

Thermal Properties and Rheological Behavior of Biodegradable Aliphatic Polycarbonate Derived from Carbon Dioxide and Propylene Oxide

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ABSTRACT: Alternating poly(propylene carbonate)s (PPCs) were synthesized from carbon dioxide and propylene oxide on a relatively larger scale. The thermal properties of the alternating PPC copolymers, with various molecular weights, were investigated with modulated differential scanning calorimetry (MDSC) and thermogravimetric analysis (TGA). The melt-flow indices of the as-made PPCs were determined in a melt-flow indexer, and the rheological properties of the PPCs were studied with a capillary rheometer. The MDSC and TGA results showed that the glass-transition temperatures of the PPCs increased with increasing molecular weight. The rheological measurements revealed that the PPCs exhibited pseudoplastic flow behavior

in the melt. The molecular weight played a key role in the rheological behavior of the PPCs. Moreover, the PPCs with high molecular weights were more sensitive to the temperature and shear rate than those with low molecular weights. The melt viscosity of the PPCs with low molecular weights decreased dramatically with increasing temperature. The flow activation energy of such PPCs diminished with an increase in the shear rate, whereas the flow activation energy of the PPCs with high molecular weights remained nearly unchanged. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 711–716, 2004

Key words: copolymerization; polycarbonates; rheology

INTRODUCTION

Carbon dioxide is the most widespread of the gaseous pollutants that cause the so-called greenhouse effect and is responsible for about 66% of global warming.^{1–3} To reduce the release of carbon dioxide, it is advantageous to employ carbon dioxide as a starting material or monomer to produce biodegradable polymeric materials. Aliphatic polycarbonates have been synthesized from carbon dioxide and propylene oxide (PO) with various catalysts, such as organometallic com-

pounds and their complexes, metallic complexes, and polymer-supporting bimetallic catalysts.^{4–12} However, the big hurdle for the commercialization of these new polymers is the low catalytic activity of the aforementioned catalysts. The exploration of catalysts with high efficiency has been the focus of much research since the 1970s.^{4–12}

In previous work, we prepared zinc glutarate catalysts via magnetic stirring and supported them on perfluorinated compounds.^{13,14} By optimizing the reaction conditions, we synthesized high-molecular-weight alternating poly(propylene carbonate) (PPC) in a very high yield (126 g of polymer/g of catalyst).¹⁴ Such PPC exhibits good biodegradability according to both soil burial and buffer solution immersion tests.¹⁵ Moreover, synthesized alternating PPCs exhibit superior thermal and mechanical properties.^{13,14,16} The glass transition and decomposition temperatures of PPCs are much higher than those of conventional PPCs containing ether bonds. Therefore, they can be melt-processed like commercial polyethylene.¹⁷ The molecular weight plays a critical role in the properties of a polymer, especially in processability and mechanical properties. It is of particular technical interest to

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understand the relationship of the molecular weight, thermal properties, and rheological behavior of synthesized ether-bond-free PPCs. Because of the practical and potentially massive application of synthesized PPC, it is important to completely understand the thermal properties and rheological properties of this new biodegradable polymer. In this study, we investigated the effects of the molecular weight on the thermal properties and processability. The effects of the molecular weight, shear rate, and temperature on the melt viscosity of PPCs were also studied with a capillary rheometer.

EXPERIMENTAL

Preparation of the aliphatic polycarbonates

Zinc glutarate was synthesized from zinc oxide and glutaric acid under magnetic stirring, as described elsewhere.¹⁸ The supported catalyst was synthesized according to previous work.^{13–16} In previous work, we successfully synthesized alternating PPCs on a relatively large scale (with a 2-L autoclave). To reproduce and determine the efficiency of the synthesized catalyst, the copolymerization of CO₂ and PO in this work was carried out in a 10-L autoclave equipped with a mechanical stirrer. Supported zinc glutarate was dried at 100°C for 24 h before the polymerization. The dry catalyst was then added to the autoclave as quickly as possible. The autoclave with the catalyst inside was further dried for another 24 h *in vacuo* at 100°C. Subsequently, the autoclave was purged with carbon dioxide and alternately evacuated three times, and this was followed by the addition of purified PO with a large syringe. The autoclave was finally pressurized to 2.6 MPa with a CO₂ cylinder. The copolymerization was performed at 60°C under stirring for 40 h. The resulting viscous mixture was removed and dissolved in an appropriate volume of methylene chloride. The residual catalyst was extracted from the product solution with dilute HCl (5%), and this was followed by three washes with distilled water. The viscous solution was concentrated with a rotary evaporator to produce a concentration of about 10 wt %. Finally, PPC was precipitated by the pouring of the concentrated PPC solution into vigorously stirred methanol. The polydispersity of the synthesized PPCs ranged from 1.92 to 3.87.

Thermal property analysis

The glass-transition temperature (T_g) was determined in a modulated differential calorimeter (MDSC), TA model 2910 (New Castle, DE, USA) at a heating rate of 20°C/min under a nitrogen flow of 100 mL/min. The thermal stabilities of the PPCs were studied with a thermogravimetric analyzer (TGA), PerkinElmer TGA-4

(Boston, MA, USA) under a nitrogen-protective atmosphere. The temperature profile was from 30 to 600°C at a heating rate of 10°C/min.

Melt-flow-index (MFI) measurements

MFIs of the alternating copolymers with various molecular weights were determined with a μ PXRZ-400B melt-flow indexer (Changchun, China) equipped with a standard die. The die had a smooth straight bore with a diameter of 2.0955 ± 0.0051 mm and a length of 8.000 ± 0.025 mm. The measurements were performed according to ASTM Standard D 1238-82. The investigated temperature ranged from 150 to 180°C. Two different loads were employed at each temperature during the melt extrusion.

Rheological measurements

The steady-shear flow behavior of the synthetic PPCs was measured with a capillary rheometer (Thermo Haake Rheoflizer MT) at 150, 160, 170, and 180°C, respectively. The length-to-diameter (L/D) ratio of the capillary was fixed at 30. For each test at a different temperature, the sample was preheated for 5 min at the temperature before the measurements. The apparent shear stress and melt viscosity were obtained from the software attached to the rheometer. The Bagley correction for the apparent shear stress was negligible because the L/D ratio of the capillary was 30 or greater.

RESULTS AND DISCUSSION

Relationship between the thermal properties and molecular weight

It is well known that different molecular structures can result from different catalysts, and zinc carboxylates can generally produce PPC with a regular molecular structure. In previous work,¹⁴ we reported that T_g of as-made alternating PPC was 25°C higher and the 5% weight-loss temperature ($TGA_{-5\%}$) was almost 100°C higher than those of PPC obtained with a complex catalyst. For an amorphous polymer, the molecular weight plays a crucial role in the thermal properties. The thermal properties of PPCs with various molecular weights are listed in Table I. T_g of the alternating PPC increased with increasing molecular weight. $TGA_{-5\%}$ increased with an increase in the molecular weight, and the increasing tendency became smaller when the molecular weight was greater than 56,000 Da. This can be explained by the idea that the main decomposition mechanism for PPC is an unzipping reaction, as disclosed in previous work.¹⁹ This showed that the thermal properties depended

TABLE I
Thermal Properties for Alternating PPC Copolymers with Various Molecular Weights

Sample	M_n (k)	T_g (°C)	TGA _{-5%} (°C; N ₂)	T_{max} °C; N ₂)
1	26.9	26.7	239.0	258.1
2	36.6	36.0	233.0	256.1
3	56.0	38.2	256.0	271.0
4	62.5	40.8	256.6	271.6
5	89.0	41.0	251.0	276.4
6	114.0	42.1	258.0	279.5
7	144.6	46.5	255.8	275.8

T_{max} = maximum weight-loss temperature.

greatly on the molecular structure and molecular weight of the PPC copolymer.

MFIs

On the basis of ASTM Standard D 1238-82, the MFIs of the PPC copolymers were determined under various testing conditions and are listed in Table II. The melt-extrusion temperatures ranged from 150 to 180°C. The MFI ratios under various load levels and at different temperature are also tabulated in Table II. As expected, the MFI of PPC decreased with increasing molecular weight and increased with increasing extrusion temperature and load. The experimental results indicated that the effect of the shear stress on the melt flowability was greater than that of the temperature. In comparison with commercial polyethylene and polypropylene, the as-prepared PPC exhibited a similar melt-flow rate or MFI at 170°C. The effects of the molecular weight, shear rate, and temperature on the melt-flow behavior of PPCs were studied in detail with a capillary rheometer and are discussed in the following section.

Rheological behavior of PPCs

Effect of the molecular weight

Figure 1 shows the plot of the melt viscosity versus the number-average molecular weight (M_n) of PPCs at

TABLE II
MFIs and MFI Ratios of Alternating PPC Copolymers

	M_n (Da)		
	56,000	89,000	114,000
MI150/2.16	0.18	0.06	0.02
MI150/21.6	10.12	4.04	1.07
(MI150/21.6)/(MI150/2.16)	56.57	69.72	57.87
MI170/2.16	0.69	0.42	0.39
MI170/21.6	39.87	29.65	—
(MI170/21.6)/(MI170/2.16)	57.53	70.59	—
(MI170/2.16)/(MI150/2.16)	3.87	7.25	20.75
MI180/2.16	1.63	1.29	1.07
(MI180/2.16)/(MI150/2.16)	9.08	22.28	58.08
(MI180/2.16)/(MI170/2.16)	2.34	3.07	2.80

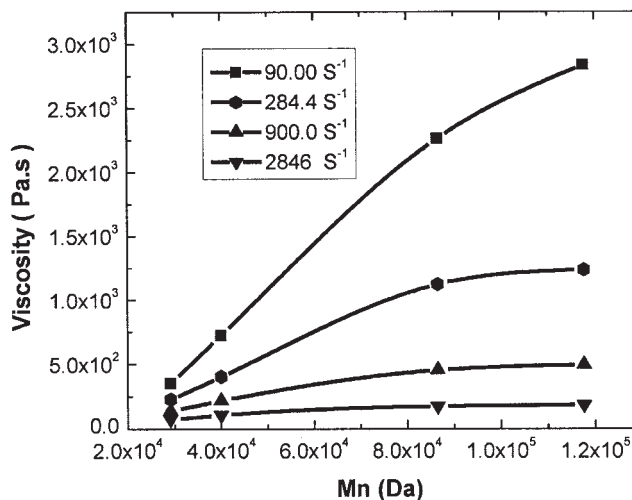


Figure 1 Melt viscosity versus M_n at different shear rates and 170°C.

different shear rates and 170°C. The melt viscosity increased with increasing molecular weight at various shear rates. However, the increasing tendency was greater at the low shear rate of 90 s⁻¹ than that at higher shear rates. For the shear rates greater than or equal to 284.4 s⁻¹, the melt viscosity increased initially with increasing M_n up to 86,590 Da and then leveled off to reach a constant value. The melt flow of thermoplastics is related to the slippage of molecular chains and the corresponding removal of the entanglements of molecular chains. The flow resistance generally increases with the tangle density. The decrease in the melt viscosity with an increasing shear rate can be attributed to the shearing-induced alignment of the molecular chain coils. Intense shearing can remove the entanglements of molecular chains, and the molecular

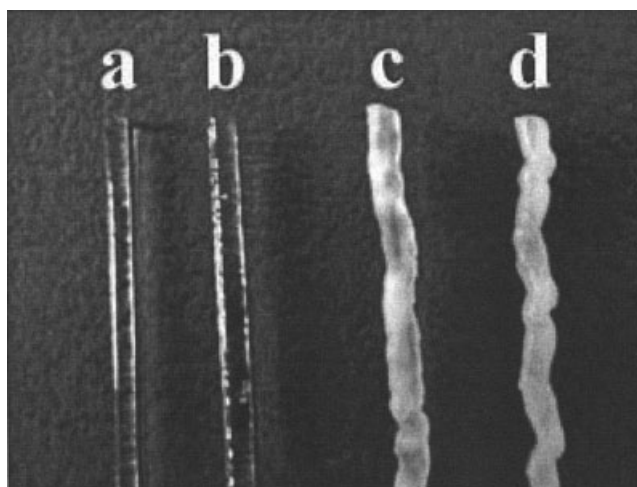


Figure 2 Effect of M_n on the appearance of PPC extrudates at a shear rate of 90 s⁻¹ and 170°C: (a) 29,130, (b) 40,000, (c) 86,590, and (d) 117,700 Da.

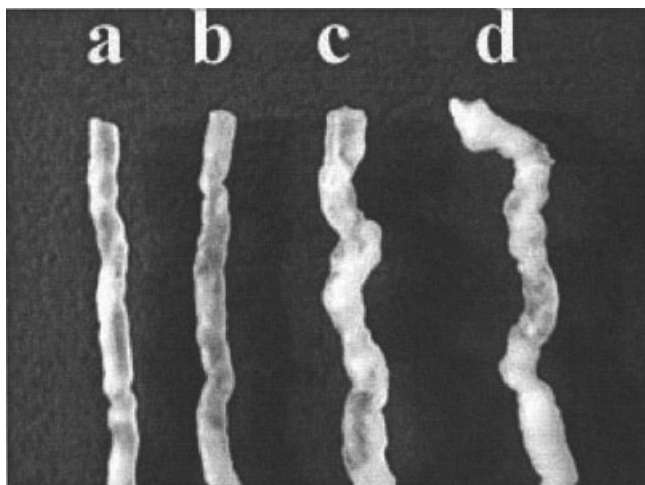


Figure 3 Effect of the shear rate on the appearance of PPC extrudates with an M_n value of 86,590 Da at 170°C: (a) 90, (b) 284.4, (c) 900, and (d) 2846 s^{-1} .

chains can be then oriented along the shear direction in case of a high shear rate.

Figures 2–4 show the typical appearances of PPC extrudates obtained under different conditions. Figure 2 shows the effect of M_n on the morphology of PPCs at a low shear rate of 90 s^{-1} and 170°C. The PPCs with lower M_n 's had smooth appearance [Fig. 2(a,b)], whereas the PPC with a higher M_n had a wavy and rough appearance [Fig. 2(c,d)]. Figures 3 and 4 indicate the effect of the shear rate and the temperature, respectively, on the morphologies of PPCs with higher molecular weights. The appearance of the extrudates deteriorated with an increasing shear rate and was improved with an increase in the temperature. In conclusion, a lower shear rate and a higher temperature were preferable. The PPC copolymers were readily

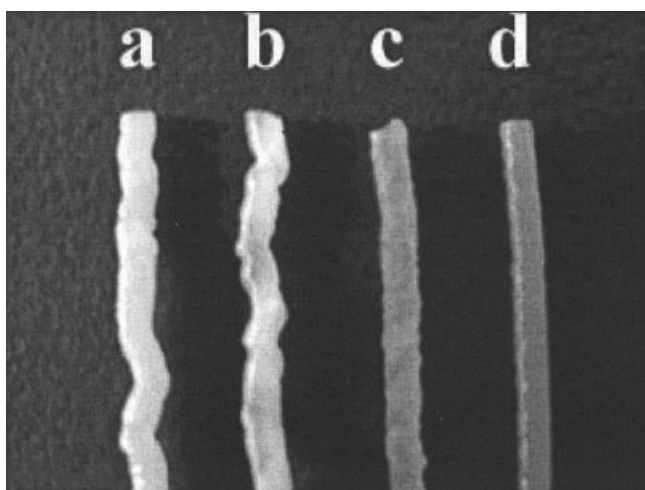


Figure 4 Effect of the temperature on the appearances of PPC extrudates with an M_n value of 117,700 Da at a shear rate of 90 s^{-1} : (a) 150, (b) 160, (c) 170, and (d) 180°C.

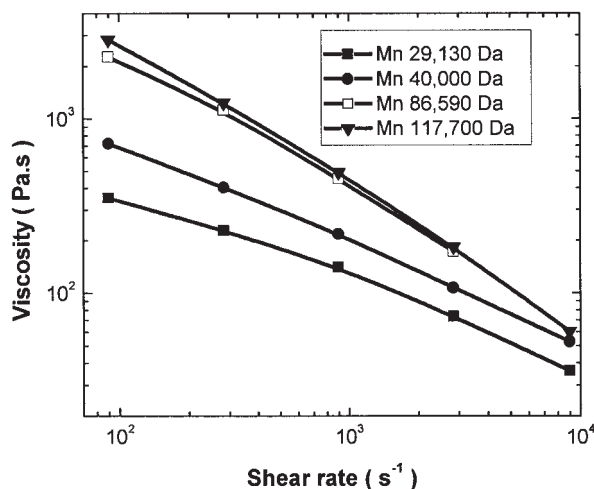


Figure 5 Melt viscosity versus the shear rate for PPCs with different M_n 's at 170°C.

melt-processed like commercial polyethylene and polypropylene from 160 to 180°C according to the molecular weight.

Effect of the shear rate

Figure 5 shows the melt viscosity versus the shear rate for PPCs with different molecular weights at 170°C. At the shear rate used, shear-thinning behavior was observed, and the shear thinning was more obvious for PPCs with high molecular weights than for those with low molecular weights. Thus, high-molecular-weight PPCs were more sensitive to the shear rates because of the entanglements of molecular chains.

For a non-Newtonian fluid, the index n can be expressed as follows:

$$n = \frac{d \log \tau}{d \log \dot{\gamma}} \quad (1)$$

where τ and $\dot{\gamma}$ are the shear stress and shear rate, respectively. The n values generally describe the characteristics of a polymeric fluid. The n values at various shear rates can be obtained by from plots of the tangent lines from the curves of $\log \tau$ versus $\log \dot{\gamma}$.²⁰ The

TABLE III
 n Values for PPCs with Various Molecular Weights at Different Shear Rates and at 170°C

M_n (Da)	Shear rate (s^{-1})				
	90.00	284.4	900.0	2846	9000
29,130	0.51	0.73	0.71	0.43	0.55
40,000	0.49	0.50	0.37	0.34	0.25
86,590	0.38	0.25	0.19	0.19	—
117,700	0.42	0.25	0.19	0.15	0.08

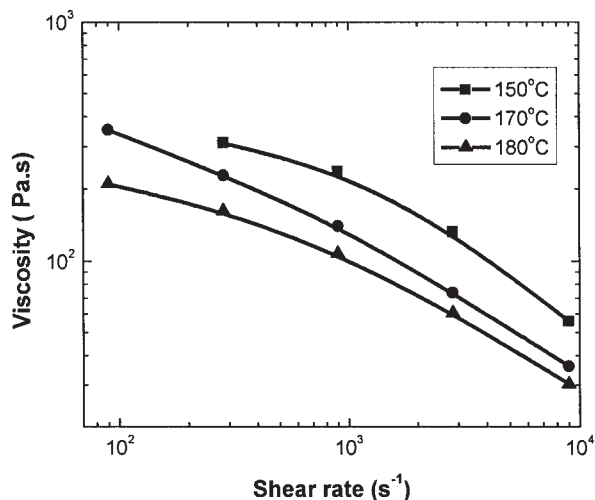


Figure 6 Melt viscosity versus the shear rate for PPCs with an M_n value of 28,900 Da at various temperatures.

n values for PPCs with various molecular weights at different shear rates and 170°C are listed in Table III. The n values were less than 1, showing a typical characteristic of a non-Newtonian fluid, that is, pseudoplastic behavior. Moreover, the n values decreased with increasing shear rate and molecular weight, and this indicated that both the shear rate and molecular weight could enhance the pseudoplasticity of the PPC melts.

Temperature dependence

Figures 6 and 7 show plots of the melt viscosity versus the shear rate for PPCs with M_n 's of 28,900 and 86,590 Da at various temperatures. These figures demonstrate that the melt viscosity was reduced dramatically

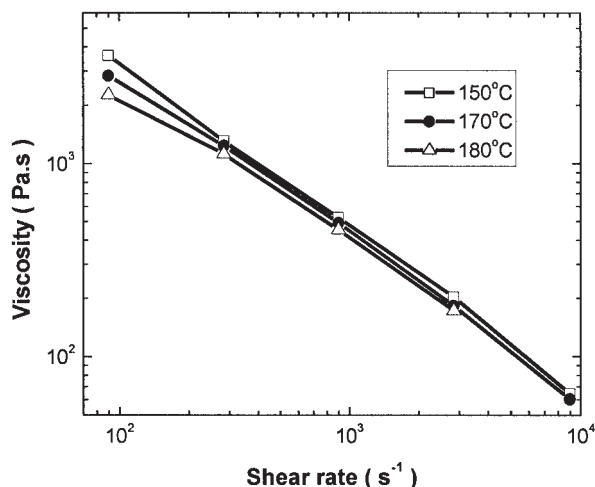


Figure 7 Melt viscosity versus the shear rate for PPCs with an M_n value of 86,590 Da at various temperatures.

TABLE IV
Activation Energies (kJ/mol) for PPCs with Various Molecular Weights at Different Shear Rates

Shear rate (s^{-1})	M_n (Da)	
	28,900	117,700
284.6	5.57	12.62
900.0	3.88	12.15
2846	3.81	13.12

as the temperature increased from 150 to 180°C, particularly for low-molecular-weight PPCs. This result was consistent with the morphology observations for the PPC with a molecular weight of 117,700 Da at different temperatures (Fig. 4). The temperature dependence of the melt viscosity can be described by an Arrhenius equation:

$$\eta = A \times \exp(E_a/RT) \tag{2}$$

where η is the melt viscosity; A is a constant; and E_a , R , and T are the activation energy for viscous flow, universal gas constant, and absolute temperature, respectively. The E_a values of PPCs, determined from the slope of $\ln \eta$ versus $1/T$ with linear regression, are listed in Table IV. The results indicated that the flow activation energies of PPCs with low molecular weights tended to decrease with an increasing shear rate. This was because shearing could remove the entanglements of polymer chains. Thus, the flow activation energies of PPCs with a high molecular weight (117,700 Da) were much higher than those of low-molecular-weight PPCs. These results showed that high-molecular-weight PPCs were more sensitive to temperature than low-molecular-weight PPCs.

The n values for PPCs with molecular weights of 29,130 and 86,590 Da, determined at various melt temperatures and different shear rates, are given in Table V. The PPCs exhibited the typical pseudoplastic behavior of a non-Newtonian fluid. The n values at various shear rates increased with increasing temper-

TABLE V
 n Values for PPCs Processed at Various Temperatures and Different Shear Rates

	Shear rate (s^{-1})			
	90.00	284.4	900.0	2846
M_n (29,130 Da)				
150°C	—	0.43	0.50	0.24
170°C	0.51	0.73	0.71	0.43
180°C	1.04	0.81	0.65	0.47
M_n (86,590 Da)				
150°C	0.15	0.21	0.18	0.15
170°C	0.38	0.25	0.19	0.19
180°C	0.33	0.32	0.22	0.20

ature, and this demonstrated that increasing the temperature could reduce the pseudoplasticity of PPC melts. Also, low-molecular-weight PPCs exhibited Newtonian fluid behavior at low shear rates and high temperatures.

CONCLUSIONS

The thermal properties of PPCs with various molecular weights were examined with modulated differential scanning calorimetry and thermogravimetric analysis. The results showed that T_g 's of PPCs increased with increasing molecular weight. The effects of the molecular weight, shear rate, and temperature on the rheological behavior of PPCs were investigated. The results showed that the melt flow of PPC had pseudoplastic flow characteristics. Moreover, the molecular weight of PPC played a crucial role in its processability. High-molecular-weight PPCs appeared to be more sensitive to the temperature and shear rate than low-molecular-weight PPCs. For low-molecular-weight PPCs, the melt viscosity decreased with increasing temperature, and the flow activation energy decreased greatly with increasing shear rate. The flow activation energy was almost constant for high-molecular-weight PPC. Finally, the pseudoplasticity of the PPC melts decreased with increasing temperature.

References

1. Kacholia, K.; Reck, R. A. *Climate Change* 1997, 35, 53.
2. Broecker, W. S. *Science* 1997, 278, 1582.
3. Meehl, G. A.; Washington, W. M. *Nature* 1996, 382, 56.
4. Rokicki, A.; Kuran, W. *J Macromol Sci Rev Macromol Chem* 1981, 21, 135.
5. Gorecki, P.; Kuran, W. *J Polym Sci Polym Lett Ed* 1985, 23, 299.
6. Nishimura, M.; Kasai, M.; Tsuchida, E. *Makromol Chem* 1978, 179, 1913.
7. Tsuchida, E.; Kasai, M. *Makromol Chem* 1980, 181, 1613.
8. Soga, K.; Uenishi, K.; Ikeda, S. *J Polym Sci Polym Chem Ed* 1979, 17, 415.
9. Chen, X.; Shen, Z.; Zhang, Y. *Macromolecules* 1991, 24, 5305.
10. Soga, K.; Hyakkoku, K.; Izumi, K.; Ikeda, S. *J Polym Sci Polym Chem Ed* 1978, 16, 2383.
11. Kobayashi, M.; Tang, Y. L.; Tsuruta, T.; Inoue, S. *Makromol Chem* 1973, 169, 69.
12. Ree, M.; Bae, J. Y.; Jung, J. H.; Shin, T. J. *J Polym Sci Part A: Polym Chem* 1999, 37, 1863.
13. Wang, S. J.; Tjong, S. C.; Du, L. C.; Zhao, X. S.; Meng, Y. Z. *J Appl Polym Sci* 2002, 85, 2327.
14. Zhu, Q.; Meng, Y. Z.; Tjong, S. C.; Zhao, X. S.; Chen, Y. L. *Polym Int* 2002, 51, 1079.
15. Du, L. C.; Meng, Y. Z.; Wang, S. J.; Tjong, S. C. *Acta Sci Nat Univ Sunyatseni* 2003, 42 (Suppl.), 5.
16. Zhu, Q.; Meng, Y. Z.; Tjong, S. C.; Wan, W. *Polym Int* 2003, 52, 799.
17. Li, X. H.; Tjong, S. C.; Zhu, Q.; Meng, Y. Z. *J Appl Polym Sci* 2003, 89, 3301.
18. Motika, S. A.; Pickering, T. L.; Rokicki, A.; Stein, B. K. *U.S. Pat.* 5,026,676 (1991).
19. Li, X. H.; Meng, Y. Z.; Zhu, Q.; Tjong, S. C. *Polym Stab Degrad* 2003, 81, 157.
20. Han, C. D. *Rheology in Polymer Processing*; Academic: New York, 1976; p 105.