Journal of Thermal Analysis and Calorimetry, Vol. 82 (2005) 293–298

THERMAL AND DYNAMIC MECHANICAL PROPERTIES OF POLY(PROPYLENE CARBONATE)

M. F. Lai, J. Li and J. J. Liu[*]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, P. R. China

Thermal and dynamic mechanical properties of carbon dioxide and propylene oxide alternative copolymer, poly(propylene carbonate) (PPC), and the end-capped PPC with maleic anhydride were investigated by means of TG and DMA. A master curve of the storage modulus *vs.* frequency can be deduced from the isochronal curves. Physical parameters of both plain and MA end-capped PPC were discussed. The results showed that for maleic anhydride (MA) end-capping PPC, an improvement of its thermal stability and mechanical properties accompanied with some modifications of the viscoelastic behavior were obtained.

Keywords: *mechanical properties, poly(propylene carbonate), thermal stability, viscoelastic properties*

Introduction

Aliphatic polycarbonate (APC), a series of novel biodegradable polymer, is the copolymers of carbon dioxide and epoxy compounds and was first synthesized by Inoue *et al.* [1–3] in 1969. APC is now considered to be a better solution to reducing CO_2 emission in industries. Fixation of CO_2 in APC is an efficient route of abating the global warming. The biodegradability of APC makes it useful in improving another environmental problem, 'white pollution', resulted from largely using plastics. Poly(propylene carbonate) (PPC) is an alternative copolymer of CO_2 and propylene oxide (PO), an important member of APC family. Several studies had been reported focusing on the properties of PPC blends [4–7] and decomposition behavior [8–9] of PPC.

From a more fundamental point of view, it is interesting to study the properties of this material at low temperatures. In this article, the viscoelastic behavior of the glass transition zone and the main part of the glassy state was studied for MA end-capped PPC, and comparison was made with PPC copolymer.

Experimental

Material

PPC and maleic anhydride (MA) end-capped PPC labeled as PPC and MA–PPC, respectively, were synthesized in our laboratory. The mass average molecular mass is 177 000 and the polydispersity index is 3.71.

NMR data were recorded at 400 MHz in a Varian Unity NMR instrument (400 MHz), and listed in parts per million downfield from tetramethylsilane (TMS). Chloroform-d_1 ($CDCl_3$) was used as the solvent. The molar fraction of CO_2 units in the copolymer products was determined by ^{1}H-NMR spectroscopy using the following equation:

$$C=\frac{A_{5.0}+A_{4.17}}{A_{5.0}+A_{4.17}+A_{3.58}}\cdot 100\% \tag{1}$$

where $A_{5.0}$ and $A_{4.17}$ were the peak area of 5.00($CH_2C\underline{H}$) and 4.17($C\underline{H}_2CH$), $A_{3.58}$ was the area of combined peak of 3.58($CH_2C\underline{H}$, $C\underline{H}_2CH$) in poly(propylene oxide) (PPO) homopolymer, respectively.

Thermogravimetry

The thermal behavior was examined with TGA-7 instrument (PerkinElmer Co., USA) by heating from room temperature up to 600°C at a heating rate of 20°C min^{-1} under a nitrogen flow.

Rheology

Viscoelastic measurements of PPC and MA-PPC melts were carried out with a Physica MC-300 Rheometer with core-plate geometry (25 mm diameter plate and 0.05 mm gap heights). The time tests were performed in a constant strain oscillatory shear mode with a small strain amplitude (γ_0=1%) at 180°C for 40 min to monitored the thermal stabilization of PPC and MA–PPC.

Mechanical property

The mechanical properties of the films were determined using a texture analyzer (Instron1121). The ten-

---

[*] Author for correspondence: jjliu@ciac.jl.cn

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

sile strength and the elongation of the films were determined with an extension rate of 50 mm min^{-1}, at room temperature according to GB/T1040-1992 method.

Viscoelastic properties

The dynamic storage modulus E' and loss factor (tanδ) were determined using a DMA-242C instrument (Netzsch Company, Germany) in a temperature range of –15 to 100°C. A tensile mode was employed. All measurements were carried out under the N_2 atmosphere at frequencies range from 2 to 33 Hz and heating rate of 3 K min^{-1}. The test specimens were 1.0×5.0×20 mm approximately.

Results and discussion

Characterization of PPC

The ^{1}H-NMR and ^{13}C-NMR spectrum for the poly(propylene carbonate) are shown in Fig. 1, that is, ^{1}H-NMR ($CDCl_3$):δ1.34 ($C\underline{H}_3$), 4.17($C\underline{H}_2CH$), 5.00($CH_2C\underline{H}$) and ^{13}C-NMR ($CDCl_3$):δ16.6($\underline{C}H_3$), 69.5($CH_2\underline{C}H$), 73.0($\underline{C}H_2CH$), 155.7($O\underline{C}OO$). From the NMR data, the as-received PPC exhibits an exact alternating molecular structure, the ratio of alternating copolymerization calculated from Eq. (1) is 98.6%. It has been reported [10] that the ^{1}H-NMR ($CDCl_3$) and ^{13}C-NMR (C_6D_6) spectrum of PPO homopolymer were as followed: δ1.16(d, $C\underline{H}_3$), 3.58($C\underline{H}_2CH$), 3.45($CH_2C\underline{H}$); 17.8($\underline{C}H_3$), 73.8($CH_2\underline{C}H$), 75.7($\underline{C}H_2CH$). The ^{1}H-NMR spectrum of PPC showed only a very slight mound in 3.45–3.58, and in the ^{13}C-NMR spectrum of PPC no chemical shift signal about the carbon atom of poly(propylene oxide) was observed. The results indicated that there is scarcely PPO homopolymer in poly(propylene carbonate).

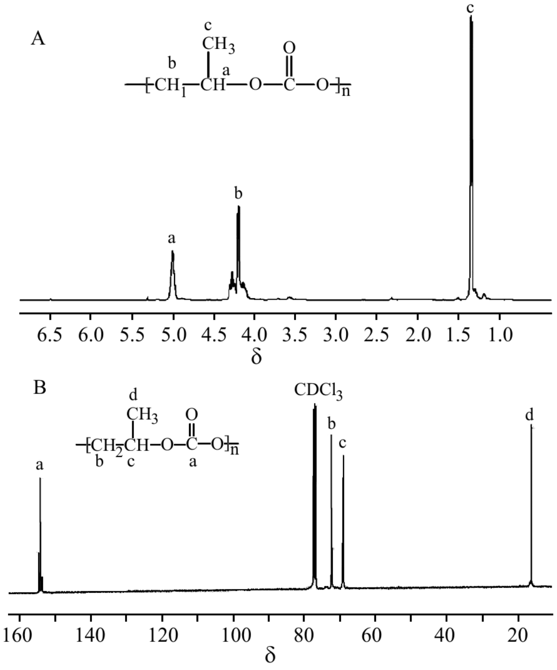

Fig. 1 A – ^{1}H-NMR and B – ^{13}C-NMR spectra of MA–PPC

Thermal stability

The thermal degradations of PPC and MA–PPC were investigated by TG. The original and derivatives of the thermogravimetric curves are presented in Fig. 2 and the relevant parameters are summarized in Table 1. The difference between their decomposition temperatures T_e, T_p and 95% mass residue were 22.8, 33.5 and 22.4°C, respectively. The results indicated that the thermal stability of MA–PPC was much better than that of PPC.

Two types of mechanisms in APC degradation had been reported elsewhere [11]: unzipping mechanism and random chain scission. It had been proved that unzipping degradation of PPC could be depressed by end capping significantly [12, 13]. Inoue [11] reported that the thermal degradation of PPC takes place in two steps: the scissions of the chains by decarboxylation followed by the unzipping reaction, while the work of Dixson [13] showed that for uncapped poly(alkylene carbonate) degradation occurs exclusively by chain unzipping; depolymerization by chain scission does not operate until the unzipping

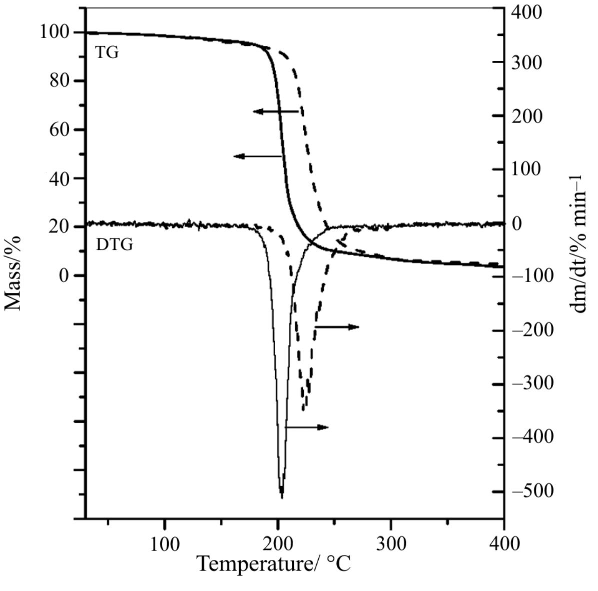

Fig. 2 TG and DTG curves of (—) – PPC and (- -) – MA-PPC

Table 1 TG results of PPC and MA–PPC

Code	T_e/°C	T_p/°C	$T_{95\%}$/°C
PPC	210.6	224.0	196.0
MA–PPC	233.4	257.5	218.4

mechanism is obviated. And pathways for thermal degradation of the capped poly(alkylene carbonate) are restricted to chain scission and subsequent unzipping. Liu [14] investigated the degradation mechanism of PPC by means of MS and ^{1}H-NMR, and found that at low temperature the dominant mechanism of degradation was unzipping and the degradation process at higher temperature was a mixture of the two mechanisms. The volatile products of unzipping degradation will result in mass loss and for random chain scission there is little mass loss detected, therefore, as showed in TG curves the 95% mass residue temperature of MA–PPC was 22.4°C higher than that of plain PPC, which means that comparing with that of PPC, the unzipping degradation of MA–PPC occurs at much higher temperature.

The decrease in molecular mass resulted from chain scission leaded to the drop of viscosity in PPC melt and can be measured by rheometer. A rheological time test was performed to detect the effect of end-capping on the degradation of PPC. The time dependence of the complex viscosity were recorded and depicted in Fig. 3. The viscosity of both of the samples decreased with time due to the thermal degradation. Obviously, at the time range of 0~30 min, the viscosity of PPC dropped more rapidly than that of MA–PPC. The decrement 60% for MA–PPC while the former dropped more than 35 times. It is well known that for the same polymer higher viscosity correspond with higher molecular weight. But chain scission was not the unique reason of viscosity decreasing, the newborn reactive groups resulted from chain scission promoted the process of unzipping and accelerated the degradation. After 30 min, the viscosity of PPC increased again which was given rise to the thermal cross-linking of the degraded polymer chains. However, no such phenomenon was observed in MA–PPC because of the insufficient degradation within test time range. The results above also proved that the thermal stability of PPC was improved significantly by end-capping.

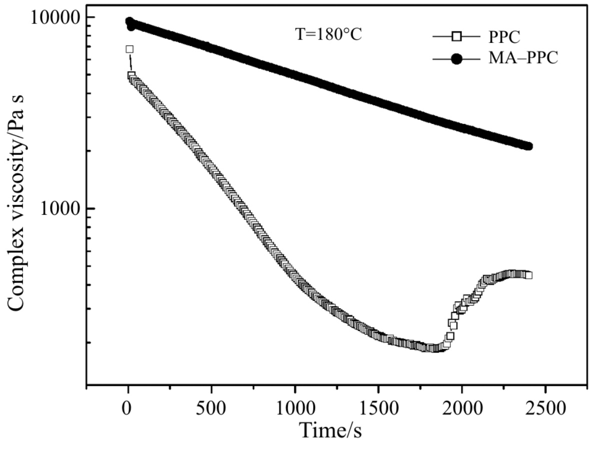

Fig. 3 Time test curves of PPC and MA–PPC

Mechanical properties

Results obtained from the tensile tests are summarized in Fig. 4 and Table 2, which show that all the tensile properties of PPC were improved after end-capped by MA. The elongation at break and the energy absorption of MA–PPC were 34 and 39% higher than that of PPC, respectively. The significant improvement of mechanical properties was attributed to stabilization resulted from the end-capping with MA.

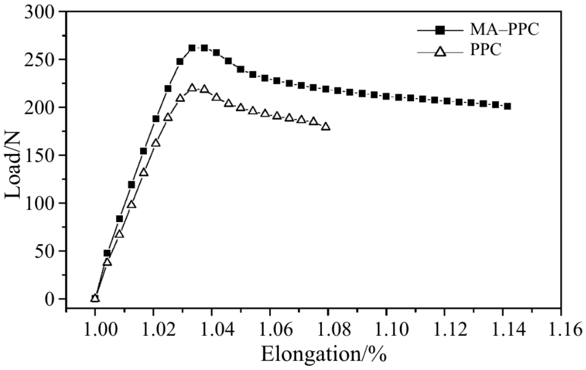

Fig. 4 Tensile test results of PPC and MA–PPC

Table 2 Tensile properties of PPC and MA–PPC

Code	σ_y/MPa	σ_b/MPa	ε/%	*E*/MPa	*Uk*/mJ
PPC	38.8	29.6	13.7	1233	450
MA–PPC	41.2	31.0	18.3	1333	625

The degradation was depressed by stabilization, which led to an elevation in mechanical properties; on the other hand, the strong interaction of the polar groups in maleic anhydride, such as carbonyl and ester, reinforced the interaction among the macromolecules. Higher value of elongation at break and fracture energy indicated that MA–PPC had better toughness.

Viscoelastic behavior

Dynamic mechanical analysis is an efficient technique to characterize the viscoelastic properties of polymer [15, 16]. Figure 5 represented the storage modulus *E'* and the loss tangent curves of PPC and MA–PPC obtained using dynamic tension technique at five frequencies, 2, 5, 10, 20 and 33 Hz. Only one symmetrical damping peak was observed within the range of experimental temperature and frequency. Both of PPC and MA–PPC showed a rather high tensile Young's modulus (about 10 MPa) after passing through the glass transition (above 90°C), which were related to the high entanglement density of macromolecules. The glass transition temperature T_g, defined as the temperature corresponding to the peak of tanδ in the glass transition region, is 41.9°C (2 Hz) for MA–PPC and

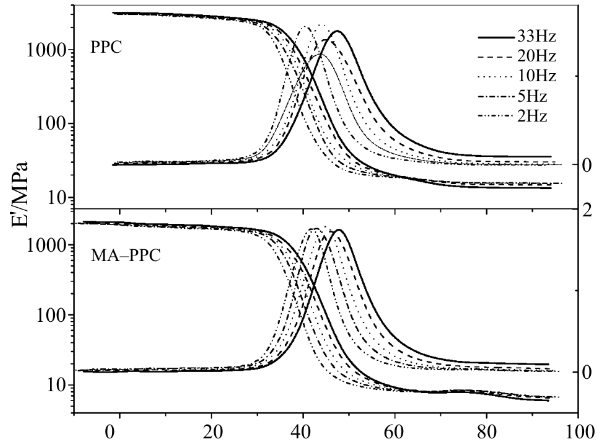

Fig. 5 Storage modulus E' and loss tangent *vs.* temperature, obtained at 2, 5, 10, 20 and 33Hz for PPC and MA–PPC

40.3°C (2 Hz) for PPC. The increase of T_g indicated that macromolecular motion had been affected by the bulky end group produced from the MA end-capping.

The master curves of PPC and MA-PPC are presented in Fig. 6. Superposition principles for the dynamic moduli can be used to obtain master curves that covers a wide range of viscoelastic properties. This technique was originally described by William, Landel and Ferry [17]. The principle of the equivalency of time and temperature is basically described by time–temperature superposition (TTS) and is shown by Eq. (2):

$$\log\alpha_T=\log\frac{\lambda_T}{\lambda_{T_0}}=-\frac{C_1^0(T-T_0)}{C_2^0+T-T_0} \quad (2)$$

The shift factor α_T is defined as the ratio of the relaxation time, λ_T, at a given temperature, T, and the relaxation time, λ_{T_0}, at the reference temperature, T_0, C_1^0 and C_2^0 are two empirical constants. The WLF (William–Landel–Ferry) equation and its derivation on the basis of free volume considerations appear to satisfactorily explain the recorded progress in viscoelasticity [17–22]. Fitting of the shift factors can be achieved, for example, by plotting $(\log\alpha_T)^{-1}$ *vs.* $(T-T_0)^{-1}$ and obtaining the two constants C_1^0 and C_2^0 from the slope and intercept of the linear fit, respectively. For PPC, C_1^0=3.941 and C_2^0=11.343 K at a reference temperature, T_0=313.4 K. For MA–PPC, C_1^0=8.153 and C_2^0=54.515 K at a reference temperature, T_0=314.9 K. It is well known that at the glass transition zone the relationship between relaxation time and temperature for polymers does not follow a simple Arrhenius law.

But it can be described by WLF equation:

$$E_a=R\frac{d(\ln a_T)}{d(1/T)}=\frac{2.303C_1^0C_2^0RT^2}{(C_2+T-T_0)} \quad (3)$$

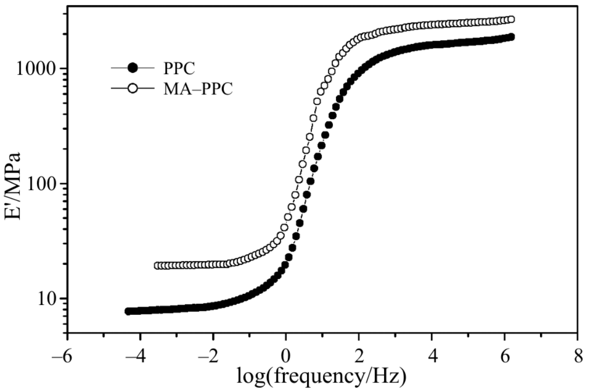

Fig. 6 Master curves of E' *vs.* frequency of PPC and MA–PPC reduced to T=313.4 K and T=314.9 K, respectively, obtained by superimposition of the data from dynamic tension experiments

where E_a is the so-called apparent activation energy of glass transition. The apparent activation energies of glass transition for PPC and MA–PPC obtained from Eq. (3) are plotted in Fig. 7. For PPC, the value of E_a was very high in glass transition zone and dropped significantly with the increase of temperature. In the temperature range of 315–350 K, the decrease of E_a covered an order of magnitude (510–46 kJ mol^{-1}). And for MA–PPC, the value of E_a in 350 K was only 2.2 times lower than that in 315 K. This result indicated that the macromolecular motion of PPC was very sensitive to temperature, while that of MA–PPC was much more stable.

In terms of the theory of free volume,

$$C_1^0=B/2.303f_0 \quad (4)$$

$$C_2^0=f_0/a_f \quad (5)$$

the ratio of free to total volume per unit mass of a material is known as the fractional free volume, f_0, the degree of thermal expansion is given by the coefficient a_f, and, for simplicity, B is taken equal to unity [19]. The value of a_f and f_0 can be obtained from Eqs 3 and 4: a_f=0.11, f_0=0.0097 K^{-1} (T_0=313.47 K) for PPC

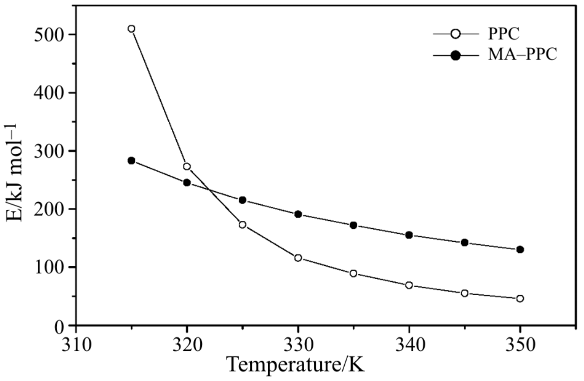

Fig. 7 Apparent activation energy *vs.* temperature in the glassy state of PPC and MA–PPC

and a_f=0.053, f_0=9.77·10^{-4} K^{-1} (T_0=314.9 K) for MA–PPC. The parameters f_g and f_0 are related to the fractional free volume at the glass transition temperature and the reference temperature, respectively. Quantitatively, their relationship is represented by:

$$f_0=f_g+a_f(T-T_0) \tag{6}$$

The value of f_g was calculated to be 0.0479 and 0.0453 for PPC and MA–PPC, respectively. Comparing with the universal value 0.025±0.003, it can be concluded that the fractional free volume of PPC was higher than that of the great majority of the systems. At the glass transition temperature, PPC and MA–PPC had similar f_g.

A single average relaxation time, τ, was used as a parameter to characterize the relaxation behavior of amorphous polymer with high symmetrical structure like PPC. In DMA spectrum, when E'' reaches its maximum, it is generally assumed that $\omega\tau=1$, $\varpi=1/2\pi f$ it is the solicitation pulsation and τ is the average value of the relaxation time for the considered temperature. According to Eq. (2), the value of τ varying with temperature at a given frequency can be obtained. Figure 8 plots the average relaxation time as a function of temperature. Comparing with MA–PPC, PPC was much sensitive to temperature; it relaxed very fast at high temperature and slowed down at lower temperature. It should be noted that the cross point of the two curves was around 40°C, which equaled to the glass transition temperature corresponding to the peak value of tanδ(2 Hz) in DMA spectra. In agreement with results discussed above, the molecular motion characters of PPC and MA–PPC were similar at the glass transition zone, but they were different both in glass state and in rubbery state, the difference between PPC and MA–PPC was much more significant. End-capping not only enhanced the thermal stability of PPC, reinforced interaction between macromolecules, but also led to some modifications on its viscoelastic properties and molecular characters.

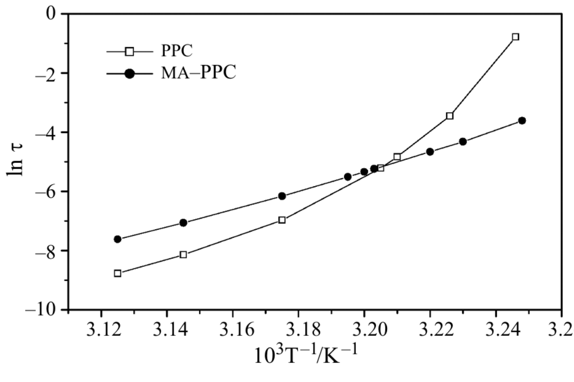

Fig. 8 Average relaxation time *vs.* temperature in the glassy state of PPC and MA–PPC

Conclusions

The thermal stability and mechanical performance of PPC can be enhanced by maleic anhydride end-capping due to the depression of unzipping degradation and chain scission. The effect of end-capping on the viscoelastic properties has been studied in the glass transition region by means of dynamic mechanical tests. It was found that the PPC and MA–PPC have a similar fractional free volume at the glass transition temperature and the T_g of PPC was a little lower than that of MA–PPC. Although the apparent active energy, E_a, and average relaxation time, τ, of both PPC and MA–PPC varied monotonically with temperature, it showed clearly that the molecular motion of PPC was much sensitive to temperature while MA–PPC was much stable.

Acknowledgements

This research is supported by the Special Funds for Major State Basic Research Project (G1999064806).

References

1 S. Inoue, H. Koinuma and T. Tsuruta, Polym. Lett., 7 (1969) 287.
2 S. Inoue, H. Koinuma and T. Tsuruta, Makromol. Chem., 130 (1969) 210.
3 S. Inoue, M. Kobayashi, H. Koinuma and T. Tsuruta, Makromol. Chem., 155 (1972) 61.
4 S. J. Wang, Y. H. Huang and G. M. Cong, J. Appl. Polym. Sci., 63 (1997) 1107.
5 S. J. Wang, Y. H. Huang and G. M. Cong, J. Appl. Polym. Sci., 64 (1997) 2457.
6 S. J. Wang, Y. H. Huang and G. M. Cong, Polym. Mater. Sci. Eng., 4 (1997) 78 (in Chinese).
7 M. Song, Y. H. Huang and G. M. Cong, Funct. Polym., 1 (1993) 51 (in Chinese).
8 W. Kuran and T. Listos, Macromol. Chem. Phys., 195 (1994) 1011.
9 H. W. Yan, W. R. Cannon and D. J. Shanefield, Ceram. Intern., 24 (1998) 433.
10 M. Ree, J. Y. Bae, J. H. Jung, T. J. Shin, Y. T. Hwang and T. Chang, Polym. Eng. Sci., 40 (2000) 1542.
11 S. Inue and J. Tsututa, Appl. Polym. Symp., 26 (1975) 257.
12 S. Y. Yang, H. Peng, B. Huang and L. B. Chen, Shi You Hua Gong, 22 (1993) 730 (in Chinese).
13 D. D. Dixon, M. E. Ford and G. J. Mantell, J. Polym. Sci., Polym. Lett. Ed., 18 (1980) 131.
14 B. Y. Liu, Synthesis Properties of Carbon Dioxide-Propylene Oxide Copolymer Using Rare Earth-based Ternary Catalyst, Thesis of Ph.D., 2001 pp. 97–99.
15 A. Danch and W. Osoba, J. Therm. Anal. Cal., 72 (2003) 641.
16 A. Danch and W. Osoba, J. Therm. Anal. Cal., 78 (2004) 923.
17 J. D. Ferry, Viscoelastic Properties of Polymers, 3rd Ed.; John Wiley & Sons, New York 1980.

18 Y. M. Goldman, Prediction of the deformation properties of polymeric and composite materials, American Chemical Society, Washington DC 1994.
19 W. Brostow, M. Kubat and M. J. Kubat, Physical properties of polymer handbook, J. E. Mark Ed, Woodbury: Institute of Physics Press, N.Y. 1996 Chap. 33.
20 J. J. Aklonis and W. J. McKnight, Introduction to polymer viscoelasticity, 2nd Ed., John Wiley & Sons, New York 1983.
21 M. C. Shen and A. Eisenberg, in H.Reiss (Ed.,) Progress in Solid State Chemistry, Pergamon Oxford 1967, pp. 407–481.
22 S. Kasapis, in S. E. Hill, D. A. Ledward and J. R. Mitchell (Eds), Functional Properties of Food Macromolecules, Aspen Publishers, Gaithersburg 1998, pp. 227–251.

Received: January 20, 2005
In revised form: April 5, 2005

DOI: 10.1007/s10973-005-6182-1