K. Macromolecules 1985, 18, 1319.
12. Sawada, H. Thermodynamics of Polymerization; Marcel Dekker: New York, 1976.