

EFFECT OF CHEMICAL STRUCTURE OF POLYCARBONATES ON ENTANGLEMENT SPACING*

Wei Ning, Wen-xiang Zhu, Bao-qing Zhang, Chun-cheng Li^{**}, Chen-yang Liu^{**} and Du-jin Wang
*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics,
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Abstract The master curves of a series of aliphatic polycarbonates (APCs) with different lengths of methylene segments in the repeat unit were obtained by dynamic rheological measurements. The plateau modulus and entanglement molecular weight were determined and cross-checked by different methods. Though having distinct difference in chemical structure of repeat units, both APCs and bisphenol-A polycarbonates have the similar entanglement weight and entanglement spacing. On the other side, the plateau modulus decreases with increasing the length of the side group of aliphatic polycarbonates with different side-chain lengths in the literature. The packing length model can explain the relationship between chain structure and entanglements.

Keywords: Aliphatic polycarbonates; Bisphenol-A polycarbonate; Plateau modulus; Entanglement; Packing length model.

INTRODUCTION

The public has been concerning with developing new biodegradable plastic materials to replace traditional general plastics to alleviate their destruction to our environment. Among biodegradable plastics, aliphatic polyesters and aliphatic polycarbonates (APCs) have drawn great attention due to their combination of biodegradability, biocompatibility and physical chemical properties^[1, 2].

The enzymatic degradation rate of biodegradable polymers is highly influenced by the ability of molecular chains to reach the active center of lipase^[3]. The ability of polymer chains to reach the active center mainly depends on the chain flexibility and crystal structures. The biodegradation rate and content mainly depend on the crystal structure, which is mainly determined by the chemical structure of the repeating unit of the biodegradable polymers^[4–7]. In contrast, the entanglement molecular weight of polymers is one of the important material parameters which determine the mechanical properties. Therefore, the “tailor-made” new copolymers can be synthesized by the controlled incorporation of repeating units with different structures to produce polymers with a range of material properties.

Inferior mechanical properties of APCs compared with polyolefins hinder the practical applications since the molecular weight (MW) of the APCs obtained was too low. Recently a series of high MW APCs with different lengths of methylene segments were synthesized *via* the two-step condensation polymerization^[8]. They are also good model polymers to build the structure and rheological properties relationship for this novel biodegradable polymer. The average molecular weight between topological entanglements M_e is one of the most

* This work was financially supported by National Natural Science Foundation of China (No. 20874109) and National High Technology Research and Development Program of China (No. 2009AA033601) and the Chinese Academy of Sciences.

** Corresponding author: Chun-cheng Li (李春成), E-mail: lichch@iccas.ac.cn
Chen-yang Liu (刘琛阳), E-mail: liucy@iccas.ac.cn

fundamental material parameters since it determines the properties of polymer melt and mechanical properties of materials^[9–11]. For example, the ratio of MW/M_e determines the chain relaxation time under certain tension rates, which also affects the tensile strength of APC elastomers^[12]. M_e is usually inferred from the plateau modulus G_N^0 , which can be determined by the calculation from the measurement results of the dynamic moduli G' and G'' in oscillatory shear experiments:

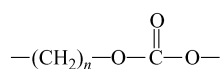
$$M_e = \frac{\rho_0 RT_0}{G_N^0} \quad (1)$$

The relationship between chain structures, rheological properties and chain entanglements of bisphenol-A polycarbonates (BPA-PC) has been extensively investigated^[13, 14]. APCs have different structures from BPA-PC on the backbone. In the present paper the master curves of APCs with different chain structures were measured by the melt rheological frequency sweep at different temperatures. The plateau modulus was determined based on the master curves by three different methods. The influence of the structure of the main chain and the side group in repeat units of biodegradable APCs was explored. The dependence of plateau modulus G_N^0 on the chain structures was analyzed by the packing length model.

EXPERIMENTAL

Materials and Sample Preparation

Aliphatic polycarbonates with different lengths of methylene segments, denoted as APC n ($n = 3–9$, the number of methylene groups in a repeat unit), were synthesized *via* the two-step condensation polymerization in dichloromethane. The synthetic procedure has been described in detail elsewhere^[8]. The chemical structure of the repeat unit is shown as Scheme 1.



Scheme 1 Repeat unit of APC n

Here n denotes the number of methylene in the repeat unit. Due to different crystallinities, as-synthesized APC3 was a soft and transparent rubber at ambient conditions, APC5 was a semi-transparent rubber and other APCs were white opaque plastics. All samples showed a good solubility in chloroform, so APCs were purified by dissolving in chloroform and precipitating in cold methanol before any measurement. The bisphenol-A polycarbonate used in this work was supplied by Idemitsu Petrochemical.

Gel Permeation Chromatography (GPC)

Molecular weight data were obtained by gel-permeation chromatography (GPC) at 40°C using a Waters 2414. In all cases, THF was used as the eluent with a flow rate of 1.0 mL/min, and sample concentrations were approximately 3.0 mg/mL. The molecular weight calibration curve was obtained with several polystyrene standards with a molecular weight in the range of 1000–100000. The results of M_n and M_w are summarized in Table 1.

Table 1. Molecular weight and molecular weight distribution parameters of APCs and BPA-PC

Sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
APC3	23	38	1.68
APC4	40	69	1.73
APC5	99	194	1.95
APC6	36	63	1.77
APC7	66	104	1.58
APC8	42	70	1.67
APC9	73	122	1.67
BPA-PC	18	35	2.10

Rheological Measurements

The purified samples were compression-molded into 1 mm thick sheets at 80°C. The round plates with 7 mm in diameter were punched down using a commercial punch. The viscoelastic behaviors were determined by the strain-controlled rheometer ARES-G2 supplied by TA Instruments. The geometries were 8 mm parallel plates. All the measurements were carried out under nitrogen atmosphere between 0.1 rad/s and 100 rad/s with 5 points per decade and temperatures ranging from 80°C to near T_g (or near T_m for those APCs with a fast crystallization rate). A strain of 5% was selected to keep all the samples deforming within their own linear viscoelastic (LVE) region. Repeat measurements at the initial temperature (80°C) after a complete frequency sweep series did not show any significant change. The TA TRIOS software was used to derive master curves at a reference temperature 80°C by a two-dimensional residual minimization technique.

RESULTS AND DISCUSSION

Master Curves and Plateau Modulus of APCs

The rheological master curves of polymers generally consist of four sections: the glass, transition, rubber plateau and terminal flow regions. Figure 1(a) clearly shows a quasi-plateau in the storage modulus versus angular frequency curve, which is the signature of entanglements. It is obvious that all the master curves of APCs, except APC6, have the approximate plateau height. There are various semi-empirical methods to extract the value of the linear viscoelastic spectrum. One of them is to determine G_N^0 from the value of G' at the frequency ω where $\tan\delta$ reaches a minimum (MIN method)^[11].

$$G_N^0 = G'(\omega)_{\tan\delta \rightarrow \text{minimum}} \quad (2)$$

The plateau region of master curves was highlighted in Fig. 1(b), APC3, APC4 and APC5 have the identical plateau modulus close to 2.0 MPa by the MIN method. Values of G_N^0 are listed in Table 2.

Table 2. Effects of chemical structure of the repeat unit on the plateau modulus and entanglement molecular weights and entangle spacing

Polymer	G_N^0 (MPa)		G_x (MPa)	G_N^0 (MPa) Wu ^c	M_e	$N_e = M_e/M_0$	$N_b = N_e \times N_{b0}$
	INT ^a	MIN ^b					
APC3	2.2	2.2	0.32	1.9	1133	11	55
APC4	2.2	2.3	0.32	1.9	1133	10	60
APC5	1.9	2.2	0.28	1.9	1312	9	63
APC6	—	—	0.33	2.0	1247	8	64
APC7	—	—	0.33	1.8	1385	8	72
APC8	—	—	0.28	1.7	1467	8	80
APC9	—	—	0.29	1.7	1467	7	63
APC2 ^d	—	—	0.20	2.0	1494	17	68
BPA-PC	2.3	2.2	0.39	2.8	1240	5	45

M_0 is the molecular weight of the repeat unit. N_{b0} is the number of chemical bonds in one repeat unit. N_e and N_b are the number of repeat units and chemical bonds between entanglement points, respectively;

^a Estimated by using “INT” method, the numerical integration over the terminal relaxation peak of $G''(\omega)$;

^b Estimated by using “MIN” method value of G' at the frequency ω where $\tan\delta$ reached a minimum;

^c Estimated by using Wu method, the ratio between the crossover modulus and the plateau modulus according to the polydispersity;

^d Estimated by Wu method based on the literature data^[16]

Because APC6, APC7, APC8 and APC9 have extremely fast crystallization rates, the data of both their plateau and flow regions could not be obtained. An empirical method based on the terminal crosspoint (G_x) of G' and G'' have been proposed by Wu^[15]. The Wu method correlates the ratio between the G_x and the plateau modulus to the polydispersity.

$$\lg\left(\frac{G_N^0}{G_x}\right) = 0.38 + \frac{2.63 \lg \frac{M_w}{M_n}}{1 + 2.45 \lg \frac{M_w}{M_n}} \quad (3)$$

The plateau modulus of APCs obtained from the Wu method is also listed in Table 2.

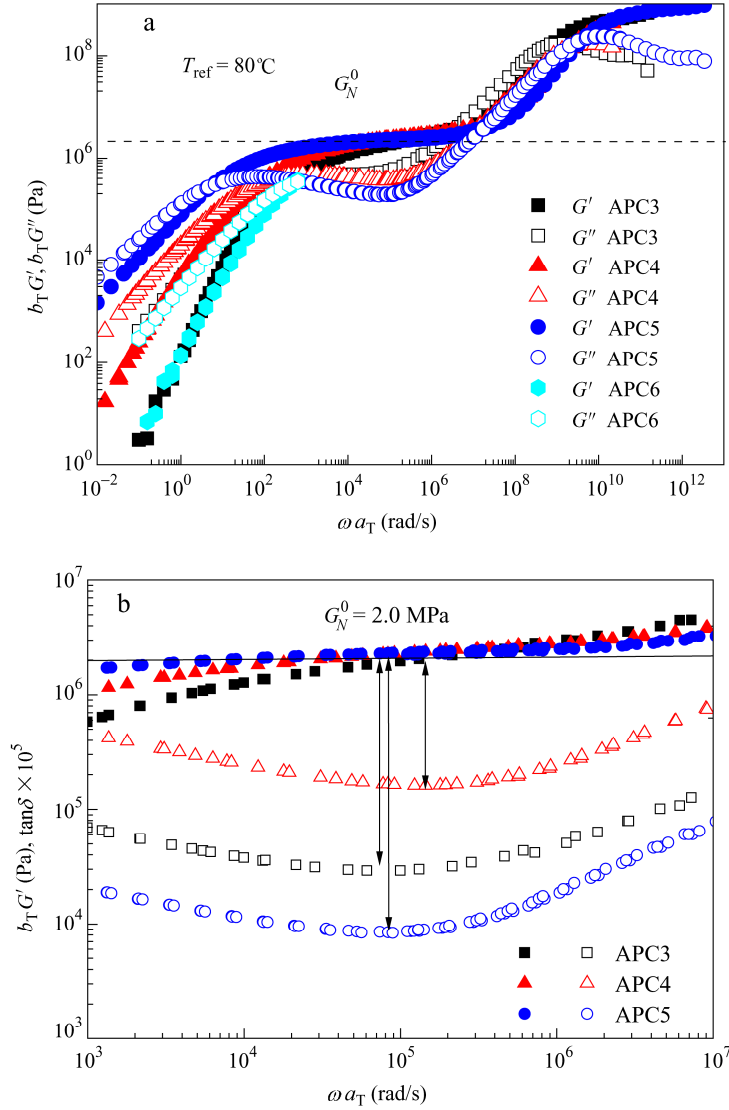


Fig. 1 (a) Plateau regions of master curves of storage moduli G' and loss moduli G'' for APCs as functions of frequency; (b) The magnification of the plateau region of master curves of the storage modulus G' (filled symbols) of APC3, APC4 and APC5
 a_T and b_T are the WLF shift factors; The plateau modulus from the minimum $\tan \delta$ method is also marked for all samples.

The third method is derived from the Krong-Kramers relation for G' and G'' ^[11]. It calculates plateau modulus by numerical integration over the terminal relaxation peak of $G''(\omega)$:

$$G_N^0 = \frac{2}{\pi} \int_{-\infty}^{+\infty} G''(\omega) d \ln \omega \quad (4)$$

This is called the “integral” method (INT). The plateau modulus of APCs calculated by the INT method is also listed in Table 2. It is clear that values obtained by different methods are consistent with each other for APC3, APC4 and APC5, which implies that the G_x method is applicable to all APCs.

Influence of Main Chain Structure on Plateau Modulus

APCs with different lengths of methylene segments in a repeat unit have the similar plateau modulus of around 2.0 MPa, as displayed in Table 2. It is interesting to compare their rheological properties with those of the bisphenol-A polycarbonate having a different main chain structure. Figure 2(a) shows the master curve of APC3 ($M_w = 38 \times 10^3$) at 80°C and that of BPA-PC ($M_w = 35 \times 10^3$) at 250°C. The glass transition temperatures T_g s are -22°C and 150°C for APC3 and BPA-PC, respectively, so the reference temperatures were chosen as *ca.* 100 K above their own T_g . In spite of a great difference in the stiffness of the repeat unit and then T_g , it is obvious that the two samples not only have the similar value of plateau modulus around 2.0 MPa, and also have a good overlapping for the whole master curves (since the number of entanglements per molecule Z , which equals to the ratio of M_w/M_e , is very close). The entanglement molecular weights for both of them are around 1200. The numbers of chemical bonds in the backbone between entanglement points are 55 and 45 for APC3 and BPA-PC, respectively. Similarly, the comparison of APC4 and BPA-PC is shown in Fig. 2 (b). The reference temperature of BPA-PC is 273°C to keep the same temperature gap between the T_g and the reference temperature of APC4, whose T_g is -43°C . The same plateau modulus can be found for APC4 and BPA-PC.

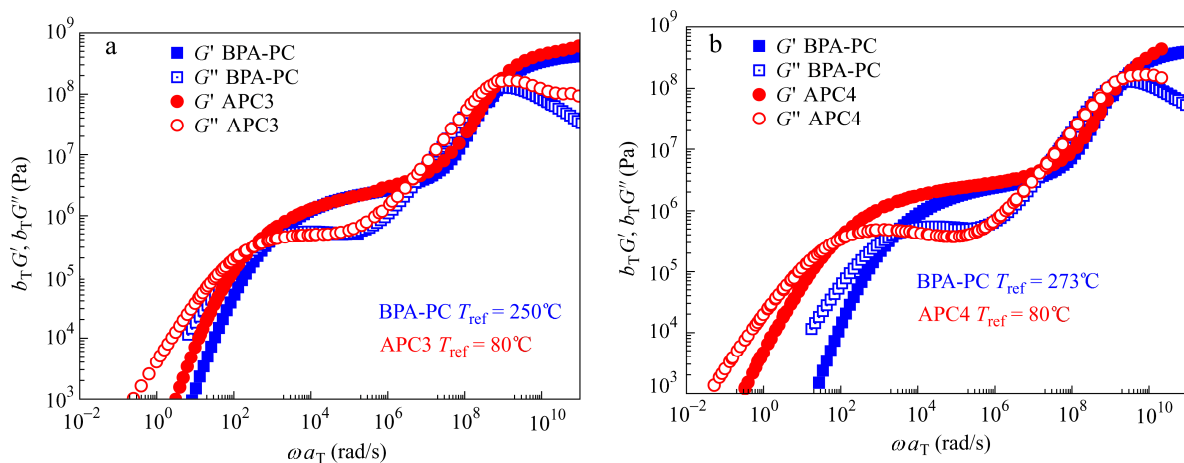


Fig. 2 Master curves of storage moluli G' and loss moluli G'' for BPA-PC and APC as functions of the shifted frequency ωa_T : (a) BPA-PC versus APC3 and (b) BPA-PC versus APC4

Table 3. Chain entanglement of flexible and semi-flexible polymers

Polymer	Repeat unit	$T_{\text{ref}} (^\circ\text{C})$	G_N^0 (MPa)	Ref.
Aliphatic polycarbonate (APC3)	$-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-$	80	2.0	—
Biphenol-A polycarbonate (BPA-PC)	$-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})-\text{O}-$	273	2.2	[11]
Poly(oxymethylene) (POM)	$-\text{CH}_2-\text{O}-$	200	1.7	[17]
Poly(ethylene oxide) (PEO)	$-\text{CH}_2-\text{CH}_2-\text{O}-$	80	1.8	[17]
Polyethylene (PE)	$-\text{CH}_2-\text{CH}_2-$	140	2.3	[17]

Furthermore, the literature data of the polyethylene (PE), which is regarded as the extreme model of APC whose number of methylene groups is infinite (so without carbonate groups), also is compared with APCs. In addition, polyoxymethylene (POM) and polyoxyethylene (PEO) have the ether linkage in the backbone. It is interesting to explore the structure-properties relationship for different polymers. The data in Table 3 show the insensitivity of entanglement effects to atomistic details. All polymers in the table have the similar plateau modulus of around 2.0 MPa. It can be understood that all four flexible polymers have similar entanglement spacing, but why BPA-PC with stiff backbones has a similar M_e remains unsettled^[14].

Influence of Side Group Structure on Plateau Modulus

Rheological properties of the homologous series of aliphatic polycarbonates with different side group lengths are investigated by Thorat and coauthors^[16]. All APCs have the same main chain structure (two methylenes in the repeat unit) but different side-chain substitutes ($n = 0, 1, 3, 4, 6$). The chemical structure of the repeat unit of APC2- n (Table 4) is shown in Fig. 3. The plateau modulus of these APCs with side groups can be determined from the data of crossover modulus G_x and the data of molecular weight. The results are listed in Table 4. The plateau modulus as a function of the number of the side-chain length is plotted in Fig. 3. The plateau modulus of the APC2- n decreases with increasing the length of the side group. APC2 which is taken as a reference polymer showed the same plateau modulus (2.0 MPa) as the APCs with different main chain structures. The APC with the longest side group has the lowest plateau modulus of only 0.02 MPa.

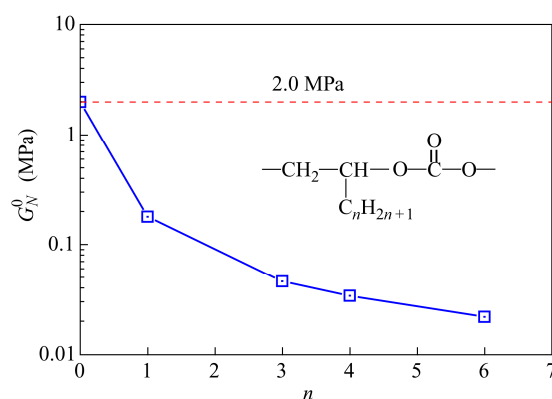


Fig. 3 Effect of the side group length on the plateau modulus of APC2s with a side group in the repeat unit

Table 4. Effect of the side group length of APC2s on the plateau modulus

Polymer	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	G_x (MPa)	G_N^0 (MPa) Wu
APC2	—	—	0.19	2.0
APC2-1	7.5	28.9	0.018	0.18
APC2-3	8.5	44.4	0.004	0.05
APC2-4	9.5	45.5	0.003	0.03
APC2-6	10.5	49.4	0.002	0.02

It is well known that the plateau modulus of ethylene- α -olefin copolymers decreases with the fraction of α -olefins and the decrease also depends on the length of the α -olefin^[18]. The packing length model^[19] can explain the relationship. The plateau modulus is inversely proportional to the third power of the packing length that increases with the chain thickness. The degree of branching and the length of the branching have a significant influence on the chain thickness. Conclusively, with the longer branching (here APC2- n) or more heavy density of branching (ethylene- α -olefin copolymers), the polymer has a lower plateau modulus and a larger entanglement spacing.

CONCLUSIONS

Rheological measurements were carried out to obtain the master curves of the series of APCs with different numbers of methylenes in the repeat unit. Based on the master curves, the plateau modulus is determined by different methods. Though having great difference in the structure of the repeat unit, APC and BPA-PC have the similar plateau modulus of 2.0 MPa. The calculated number of repeat units and chemical bonds tends to be constant for many flexible polymers with different chemical structure. In addition, both flexible polyoxymethylene (POM) and polyoxyethylene (PEO) which have the ether linkage in the backbone also show the approximate plateau modulus of 2.0 MPa. In contrast, the plateau modulus decreases with increasing the length of the side group of APCs with different side group length in the literature. Similar with the ethylene- α -olefin copolymers, the decreasing of the plateau modulus can be attributed to the increasing of the chain thickness according to the packing length model.

REFERENCES

- 1 Artham, T. and Doble, M., *Macromol. Biosci.*, 2008, 8(1): 14
- 2 Su, W., Feng, J., Wang, H.F., Zhang, X.Z. and Zhuo, R.X., *Polymer*, 2010, 51: 1010
- 3 Herzog, K., Müller, R.J. and Deckwer, W.D., *Polym. Degrad. Stab.*, 2006, 91: 2486
- 4 Wang, S.G. and Qiu, B., *Acta Polymerica Sinica* (in Chinese), 1993, (5): 620
- 5 Chen, D.R., Bei, J.Z. and Wang, S.G., *Acta Polymerica Sinica* (in Chinese), 1999, (5): 620
- 6 Lentz, R.W., Gross, R.A., Brandl, H. and Fuller, R.C., *Chinese J. Polym. Sci.*, 1989, 7(4): 289
- 7 Wang, B.T., Zhang, Y., Song, P.A., Guo, Z.H., Cheng, J. and Fang, Z.P., *Chinese J. Polym. Sci.*, 2010, 28(3): 405
- 8 Zhu, W.X., Huang, X., Li, C.C., Xiao, Y.N., Zhang, D. and Guan, G.H., *Polym. Int.*, 2011, 60: 1060
- 9 Watanabe, H., *Prog. Polym. Sci.*, 1999, 24: 1253
- 10 Mcleish, T.C.B., *Adv. Phys.*, 2002, 51(6): 1379
- 11 Liu, C.Y., He, J.S., van Ruymbeke, E., Keunings, R. and Bailly, C., *Polymer*, 2006, 47(13): 4461
- 12 Pego, A.P., Grijpma, D.W. and Feijen, J., *Polymer*, 2003, 44: 6495
- 13 Liu, C.Y., Li, C.X., Chen, P., He, J.S. and Fan, Q.R., *Polymer*, 2004, 45(8): 2803
- 14 Everaers, R., Sukumaran, S.K., Grest, G.S., Svaneborg, C., Sivasubramanian, A. and Kremer, K., *Science*, 2004, 303(5659): 823
- 15 Wu, S., *J. Polym. Sci. Part B: Polym. Phys.*, 1989, 27(4): 723
- 16 Thorat, S.D., Phillips, P.J., Semenov, V. and Galkh, A., *J. Appl. Polym. Sci.*, 2004, 93(2): 534
- 17 James, E.M., "Physical properties of polymers handbook", 2nd ed., Springer, New York, 2005, p. 451
- 18 Lohse, D.J., *J. Polym. Sci. Part C: Polym. Rev.*, 2005, 45: 289
- 19 Fetters, L.J., Lohse, D.J., Richter, D., Witten, T.A. and Zirkel, A., *Macromolecules*, 1994, 27: 4639