Polymer 49 (2008) 2817–2824

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Optimizing polymer reactivities for the solid-state polycondensation of AA and BB type monomers

Yuesheng Ye, Kyu Yong Choi*

Department of Chemical and Biomolecular Engineering, University of Maryland, Building 090, College Park, MD 20742, United States

ARTICLE INFO

Article history:
Received 5 February 2008
Received in revised form 4 April 2008
Accepted 12 April 2008
Available online 24 April 2008

Keywords:
Solid-state polymerization
Optimization
Bisphenol A polycarbonate

ABSTRACT

A new method is presented to optimize the reactivities of a prepolymer for the solid-state polymerization of AA and BB type monomers to obtain high molecular weight polymers. The proposed method consists of blending the prepolymers of different end group mole ratios to maintain optimal reaction stoichiometry, and developing a computational procedure to calculate the molecular weight of the polymer in the solid-state polymerization. A molecular species model is used to calculate the molecular weight moments of the optimized prepolymer and to calculate the molecular weight development in a solid-state polymerization. The molecular weight moments of different polymer species in the prepolymer mixture are estimated by performing the dynamic simulations of a melt prepolymerization process model in conjunction with a numerical optimizer. The model simulation results show that the proposed method offers a significantly improved process performance to obtain high molecular weight condensation polymers in a solid-state polymerization. Bisphenol A polycarbonate is selected as an example to illustrate the proposed method.

1. Introduction

The solid-state polymerization is an important industrial process for the production of high molecular weight engineering and specialty condensation polymers such as polyethylene terephthalate, bisphenol A polycarbonate, and nylons. In a typical solid-state polycondensation process, the molecular weight of relatively low molecular weight semicrystalline prepolymers is increased at a temperature above the polymer's glass transition temperature but below its melting point. Volatile polycondensation byproducts are removed from the polymer particles of several hundred microns by inert purge gas or vacuum. Although the solid-state polymerization is a very effective way to increase the molecular weight of the condensation polymer, the solid-state polymerization rate is inherently very slow because the mobility of polymer chain segments is low in the solid state. Therefore, a long reaction time is required to attain a high polymer molecular weight. Also, a large consumption of energy is required to purge the condensation byproducts from the polymer particles. For the industrial production of high molecular weight condensation polymers by solid-state polymerization, continuous reactors such as rotary drum-type reactors, fixed-bed reactors, fluidized bed reactors, stirred bed reactors, and moving packed-bed reactors are used. Because of its industrial importance, the solid-state polymerization processes have been the subject of many experimental and theoretical modeling studies in recent years [1–19].

There are several factors that affect the rate of solid-state polymerization in a polymer particle. For example, the intraparticle mass transfer (diffusion) resistance for the removal of condensation byproducts is often a rate-controlling process. The smaller the polymer particle is, the smaller the intraparticle diffusion resistance is for the condensation byproducts; however, if the polymer particles are too small, they are difficult to be processed in a continuous solid-state polymerization reactor.

The stoichiometric imbalance of the functional end groups of the prepolymer is another important factor. In a classical linear step-growth polymerization process, it has been well known that high molecular weight polymers can be obtained when the reactive end group ratio is maintained at its stoichiometric value (i.e., 1.0). For the polymers derived from AB type monomers (A and B are different reactive end groups), the concentrations of both A and B groups are always same and the stoichiometric ratio is maintained throughout the polymerization. If some side reactions occur, the molar ratio of end groups even in AB type polymerization system can deviate from the stoichiometry, affecting the rate of solid-state polymerization [7].

When AA and BB type monomers are polymerized in a high-temperature melt polycondensation process, the deviation from the stoichiometric end group ratio can cause a serious problem if one of the monomers is more volatile than the other and a partial loss of the more volatile monomer occurs during the polymerization. A good

---

* Corresponding author. Tel.: +1 301 405 1907; fax: +1 301 405 0523.
E-mail address: choi@umd.edu (K.Y. Choi).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.04.031

Nomenclature

A_0	AA monomer
A_n	polymeric species A
B_0	BB monomer
B_n	polymeric species B
C_n	polymeric species C
d_p	particle diameter, mm
D_p	diffusivity of phenol, $cm^2\,s^{-1}$
$[E_A]_0$	initial concentration of A group in prepolymer, $mol\,L^{-1}$
$[E_A]_I$	concentration of A group in prepolymer I, $mol\,L^{-1}$
$[E_A]_{II}$	concentration of A group in prepolymer II, $mol\,L^{-1}$
$[E_B]_0$	initial concentration of B group in a prepolymer, $mol\,L^{-1}$
$[E_B]_I$	concentration of B group in prepolymer I, $mol\,L^{-1}$
$[E_B]_{II}$	concentration of B group in prepolymer II, $mol\,L^{-1}$
K	equilibrium constant
k_1	forward reaction rate constant, $L\,mol^{-1}\,min^{-1}$
k_2	reverse reaction rate constant, $L\,mol^{-1}\,min^{-1}$
k_c	crystallization rate constant, min^{-1}
$\overline{M}_n$	number-average molecular weight
$\overline{M}_{n,0}$	number-average molecular weight of prepolymer
$\overline{M}_w$	weight-average molecular weight
$\overline{M}_{w,0}$	weight-average molecular weight of prepolymer
$\overline{M}_{w,cal}$	calculated weight-average molecular weight
$\overline{M}_{w,exp}$	experimentally measured weight-average molecular weight
n	number of repeating units
$[P]$	concentration of phenol at time t, $mol\,L^{-1}$
r	distance from particle center, mm
r_a	mole ratio of end group at the beginning of melt prepolymerization
r'_a	mole ratio of end group in prepolymer
$r'_{a,cal}$	calculated mole ratio of end groups in prepolymer
$r'_{a,exp}$	experimentally measured mole ratio of end groups in prepolymer
r_m	initially changed monomer ratio ([DPC]/[BPA]) in prepolymerization reactor
R	particle radius, mm
t	reaction time, min
w_1	weight fraction of prepolymer I in a polymer blend
w_2	weight fraction of prepolymer II in a polymer blend
x_c	degree of polymer crystallinity
ρ	density of bisphenol A polycarbonate, $g\,cm^{-3}$
$\mu_{i,j}$ ($i = A, B, C$; $j = 0, 1, 2$)	j-th molecular weight moment of polymeric species i

example is a semibatch melt transesterification of bisphenol A (BPA) and diphenyl carbonate (DPC) for the synthesis of polycarbonate. The semibatch reactor is operated at 180–230 °C and at reduced pressure (20–100 mmHg) with a reflux condenser [20,21]. Although the vapor pressure of bisphenol A is negligibly small at such reaction temperature, the vapor pressure of DPC is as high as 114 mmHg at 230 °C. As the melt polymerization proceeds, DPC vaporizes together with phenol (condensation byproduct) as high temperature and low pressure are applied from the beginning of the polymerization. Although most of the vaporized diphenyl carbonate is condensed and refluxed back to the reactor, a small amount of diphenyl carbonate might be lost from the reactor. The partial loss of DPC causes the deviation of the reactive end groups from the optimal ratio, making it difficult to obtain high polymer molecular weight. When the prepolymer with a stoichiometrically imbalance end group ratio is later used as a precursor for the solid-state polymerization process, the maximum molecular weight obtainable becomes severely limited [16,19].

To prevent the deviation of the end group ratio from the stoichiometry in the prepolymerization stage, a small excess of more volatile monomer (e.g., diphenyl carbonate in a polycarbonate process) can be used to pre-compensate for its evaporative loss [20,21]. However, keeping the end group ratio at its target value of 1.0 is often a challenge. For example, in a semibatch process, it is difficult to monitor the end group concentrations in the reaction mixture online and to make any corrective control actions to keep the end group ratio at its optimal target value. The inability of controlling the end group ratio during the prepolymerization stage can be the source for the inconsistency in the molecular weight of the polymer produced by both the prepolymerization and the solid-state polymerization processes.

In this paper, we present a new method to optimize the end group mole ratio in a prepolymer for the solid-state polymerization of AA-BB type condensation polymers. In the proposed method, a detailed reaction kinetic model is used to modify the end group ratio in the prepolymer precursor to its most favorable value by blending the two prepolymers of different molecular weights and different end group ratios. Then, the optimized and homogeneously mixed prepolymer is used for the subsequent solid-state polymerization. A dynamic melt prepolymerization model is used in conjunction with a numerical optimization package to estimate the molecular weight moments of polymeric species in the prepolymers. The proposed method is illustrated through numerical model simulations.

2. Model development

Let us consider a condensation polymer polymerized from AA and BB monomers. A and B represent the reactive end groups. Here, we assume that a partial loss of one of the monomers occurs during the high-temperature melt prepolymerization process, causing the molar ratio of A and B groups in the polymer to deviate from the stoichiometric value (i.e., 1.0). As mentioned earlier, the molecular weight of the polymer (prepolymer) with a non-stoichiometric end group mole ratio is difficult to increase by the solid-state polymerization. However, if we can modify the end group mole ratio of the prepolymer to its stoichiometric ratio, the molecular weight of the polymer can be increased more effectively in the subsequent solid-state polymerization process. The modification of the end group mole ratio in the prepolymer can be made by mixing two or more prepolymers of different end group ratios. It is required that one of the polymers should have more A groups than B groups and the other polymer should have more B groups than A groups.

Consider mixing W_1 g of prepolymer I and W_2 g prepolymer II with different mole ratios of the functional end groups (e.g., $[E_A]_I/[E_B]_I > 1.0$; $[E_A]_{II}/[E_B]_{II} < 1.0$) to make the mole ratio of the end groups, $[E_A]/[E_B]$, to be unity in the mixture. Here, $[E_A]$ and $[E_B]$ are the total concentrations of A groups and B groups in the reaction mixture of polymer molecules of different chain lengths. The weight fraction of the prepolymer I (w_1^*) needed to keep the end group ratio of 1.0 is easily calculated as

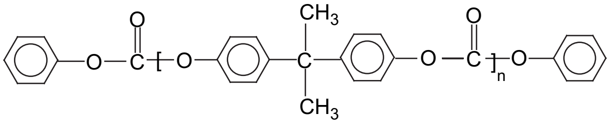
$$w_1^* = \frac{[E_A]_{II} - [E_B]_{II}}{([E_B]_I - [E_B]_{II}) - ([E_A]_I - [E_A]_{II})} \tag{1}$$

The prepolymer mixture is then polymerized in the solid state to a high molecular weight polymer. Before the solid-state polymerization, the two prepolymers should be mixed by, for example, melting so that the polymer molecules from the two different batches are mixed homogeneously at a molecular level.

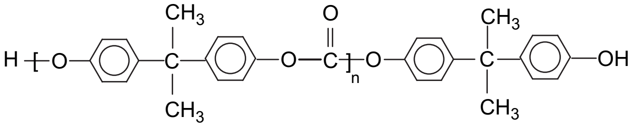
To predict the performance of the solid-state polymerization for the prepolymer mixture according to Eq. (1), a dynamic reaction model is needed. Generally, the following data will be available for the prepolymers: average molecular weights, molecular weight distributions (measured by gel-permeation chromatography), and the endgroup concentrations (measured by ^{13}C NMR spectroscopy). Unfortunately, little is known in the literature about the method to calculate the molecular weight of the polymer when a mixture of prepolymers undergoes a solid-state polymerization. In the following, we shall present a method to carry out such calculations.

In this work, we use the molecular species model where each reacting species is identified by the type of end groups and its chain length. For example, the following three polymeric species can be defined for bisphenol A polycarbonate [16,19–22].

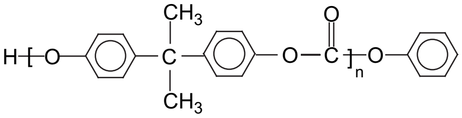
A_n:



B_n:



C_n:



In the above example, the two reactive end groups are the phenyl carbonate group and the hydroxyl group. Note that A_0 represents the AA monomer with two terminal A groups and B_0 represents the BB monomer with two terminal B groups. The polycondensation reactions between these polymeric species can be represented by the following reaction equations:

$$A_n + B_m \leftrightharpoons C_{n+m+1} + P \quad (n, m \geq 0) \tag{2.1}$$

$$A_n + C_m \leftrightharpoons A_{n+m} + P \quad (n \geq 0, m \geq 1) \tag{2.2}$$

$$B_n + C_m \leftrightharpoons B_{n+m} + P \quad (n \geq 0, m \geq 1) \tag{2.3}$$

$$C_n + C_m \leftrightharpoons C_{n+m} + P \quad (n, m \geq 1) \tag{2.4}$$

where n and m are the chain lengths, and P is the condensate (e.g., P = phenol for bisphenol A polycarbonate process). Note that the unreacted monomers (A_0 and B_0) remaining in the reaction mixture are included in the kinetic scheme. The above reactions are reversible, and hence, the condensate (P) should be removed from the reaction mixture by inert purge gas or vacuum to suppress the reverse reactions.

To calculate the molecular weight averages of the polymer, the k-th molecular weight moments are defined for each polymeric species as follows:

$$\mu_{A,k} = \sum_{n=1}^{\infty} n^k[A_n], \quad \mu_{B,k} = \sum_{n=1}^{\infty} n^k[B_n], \quad \mu_{C,k} = \sum_{n=1}^{\infty} n^k[C_n] \tag{3}$$

where $[A_n]$, $[B_n]$ and $[C_n]$ represent the concentrations of corresponding species. The number-average and the weight-average molecular weights of the polymer are calculated as

$$\overline{M}_n = w_m \frac{\mu_1}{\mu_0}, \quad \overline{M}_w = w_m \frac{\mu_2}{\mu_1} \tag{4}$$

where w_m is the molecular weight of a repeating unit, μ_0, μ_1, and μ_2 are the sums of the zero-th, first, and second moments of the three different molecular weight species. Here, we assume that the contributions of the chain end units to the overall molecular weight of the polymer are negligible as the chain length is sufficiently large.

For the solid-state polymerization in a single polymer particle, there can be a radial concentration distribution of functional end groups if there exists a strong diffusion resistance for the volatile condensation byproducts. The intraparticle compositional nonuniformity leads to the radial distribution of polymer chain lengths. The overall molecular weight averages in a particle then are calculated as

$$\overline{M}_n = R^3 \left(3 \int_0^R \frac{r^2}{\overline{M}_n(r)} \mathrm{d}r \right)^{-1} \tag{5.1}$$

$$\overline{M}_w = \frac{1}{R^3} \left(3 \int_0^R r^2 \overline{M}_w(r) \mathrm{d}r \right) \tag{5.2}$$

where r is the radial position in the particle, R is the particle radius, $\overline{M}_n(r)$ and $\overline{M}_w(r)$ are the number-average and weight-average molecular weights of the polymer particle [19].

The kinetic model for the solid-state polymerization in a spherical particle takes the following form [20]:

Condensate:

$$\begin{aligned}\frac{\partial[P]}{\partial t} = {} & \frac{k_1}{1-x_c}\Bigg[4\left([A_0] + \sum_{n=1}^{\infty}[A_n]\right)\left([B_0] + \sum_{n=1}^{\infty}[B_n]\right) \\ & + 2\sum_{n=1}^{\infty}[C_n]\left([A_0] + \sum_{n=1}^{\infty}[A_n] + [B_0] + \sum_{n=1}^{\infty}[B_n]\right) \\ & + \left(\sum_{n=1}^{\infty}[C_n]\right)^2\Bigg] + \frac{k_2[P]}{1-x_c}\Bigg[\sum_{n=1}^{\infty}[C_n] - 2\left(\sum_{n=1}^{\infty}n[A_n]\right. \\ & \left. + \sum_{n=1}^{\infty}n[B_n] + \sum_{n=1}^{\infty}n[C_n]\right)\Bigg] + D_P\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[P]}{\partial r}\right)\right)\end{aligned} \tag{6}$$

AA monomer:

$$\begin{aligned}\frac{\partial[A_0]}{\partial t} = {} & \frac{-2k_1[A_0]}{1-x_c}\Bigg[2[B_0] + \sum_{n=1}^{\infty}(2[B_n] \\ & + [C_n])\Bigg] + \frac{k_2[P]}{1-x_c}\sum_{n=1}^{\infty}(2[A_n] + [C_n])\end{aligned} \tag{7}$$

BB monomer:

$$\begin{aligned}\frac{\partial[B_0]}{\partial t} = {} & \frac{-2k_1[B_0]}{1-x_c}\Bigg[2[A_0] + \sum_{n=1}^{\infty}(2[A_n] \\ & + [C_n])\Bigg] + \frac{k_2[P]}{1-x_c}\sum_{n=1}^{\infty}(2[B_n] + [C_n])\end{aligned} \tag{8}$$

Polymer species:

$$\begin{aligned}\frac{\partial[A_n]}{\partial t} = {} & \frac{2k_1}{1-x_c}\Bigg[-2[A_n][B_0] - [A_n]\sum_{m=1}^{\infty}(2[B_m] \\ & + [C_m]) + \sum_{r=1}^{n}[A_{n-r}][C_r]\Bigg] + \frac{k_2[P]}{1-x_c}\Bigg[\sum_{r=n+1}^{\infty}([C_r] \\ & + 2[A_r]) - 2n[A_n]\Bigg] \quad (n > 1)\end{aligned} \tag{9}$$

$$\frac{\partial[\mathrm{B}_n]}{\partial t} = \frac{2k_1}{1-x_\mathrm{c}}\left[-2[\mathrm{B}_n][\mathrm{A}_0] - [\mathrm{B}_n]\sum_{m=1}^{\infty}(2[\mathrm{A}_m] + [\mathrm{C}_m]) + \sum_{r=1}^{n}[\mathrm{B}_{n-r}][\mathrm{C}_r]\right] + \frac{k_2[\mathrm{P}]}{1-x_\mathrm{c}}\left[\sum_{r=n+1}^{\infty}([\mathrm{C}_r] + 2[\mathrm{B}_r]) - 2n[\mathrm{B}_n]\right] \quad (n>1) \tag{10}$$

$$\frac{\partial[\mathrm{C}_n]}{\partial t} = \frac{2k_1}{1-x_\mathrm{c}}\left[2\sum_{r=0}^{n-1}[\mathrm{A}_{n-r-1}][\mathrm{B}_r] - ([\mathrm{A}_0] + [\mathrm{B}_0])[\mathrm{C}_n] - [\mathrm{C}_n]\sum_{m=1}^{\infty}([\mathrm{A}_m] + [\mathrm{B}_m] + [\mathrm{C}_m]) + \frac{1}{2}\sum_{r=1}^{n-1}[\mathrm{C}_{n-r}][\mathrm{C}_r]\right] + \frac{k_2[\mathrm{P}]}{1-x_\mathrm{c}}\left[-(2n-1)[\mathrm{C}_n] + 2\sum_{r=n}^{\infty}([\mathrm{A}_r] + [\mathrm{B}_r]) + 2\sum_{r=n+1}^{\infty}[\mathrm{C}_r]\right] \quad (n>1) \tag{11}$$

In the above equations, k_1 is the effective forward reaction rate constant and k_2 is the effective reverse rate constant. The catalyst concentration has been incorporated into these rate constants [19]. x_c is the degree of polymer crystallinity and $1-x_\mathrm{c}$ represents the fraction of the particle that is amorphous. The reaction is assumed to occur only in the amorphous phase. It is also assumed that x_c is independent of radial position. To calculate the molecular weight averages of the polymer, the molecular weight moment equations are derived and solved for the polymer species. The following equations illustrate the zero-th, first, and the second molecular weight moments for the A_n species. The molecular weight moments for the B_n and C_n species can also be derived similarly.

$$\frac{\partial\mu_{\mathrm{A},0}}{\partial t} = \frac{2k_1}{1-x_\mathrm{c}}[-2\mu_{\mathrm{A},0}(\mu_{\mathrm{B},0} + [\mathrm{B}_0]) + \mu_{\mathrm{C},0}[\mathrm{A}_0]] + \frac{k_2[\mathrm{P}]}{1-x_\mathrm{c}}(\mu_{\mathrm{C},1} - \mu_{\mathrm{C},0} - 2\mu_{\mathrm{A},0}) \tag{12}$$

$$\frac{\partial\mu_{\mathrm{A},1}}{\partial t} = \frac{2k_1}{1-x_\mathrm{c}}[-2\mu_{\mathrm{A},1}(\mu_{\mathrm{B},0} + [\mathrm{B}_0]) + \mu_{\mathrm{C},1}(\mu_{\mathrm{A},0} + [\mathrm{A}_0])] + \frac{k_2[\mathrm{P}]}{2(1-x_\mathrm{c})}[\mu_{\mathrm{C},2} - \mu_{\mathrm{C},1} - 2(\mu_{\mathrm{A},2} + \mu_{\mathrm{A},1})] \tag{13}$$

$$\frac{\partial\mu_{\mathrm{A},2}}{\partial t} = \frac{2k_1}{1-x_\mathrm{c}}[-2\mu_{\mathrm{A},2}(\mu_{\mathrm{B},0} + [\mathrm{B}_0]) + \mu_{\mathrm{C},2}(\mu_{\mathrm{A},0} + [\mathrm{A}_0]) + 2\mu_{\mathrm{A},1}\mu_{\mathrm{C},1}] + \frac{k_2[\mathrm{P}]}{6(1-x_\mathrm{c})}[2\mu_{\mathrm{C},3} - 3\mu_{\mathrm{C},2} + \mu_{\mathrm{C},1} - 8\mu_{\mathrm{A},3} - 6\mu_{\mathrm{A},2} + 2\mu_{\mathrm{A},1}] \tag{14}$$

In the above model, we assume that the condensate P is the only diffusant in the polymer particle. The following boundary conditions are used for P: at $r=0$ (particle center), $\partial[\mathrm{P}]/\partial r = 0$; at $r=R$ (particle surface), $[\mathrm{P}]=0$. The second boundary condition represents the situation that (i) there is no significant mass transfer resistance between the purge gas and the particle gas; (ii) the purge gas flow rate relative to the rate of production of phenol is so high that the concentration of phenol in the gas stream is essentially zero at all points in the reactor.

To solve the model equations for the solid-state polymerization, the initial values of the molecular weight moments for three polymeric species (e.g., $\mu_{\mathrm{A},k}$, $\mu_{\mathrm{B},k}$, $\mu_{\mathrm{C},k}$; $k=0,1,2$) in each prepolymer need to be known. In practice, each prepolymer's molecular weight averages, molecular weight distributions, and end group concentrations or end group ratio can be measured experimentally; however, it is impossible to measure the concentrations of three different polymeric species (i.e., A_n, B_n, and C_n) or their molecular weight moments. But if the molecular weight moments of these polymer species in each prepolymer are not known, we cannot solve the solid-state polymerization model to predict the reaction rate and polymer molecular weight with reaction time. This is the major technical challenge that we will address in the following discussion.

The first step in our proposed method is to estimate the molecular weight moments of the polymer species in a prepolymer sample. If the molecular weight averages ($\overline{M}_{\mathrm{n},0}$) and the mole ratio of the end groups ($r'_\mathrm{a} = [\mathrm{E_A}]_0/[\mathrm{E_B}]_0 > 1$) in a prepolymer are known, the initial end group mole ratio ($r_\mathrm{a} = [\mathrm{E_A}]/[\mathrm{E_B}]$) at the beginning of prepolymerization can be calculated as [19]:

$$r_\mathrm{a} = \frac{1 - r'_\mathrm{a} - (1 + r'_\mathrm{a})(2\overline{M}_{\mathrm{n},0}/w_m)}{r'_\mathrm{a} - 1 - (1 + r'_\mathrm{a})(2\overline{M}_{\mathrm{n},0}/w_m)} \tag{15}$$

where w_m is the molecular weight of a repeating unit. It should be noted that Eq. (15) was obtained with an assumption that no loss of any monomers occurred during the prepolymerization (later in this paper, we shall discuss the case where a fraction of one of the two monomers is lost by evaporation during the prepolymerization process). Also, we assume that no side reactions occur. The conversion of the limiting end group at the end of the prepolymerization stage can also be calculated as

$$p = 1 - \frac{1 + r_\mathrm{a} + (r_\mathrm{a} - 1)(2\overline{M}_{\mathrm{n},0}/w_m)}{2r_\mathrm{a}(2\overline{M}_{\mathrm{n},0}/w_m)} \tag{16}$$

After the initial reaction conditions are estimated, a dynamic model for the prepolymerization process is used to calculate the molecular weight moments for a given prepolymer. For example, for a bisphenol A polycarbonate prepolymerization process, a dynamic process model has been developed for a semibatch reactor system and verified experimentally [20,21]. The prepolymerization process model is solved so as to match the experimentally observed molecular weight averages and end group mole ratio. After such model simulation is carried out successfully for each prepolymer, the molecular weight moments of a mixture of two prepolymers can be calculated from the moment values for each prepolymer as follows:

$$\mu_{\mathrm{i},k} = w_1\mu_{\mathrm{i},k}(\mathrm{I}) + w_2\mu_{\mathrm{i},k}(\mathrm{II}) \quad (\mathrm{i} = \mathrm{A,B,C};\ k = 0,1,2) \tag{17}$$

where w_1 and w_2 denote the weight fractions of prepolymer I and prepolymer II, respectively. These molecular weight moment values are used as the initial conditions to solve the solid-state polymerization model Eqs. (6)–(14).

3. Results and discussion

In this section, we shall present the numerical simulation examples to show the performance of the proposed method. For the purpose of illustration, we use the synthesis of bisphenol A polycarbonate as an example.

3.1. Simulation of a prepolymerization process

Let us designate DPC as AA monomer and bisphenol A as BB monomer (i.e., A = phenyl carbonate group, B = hydroxyl group). The semibatch reactor model available elsewhere is used to simulate a melt prepolymerization process with $\mathrm{LiOH{\cdot}H_2O}$ catalyst [20,21]. We will use two different initial charge ratios of DPC and BPA to generate the simulated prepolymers of different molecular weights and end group mole ratios. At the end of prepolymerization, one of the prepolymers will have an excess amount of the phenyl carbonate group (A) and the other prepolymer will have an excess amount of the hydroxyl end group (B). The amounts of the two prepolymers to obtain the overall end group ratio of 1.0 are calculated using Eq. (1).

The following semibatch reactor conditions are used for the model simulations: reactor volume = 4 L, reaction temperature = 230 °C, pressure = 5 mmHg, reflux column temperature = 80 °C, catalyst ($LiOH \cdot H_2O$) concentration = 8×10^{-5} mol/L, initial charge of BPA = 6.75 mol, and reaction time = 120 min. The amount of initial charge of DPC is determined by a specific DPC/BPA charge ratio (r_m). The prepolymerization reactor model used in this work incorporates the vapor–liquid equilibrium data for a binary mixture of phenol and diphenyl carbonate [21]. The vapor–liquid equilibrium data are also used in conjunction with the Wilson equation to calculate the exact amounts of diphenyl carbonate and phenol returned from a reflux column to the reactor. The activity coefficients of the volatile species are estimated using the Flory–Huggins equation. The parameters used for the modeling of melt polymerization in a semibatch reactor are given in Table 1.

Table 1
Model parameters for model simulations

Parameters for melt prepolymerization at 230 °C [21]	Unit
$k_1 = 0.0708$	$L\ mol^{-1}\ min^{-1}$
$k_2 = 0.0361$	$L\ mol^{-1}\ min^{-1}$
Vapor pressure of diphenyl carbonate	mmHg
$\ln P_{DPC}^{sat} = -(1.48 \times 10^4/RT) + 19.55$	
Parameters for solid-state polymerization at 200 °C [19]	
$k_1 = 0.0608$	$L\ mol^{-1}\ min^{-1}$
$k_1 = 0.0434$	$L\ mol^{-1}\ min^{-1}$
$D_P = 1.8 \times 10^{-7}$	$cm^2\ min^{-1}$
$x_c = 0.25$	

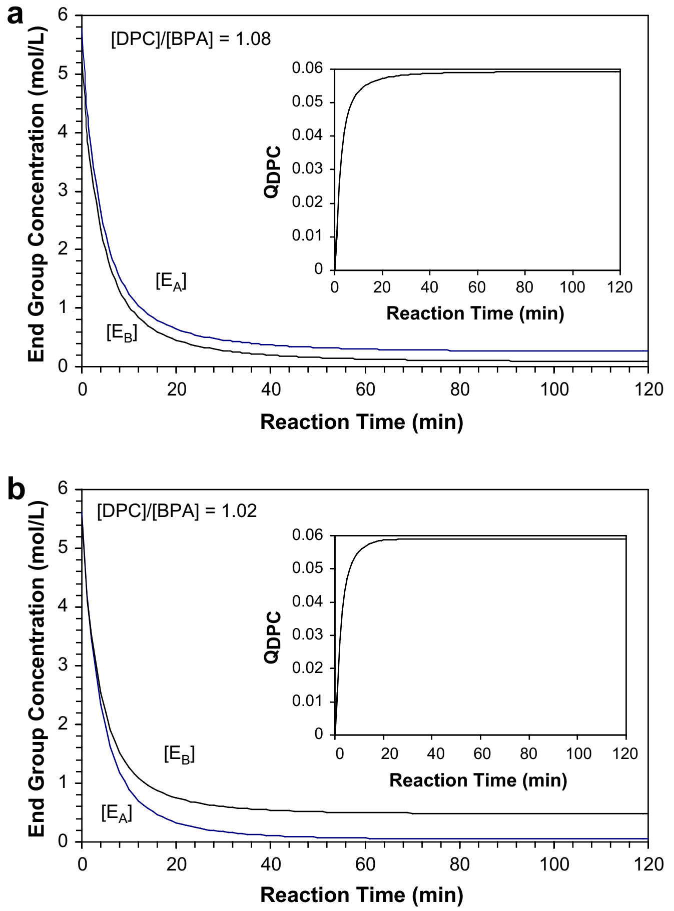


Fig. 1. Model calculated end group concentrations in a semibatch melt prepolymerization process for different monomer ratios ($[E_A]$ = diphenyl carbonate end group, $[E_B]$ = hydroxyl end group, Q_{DPC} = fraction of DPC loss).

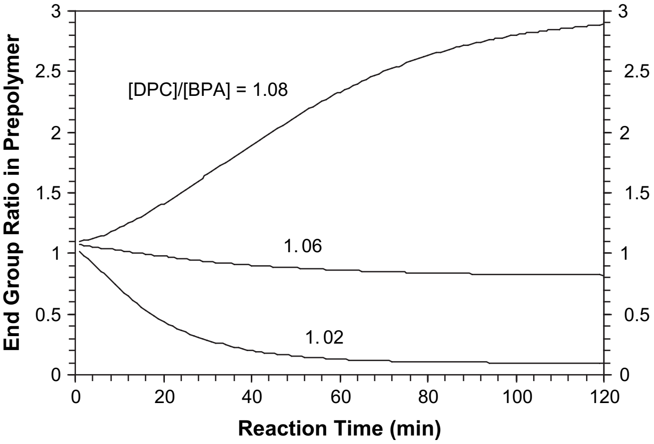


Fig. 2. Effect of initially changed monomer ratio on the ratio of end groups in a semibatch melt polymerization process (model calculations).

Fig. 1 shows the effect of initial monomer ratios on the concentrations of end groups during the melt polymerization in a semibatch reactor. In case (a) where 8% excess amount of DPC is used, the final prepolymer has more A groups than B groups even with ~6% loss of original DPC monomer by evaporation (inset). However, when the initial [DPC]/[BPA] ratio is 1.02 (case (b)), the concentration of the hydroxyl end group ($[E_B]$) becomes larger than the phenyl carbonate group concentration ($[E_A]$) as soon as the reaction starts. It is because of the evaporative loss of diphenyl carbonate through the reflux condenser.

Fig. 2 shows the profiles of the end group mole ratios during the prepolymerization for three different initial DPC/BPA mole ratios. For the initial monomer ratio of 1.02 ([DPC]/[BPA]), the mole ratio of the phenyl carbonate end group to the hydroxyl end group decreases to 0.097 after 120 min whereas for the initial monomer ratio of 1.08, the end group ratio increases to 2.888 after 120 min. In the latter case, we can see that the loss of DPC has been overcompensated by using too much excess amount of DPC. Fig. 2 also shows that if the initial mole ratio of 1.06 is used, the end group ratio is much closer to 1.0 than the other two cases. The molecular weight profiles for these three cases are shown in Fig. 3. It is clearly observed that the deviation of the end group mole ratio from the stoichiometric value results in a large decrease in the polymer molecular weight.

The simulation examples of the prepolymerization shown in Figs. 1–3 illustrate that using an excess amount of DPC is necessary

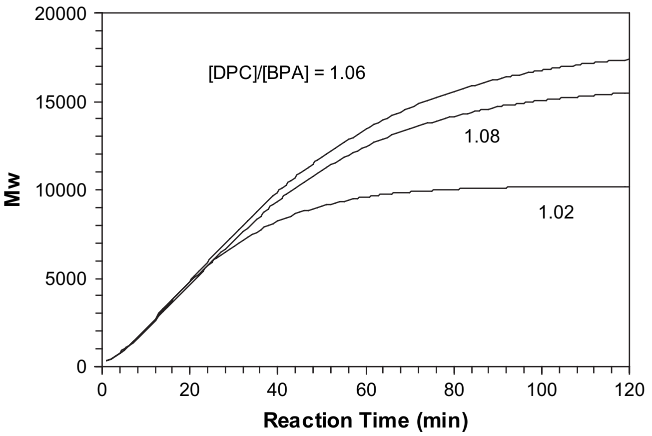


Fig. 3. Effect of initially changed monomer ratio on the weight-average molecular weight in a semibatch melt polymerization process (model calculations).

to compensate for the evaporative loss during the reaction but it will be desirable to use the optimal amount of DPC.

3.2. *Numerical identification of initial prepolymerization conditions*

Now, let us assume that the two prepolymers of drastically different end group mole ratios as illustrated in the previous section are mixed before the solid-state polymerization. They are mixed such that the end group mole ratio becomes 1.0. The amount of each prepolymer can be calculated using Eq. (1). If this mixture is used in the subsequent solid-state polymerization, high molecular weight can be obtained in much shorter time than using either of these two prepolymers separately.

To predict the polymer molecular weight of the mixture in the solid-state polymerization, we need to know the molecular weight moments of the prepolymer mixture. If the end group mole ratio ($r_a = [E_A]/[E_B]$) and polymer molecular weight values are available for a prepolymer, we can estimate the initial monomer ratio (or the end group ratio) at the beginning of prepolymerization using Eq. (15) for each prepolymer. However, the actual amounts of the two monomers charged into the reactor will be different from the values calculated by Eq. (15) because the effect of evaporative partial loss of one of the two monomers (DPC) was not considered in deriving Eqs. (15) and (16). Therefore, to estimate the molecular weight moments for the three polymeric species (A_n, B_n, and C_n) in the prepolymer, we need to develop a method to estimate the actual initial conditions (i.e., initial DPC/BPA mole ratio) for the prepolymerization stage.

To calculate the initial prepolymerization conditions, we shall use a semibatch prepolymerization model and a numerical optimization technique. Here, we determine the initial mole ratio of the monomers with the amount of less volatile monomer (i.e., BPA) held constant. The following objective function is defined:

$$\text{Obj} = \left(\frac{\overline{M}_{\text{w,cal}} - \overline{M}_{\text{w,exp}}}{\overline{M}_{\text{w,exp}}}\right)^2 + \left(\frac{r'_{\text{a,cal}} - r'_{\text{a,exp}}}{r'_{\text{a,exp}}}\right)^2 \qquad (18)$$

where $\overline{M}_{\text{w,cal}}$, ($\overline{M}_{\text{w,exp}}$) and $r'_{\text{a,cal}}$, ($r'_{\text{a,exp}}$) are the calculated (experimentally measured) weight-average molecular weight and initial end group mole ratio. The semibatch prepolymerization reactor model is used in conjunction with a numerical optimization routine ("fminsearch") from MATLAB® optimization toolbox to minimize the objective function. "fminsearch" is an unconstrained nonlinear optimization routine where the simplex method is used. The initial end group mole ratio estimated from Eq. (15) is used as an initial guess. Since the polymer molecular weight is a function of conversion or reaction time, the reaction time is also included as one of the optimization variables. The prepolymerization model (semibatch process) is solved using an ordinary differential equation solver "ode45" in MATLAB®. The prepolymer properties used as simulated experimental data are shown in Table 2. Table 3 shows the calculated values of end group ratio in the prepolymers for several different values of the initial guesses. Notice that the optimizer converges to the optimal point very well.

Table 2
Simulations of prepolymerization and prepolymer properties

	Parameter	Prepolymer I	Prepolymer II
Prepolymerization conditions	Initially charged [DPC]/[BPA]	1.08	1.02
	Prepolymerization time (min)	120	120
Prepolymer properties	$r'_a([E_A]/[E_B])$	2.888	0.097
	$\overline{M}_n$	7881	5196
	$\overline{M}_w$	15,470	10,200
Polymer blend properties	w_1^* (optimal fraction of prepolymer I)	0.721	
	$\overline{M}_{n,\text{mix}}$	6052	
	$\overline{M}_{w,\text{mix}}$	13,166	

Table 3
Numerically identified initial reaction conditions of prepolymerization

Prepolymer properties	Initial guess	Optimized results		
	$[E_A]_0/[E_B]_0$	No. of iteration	$[E_A]_0/[E_B]_0$	$\overline{M}_w$
Prepolymer I	1.016[a]	61	2.8879	15,470
$[E_A]_0/[E_B]_0 = 2.888$	1.05	42	2.8869	15,468
$\overline{M}_w = 15,470$	1.10	63	2.8856	15,473
Prepolymer II	0.9605[a]	57	0.0971	10,200
$[E_A]_0/[E_B]_0 = 0.097$	1.05	63	0.0970	10,208
$\overline{M}_w = 10,200$	1.10	84	0.0971	10,207

Note: to ensure convergence, 200 min of reaction time was used in all optimization calculations.

[a] These values were calculated using Eq. (15) assuming no loss of DPC during semibatch polymerization simulations.

3.3. *Simulation of solid-state polymerization with an optimized prepolymer blend*

The weight fractions of the two prepolymers for optimal blending are determined by Eq. (1). The polymer blend should be mixed to a homogeneous mixture, for example, by dissolving the blend in a solvent or melting the blend. Then, the new homogeneous prepolymer is converted to small particles and crystallized. In the case of bisphenol A polycarbonate, the crystallization step is crucial for the solid-state polymerization to avoid the fusion of prepolymer particles during the solid-state polymerization [14,19,23,24]. The solid-state polymerization model equations are solved using a partial differentiation equation solver "pdepe" in MATLAB®. The parameters used to solve the solid-state polymerization model for bisphenol A polycarbonate are given in Table 1.

In our first series of solid-state polymerization simulations, we investigate a kinetically controlled case, i.e., no intraparticle diffusion limitations for the condensate removal. Fig. 4 shows the weight-average molecular weight profiles during the solid-state polymerization for prepolymer I, prepolymer II, and the optimized prepolymer blend (weight fraction of prepolymer I = 0.72). It is seen that the molecular weight of the optimized prepolymer mixture increases almost linearly to very high values with reaction time whereas the molecular weights of prepolymer I and prepolymer II quickly level off because of stoichiometric imbalance of the end groups. It is quite remarkable that the modification of the end group ratio by optimally blending the two prepolymers results in

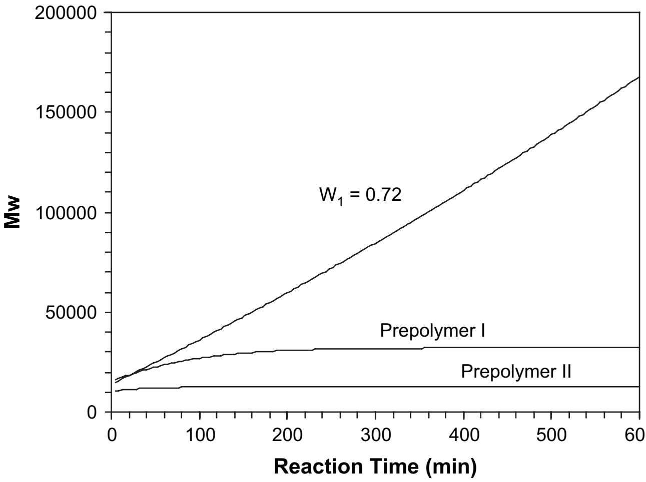


Fig. 4. Model calculated weight-average molecular weight profiles for end group optimized prepolymer blend and prepolymers during the solid-state polymerization ($T = 200\ ^\circ$C, without intraparticle diffusion resistance).

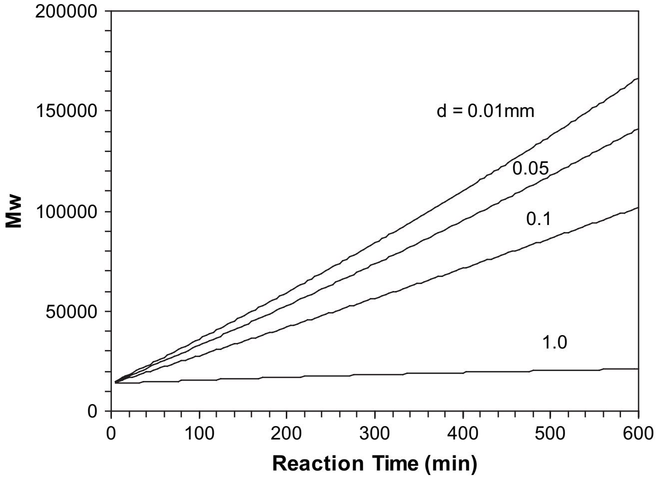


Fig. 5. Effect of particle size effect on the weight-average molecular weight with end-group optimized polymer blend ($w_1 = 0.72$) (model calculations).

such a huge increase in molecular weight as illustrated in Fig. 4. Here, it is pointed out that the molecular weight profile of the prepolymer mixture as shown in Fig. 4 can be predicted only if we have a computational model as developed in this work.

The solid-state polymerization model has also been used to simulate the reaction process in presence of the intraparticle diffusion resistance for the removal of condensation byproduct (i.e., phenol). The results are shown in Fig. 5 for different polymer particle sizes. Our model simulation results indicate negligible effect of intraparticle diffusion resistance for the polymer particles smaller than 0.01 mm in diameter. Even with the optimized end group reactivities in the blended prepolymer, the molecular weights that are reached at a fixed reaction time decrease as particle size is increased. However, compared with Fig. 4, the final molecular weights are still larger than those obtainable with prepolymer I and prepolymer II without mixing. If the particle size is too large (e.g., 1.0 mm), Fig. 5 shows almost no effect of end group optimization because the intraparticle diffusion limitation dominates the solid-state polymerization kinetics.

Finally, we have investigated the sensitivity of the results of model simulations to the deviation of the end group ratio from the true values. The reason why we perform this sensitivity analysis is because there can be some measurement errors in the measurements of end group concentrations in prepolymers. Several end-group analysis techniques reported in the literature include titration, infrared, ultraviolet (UV), gel-permeation chromatography with UV, reversed-phase HPLC, and nuclear magnetic resonance (NMR) spectroscopy [25,26]. Among these techniques, ^{13}C NMR analysis is regarded as the most reliable method to obtain accurate end-group concentrations [26]. However, even the ^{13}C NMR analysis may not be completely free from the measurement or interpretational errors. Therefore, it would be worthwhile to assess the effect of measurement errors in the end-group concentrations.

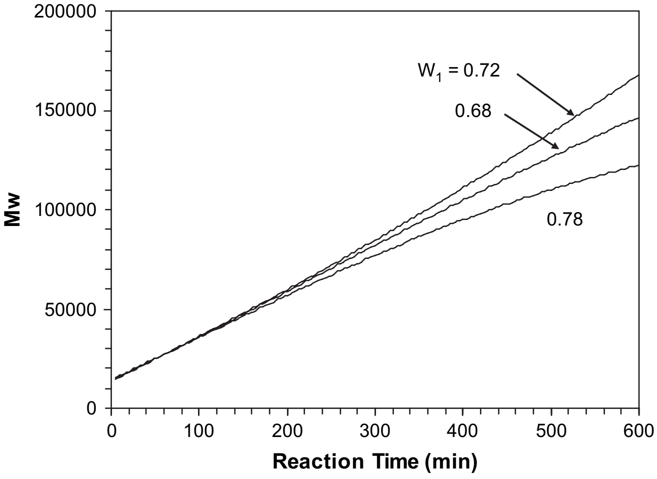


Fig. 6. Effect of measurement errors in designing end-group optimized prepolymer blends on the performance of solid-state polymerization after blending: $w_1 = 0.72$, weight fraction of optimized blend; 0.68, +20% error in end group concentration measurements (Case 1); 0.78, −20% error in end group concentration measurements (Case 2) (model calculations).

Table 4 and Fig. 6 show the numerical simulation results when ±20% error in the end group mole ratios are assumed in both prepolymer I and prepolymer II (Case 1 and Case 2). Here, we assume that there are no measurement errors in the molecular weight averages, although this assumption may not be always valid in reality. With the erroneous end group mole ratios (0.68 and 0.78), the molecular weight moment values of the prepolymers were calculated using the same methods as presented already. Because of the errors, the calculated weight fraction of prepolymer I is different from the exact value of 0.72. Fig. 6 shows that indeed, the errors in the end group concentrations result in different weight fraction of prepolymer I, which eventually causes the final molecular weight lower than the optimal value (i.e., $w_1 = 0.72$) after 600 min of solid-state polymerization. However, the molecular weights for $w_1 = 0.68$ and 0.78 are still higher than those obtainable with each individual prepolymer without mixing.

4. Concluding remarks

In this work, we have presented a new method to optimize the prepolymer properties to improve the efficiency of the solid-state polymerization for a step-growth polymerization process with AA and BB type monomers. The idea is to mix two or more prepolymers of different end group mole ratios to bring the overall end group ratio to the stoichiometry value as closely as possible. The use of a simple mixing rule yields the optimal composition of the prepolymer mixture but the technical challenge is to predict the polymer molecular weight in the subsequent solid-state polymerization. We employed a molecular species model to simulate a solid-state polymerization process for an illustrative system of bisphenol A polycarbonate process. To solve the molecular species

Table 4
Effect of the errors in end group concentration measurements on the performance of solid-state polymerization

Parameter	Optimized Blend		Case 1 (+20% error in end group concentrations)		Case 2 (−20% error in end group concentrations)	
	Prepolymer I	Prepolymer II	Prepolymer I	Prepolymer II	Prepolymer I	Prepolymer II
$[E_A]_0/[E_B]_0$	2.888	0.097	3.466	0.1164	2.310	0.078
$\overline{M}_w$	15,470	10,200	15,470	10,200	15,470	10,200
w_1^*	0.72		0.68		0.78	
After solid-state polymerization (t = 600 min)						
$\overline{M}_w$	167,839		146,467		122,288	

model for the solid-state polymerization, the initial values of the molecular weight moments for different polymeric species in a prepolymer need to be known. Since it is impossible to measure these quantities experimentally, we have used a dynamic reaction model for a semibatch melt prepolymerization process. Here, for a given prepolymer of known molecular weight averages and end group concentrations, the initial monomer ratio is estimated using a numerical optimization technique. The semibatch prepolymerization model then is solved until the model-predicted molecular weight of the polymer matches the measured value. The molecular weight moment values calculated for each prepolymer are used to initialize the molecular weight moment equations of the prepolymer blend to simulate the solid-state polymerization process. Our model simulation results for the bisphenol A polycarbonate process indicate that the polymer molecular weight can be increased quite significantly if the optimized end group mole ratio of the prepolymer blend is used. Even in presence of the intraparticle diffusion resistance, the enhancement in the molecular weight with the optimized prepolymers is quite significant unless the polymer particle size is too large. The effect of measurement errors in the end group concentration of the prepolymer has also been investigated and the results suggest that the proposed method offers a robust performance of the solid-state polymerization. It should be noted that the implementation of the proposed technique requires the availability of a high-quality model of a melt prepolymerization process. The techniques to develop such reaction models can be found in literature for certain polycondensation systems.

References

[1] Ravindranath K, Mashelkar R. J Appl Polym Sci 1990;39(6):1325–45.
[2] Devotta I, Mashelkar RA. Chem Eng Sci 1993;48(10):1859–67.
[3] Mallon FK, Ray WH. J Appl Polym Sci 1998;69(6):1233–50.
[4] Yao Z, Ray WH. AIChE J 2001;47(2):401–12.
[5] Duh B. J Appl Polym Sci 2001;81(7):1748–61.
[6] Lee EH, Yeo YK, Choi KY, Kim HY. J Chem Eng Jpn 2003;36(8):912–25.
[7] Kim TY, Jabarin SA. J Appl Polym Sci 2003;89(1):213–27.
[8] Wang X, Deng D. J Appl Polym Sci 2002;83(14):3133–44.
[9] Yao KZ, McAuley KB, Berg D, Marchildon EK. Chem Eng Sci 2001;56(16):4801–14.
[10] Yao KZ, McAuley KB. Chem Eng Sci 2001;56(18):5327–42.
[11] Yao KZ, McAuley KB, Marchildon EK. J Appl Polym Sci 2003;89(14):3701–12.
[12] Algeri C, Rovaglio M. Ind Eng Chem Res 2004;43(15):4253–66.
[13] Rovaglio M, Algeri C, Manca D. Ind Eng Chem Res 2004;43(15):4267–77.
[14] Gross SM, Flowers D, Roberts GW, Kiserow DJ, DeSimone JM. Macromolecules 1999;32(9):3167–9.
[15] Goodner MD, DeSimone JM, Kiserow DJ, Roberts GW. Ind Eng Chem Res 2000;39(8):2797–806.
[16] Goodner MD, Gross SM, DeSimone JM, Roberts GW, Kiserow DJ. J Appl Polym Sci 2001;79(5):928–43.
[17] Shi C, Gross DM, DeSimone JM, Kiserow DJ, Roberts GW. Macromolecules 2001;34(7):2060–4.
[18] Gross SM, Roberts GW, Kiserow DJ, DeSimone JM. Macromolecules 2001;34(12):3916–20.
[19] Ye Y, Machado B, Choi KY, Kim JH, Woo BG. Ind Eng Chem Res 2005;44(8):2494–505.
[20] Kim YS, Choi KY. J Appl Polym Sci 1993;49(5):747–64.
[21] Woo BG, Choi KY, Song KH, Lee SH. J Appl Polym Sci 2001;80(8):1253–66.
[22] Hersh SN, Choi KY. J Appl Polym Sci 1990;41(5–6):1033–46.
[23] Fukuoka S, Watanabe T, Dozono T. US Patent 4,948,871; 1990.
[24] Sivaram S, Sehra JC, Iyer VS, Ravindranath K. US Patent 5,266,659; 1993.
[25] Schilling FC, Ringo WM, Sloane NJA, Bovey FA. Macromolecules 1981;14:532–7.
[26] Kim J, Gracz HS, Roberts GW, Kiserow DJ. Polymer 2008;49:394–404.