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Polymer 42 (2001) 8355–8359

polymer

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Relationship between the end-cap structure of polycarbonates and their impact resistance

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Received 9 January 2001; accepted 18 April 2001

Abstract

Using various phenols as the end-capping agent, polycarbonates (PCs) with the same degrees of polymerization were prepared by phosgenation of bisphenol A. The end-capping agents greatly affected the fluidity, thermal resistance and impact resistance of the PCs. It was found that, compared to commercially available PCs end-capped with 4-*tert*-butylphenol, the PCs end-capped with 4-*tert*-octylphenol or 4-α-cumylphenol were superior in impact strength with a better balance of fluidity, thermal resistance and impact resistance. From the results of dynamic mechanical measurements, improvement in performance is explained by the high mobility of my prepared PCs as compared to commercial ones, that is, energy dissipation occurs significantly in the polymer molecule, and contributes to the improvement in impact resistance.

Keywords: End-cap structure; Polycarbonates; Impact resistance

1. Introduction

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance and transparency [1,2]. In commercially available PCs, the monomer is bisphenol A (BPA) and the degrees of polymerization are less than 100 (less than 60 for the injection grade). Consequently, the terminal structure of the PC chains with the end-capping groups is presumed to play a somewhat noticeable role in behavior and influence their properties.

In the latest studies on the modification of polymers, there are several reports on the syntheses of block copolymers by the end-capping method [3–7]. In connection with my study, it has been reported that PCs end-capped with benzophenone derivatives have good weather resistance [8], and those end-capped with *p*-alkylphenol having a branched C_8 or C_9 alkyl group show a high melt-flow rate [2].

Recently, the demand for optical disks where PCs are used as substrates of CDs and DVDs has drastically increased. To decrease birefringence, molecular weights of PCs are made to decrease and mold temperatures to increase as much as possible. Accordingly, disks, especially DVDs of 0.6 mm thick, are apt to break frequently in the molding process, and this requires developing such PCs with a better balance of fluidity and impact resistance. Although PCs, in general, have excellent impact resistance, decreasing the molecular weight or lowering the destruction test temperature leads to producing brittle fractures in PCs, and their impact resistance falls abruptly. Thus, the situations conflict: when PCs with higher molecular weights are used to improve impact resistance, the fluidity decreases, and when the fluidity of PCs is increased by using alkyl phenols as end-capping agents, thermal resistance decreases. Thus, the development of new PCs with higher levels of fluidity, thermal resistance and impact resistance than the conventional PCs is desired.

This paper describes the preparation for trial PCs using various new end-capping agents and the successful synthesis of PCs that have a better balance of fluidity, thermal resistance and impact resistance than the conventional PCs end-capped with 4-*tert*-butylphenol.

2. Experimental

2.1. Materials

All the materials were commercially available and used without further purification. As end-capping agents, 4-*tert*-butylphenol (TBP), 4-*tert*-octylphenol (TOP), 4-α-cumylphenol (CP), 4-*tert*-amylphenol (TAP), 4-phenylphenol (PP), 4-cyclohexylphenol (CHP), 4-benzylphenol (BP),

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0032-3861/01/$ - see front matter
PII: S0032-3861(01)00345-7

4-phenoxyphenol (POP), 4-(benzyloxy)phenol (BOP), 4-*n*-butoxyphenol (NBP), 4-cyanophenol (CP), 4-acetylphenol (AP), 4-*n*-hexyloxyphenol (HOB), 4-(2-methoxyethyl)-phenol (MEP), 4-fluorophenol (FP), 1-naphthol (1-N), 2-naphthol (2-N), methyl 4-hydroxybenzoate (MHB) and methyl 4-hydroxyphenylacetate (MHPA) were used.

2.2. Preparation of the PC oligomer

Sodium dithionite (120 g, 0.69 mol) and BPA (60 kg, 263 mol) were dissolved in 5 wt% aqueous sodium hydroxide (400 l). This solution, dichloromethane and phosgene were introduced through an orifice plate at 25°C with a flow rate of 138, 69 l/h and 10.7 kg/h (108 mol/h), respectively, into a tubular reactor with an inner diameter of 10 mm and a length of 10 m. This procedure was continued for 3 h. Since phosgene is a toxic, irritating gas, it was dealt with only in an efficient fume hood. After allowing the reaction solution to stand for a certain time, the organic phase was separated to obtain a PC oligomer solution with an oligomer concentration of 311 g/l and a chloroformate (CF) group concentration of 0.72 mol/l.

2.3. Preparation of PCs capped with phenols

A solution of TBP (79.8 g, 0.531 mol) in dichloromethane (400 ml), aqueous 5.8 wt% sodium hydroxide (0.6 l) and triethylamine (3.76 g, 37.2 mmol) were added to the PC oligomer solution (9 l, CF: 6.48 mol). The solution was stirred at 300 rpm at room temperature for 1 h. Then, a solution of sodium dithionite (1.2 g, 6.9 mmol), BPA (611 g, 2.67 mol) and sodium hydroxide (3.57 g, 8.93 mmol) in water (5 l), and dichloromethane (10 l) were added and stirred at 500 rpm at 23°C for 2 h. Dichloromethane (5 l) and water (5 l) were added, and the solution was kept to stand for a certain time. The organic phase separated was washed successively with 0.01 M aqueous sodium hydroxide (5 l), 0.1 M aqueous hydrochloric acid (5 l), and water (5 l). Thereafter, the dichloromethane was evaporated off to obtain PC in a flake form.

The resulting PC was dried for 12 h at 120°C, and pelletized with tris(nonylphenyl) phosphite as an oxidation inhibitor (200 wtppm) by an extruder at 280°C. The pellets obtained were dried for 24 h at 120°C.

2.4. Molding

The resulting pellets were injection molded to produce test pieces using IS-100-EN manufactured by Toshiba Machine. The conditions were a cylinder temperature of 290°C, mold temperature of 80°C, injection pressure of 100 MPa, injection rate of 30 cm^3/s and dwelling time of 12 s. The test pieces were subject to measurement of the heat distortion temperature (HDT) and the Izod impact test after leaving for 48 h at 23°C.

Also, the obtained pellets were press-molded with mirror finished aluminum sheets at 290°C, and the resulting molding (1 mm thick) was subject to dynamic mechanical measurement after leaving for 48 h at 23°C.

2.5. Measurement

The average viscosity molecular weight (M_v) of the end-capped PC was obtained by measuring the viscosity of the polymer–dichloromethane solution with different concentrations at 20°C using an Ubbellohbe viscometer, then deriving the intrinsic viscosity [η] by extrapolation, and substituting it in the following equation [1]:

$$[\eta] = 1.23 \times 10^{-5} M_v^{0.83} \quad (1)$$

The molecular weight and the molecular weight distribution were determined by gel permeation chromatography (GPC, Waters 410) with polystyrene gel columns (Tosoh TSK-GEL GMH6) at 40°C using THF. The molecular weight calculation was from a standard procedure based on the universal calibration curves for PC.

The glass-transition temperature (T_g) was measured with a differential scanning calorimeter (Perkin–Elmer DSC 7). The polymer specimens (ca. 10 mg) were heated from 50 to 260°C at a scanning rate of 40°C/min under a nitrogen atmosphere.

The flow value, the HDT and the Izod impact value were measured as indices for fluidity, thermal resistance and impact resistance in conformity to JIS K 7210, JIS K 7191 and JIS K 7110, respectively. Regarding the Izod impact test, 10 specimens were tested and the values obtained are shown in Table 1 with the rate of ductile fracture.

The ^{13}C NMR spectrum was recorded with a JEOL EX-400 NMR spectrometer operating at 100 MHz. The polymer solution prepared had a concentration of 100 mg/ml in $CDCl_3$.

The dynamic mechanical spectra were measured in tension–tension mode using a viscoelastic spectrometer (Iwamoto Seisakusho VES-F(HF)-III). The conditions were 0.1% maximum strain with a slight protension, a frequency of 100 Hz and the temperature rise of 2°C/min. The specimens were cut into a rectangular shape approximately 40 mm long, 4 mm wide and 1 mm thick for testing.

3. Results and discussion

3.1. Preparation of the end-capped PC

The synthesis of PCs with various end-capping groups was carried out according to Scheme 1, where the degree of polymerization was kept constant by using the same molar quantity of phenols. The two-step method was used to prepare PCs. The first step was precondensation between phenols and part of the PC oligomers, which have the CF group at their ends. The second step was polycondensation between BPA and prepolymers. The characterization and properties of the end-capped PCs are summarized in Table 1. In the table, the PCs, except for those end-capped

Table 1
Characterization and properties of end-capped PCs

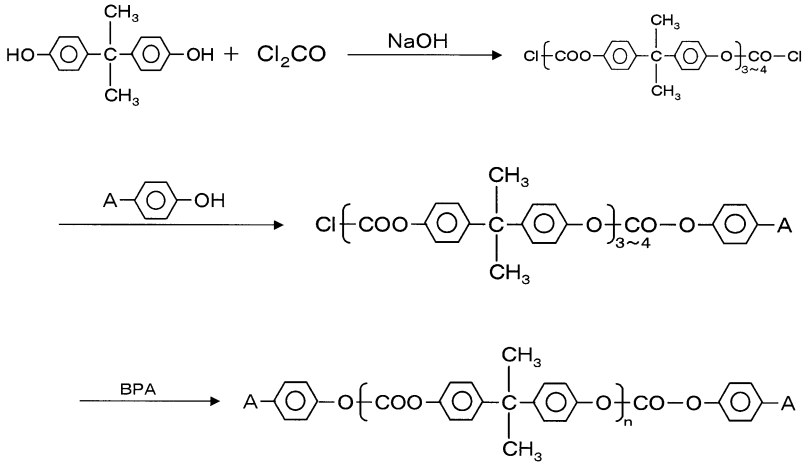
Run	End-capping agent	M_v	GPC[a]			T_g (°C)	Flow value[b] ($\times 10^{-2}$ ml/s)	HDT[c] (°C)	Izod impact value[d] (%)			
			M_n	M_w	M_w/M_n				23°C	0°C	−5°C	−10°C
1	TBP	19,100	11,200	23,500	2.10	150	10.6	132	100	80	30	10
2	TOP	19,700	12,300	25,500	2.07	149	9.3	131	100	100	100	80
3	CP	19,500	11,000	23,900	2.19	147	10.2	131	100	100	90	40
4	TAP	19,100	11,300	23,700	2.11	148	11.0	132	100	100	40	10
5	PP	19,200	10,800	23,500	2.17	148	10.3	131	100	90	40	10
6	CHP	19,000	10,900	23,500	2.15	149	10.6	132	100	80	40	10
7	BP	19,800	11,400	24,600	2.16	144	9.8	128	100	70	30	10
8	POP	19,400	11,200	24,300	2.16	145	10.4	129	100	80	30	10
9	BOP	19,100	10,900	23,600	2.17	147	11.8	127	100	50	20	0
10	NBP	19,000	10,800	23,300	2.15	144	12.8	129	100	60	10	0
11	CP	20,000	12,700	25,200	1.99	149	8.8	131	100	40	10	0
12	AP	21,100	12,100	26,100	2.16	147	7.6	130	80	80	0	0
13	HOP	18,900	11,200	23,400	2.09	142	13.3	126	100	100	30	10
14	MEP	19,300	11,600	24,200	2.08	141	13.1	126	100	80	30	10
15	FP	19,000	12,100	23,700	1.96	144	12.4	129	100	10	0	0
16	1-N	18,800	11,500	22,900	1.99	145	12.0	129	60	10	0	0
17	2-N	18,800	11,700	23,300	1.98	146	11.9	129	80	10	10	0
18	MHB	19,400	11,200	24,100	2.00	143	11.3	128	100	10	0	0
19	MHPA	31,100	19,800	41,400	2.09	151	1.2	132	100	90	80	–

[a] Calculated by using calibration curve for PC.
[b] Measured in conformity to JIS K 7210.
[c] Measured in conformity to JIS K 7191.
[d] Measured in conformity to JIS K 7110. Rate of ductile fracture.

with MHPA, have similar M_v and GPC data, and this indicates that the degree of polymerization is almost equal. It seems that MHPA is hydrolyzed to 4-hydroxyphenylacetic acid during the reaction, and the resulting carboxylic acid groups react with the CF group of the PC oligomers, giving PCs with higher degrees of polymerization. On the other hand, hydrolysis of aromatic esters seems to be more difficult when compared to that of aliphatic esters because of the conjugation of the ester bond with the aromatic ring. This implies that MHB acts as a useful end-capping agent of PCs.

3.2. Polymer characterization

The structures of the end-capped PCs were characterized by IR and ^{13}C NMR spectroscopes. The IR spectra of the PCs showed characteristic carbonate bonds at 1770 and 1230–1260 cm^{-1}. The ^{13}C NMR spectrum of the PC end-capped with TOP (TOP–PC) is shown in Fig. 1. The numbers in the figure correspond to the terminal carbons. The signals for the carbon nuclei of C11, C10, C9, C7, C8, C2, and C3 are observed at 31.4, 31.7, 32.2, 38.3, 56.9,



Scheme 1.

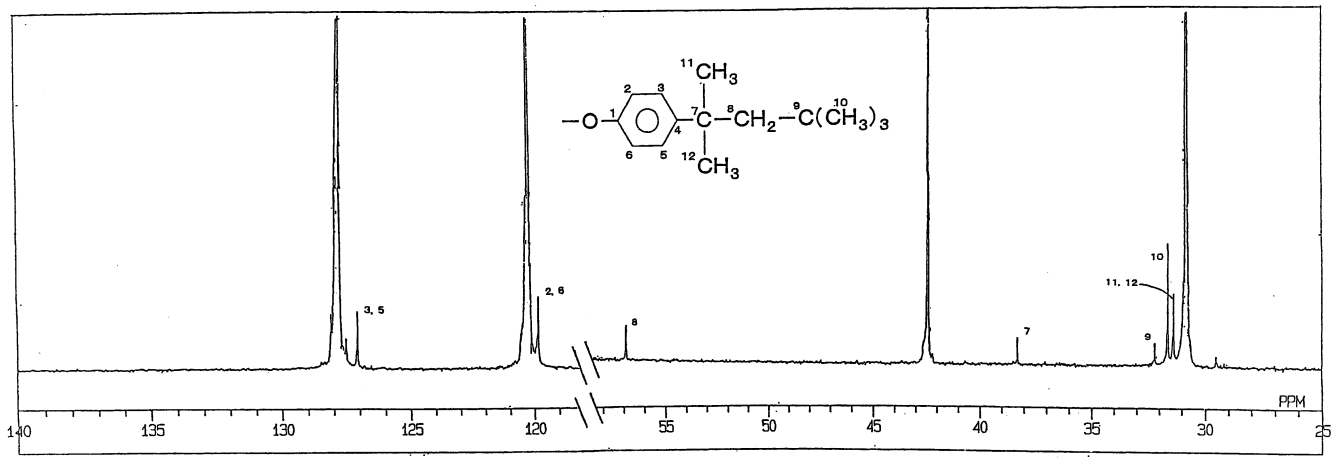
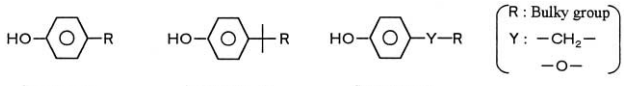


Fig. 1. ^{13}C NMR spectrum of TOP–PC.

119.8, and 127.1 ppm, respectively. These findings clearly indicate the formation of the end-capped PCs.

3.3. End-cap structure of the PC

The PCs end-capped with bulky groups are anticipated to have a higher impact resistance. This is considered as follows: the end-cap structure of such PCs, though occupying a large volume, is not so rigid and allows a relatively free molecular movement inside (free volume). As a result, shear deformation (ductile fracture) may happen more easily than crazing (brittle fracture) under stress, which would contribute to improving impact resistance. The properties of the PCs are summarized in Table 1 (Runs 1–9). Three types of end-cap structures are illustrated as follows. In Structure 2, the PC has an isopropyliden group between its aromatic ring and bulky alkyl group, and gives high impact resistance at low temperatures while maintaining thermal resistance. On the other hand, in Structure 1, which represents TAP–PC, PP–PC or CHP–PC, the bulky alkyl group is directly bonded to the aromatic ring. These PCs have properties similar to those of TBP–PC. In Structure 3, which represents BP–PC, POP–PC or BOP–PC, the bulky alkyl group and the aromatic ring are united with a flexible bond (–CH_2– or –O–). The PCs of Structure 3 do not show impact resistance as high as Structure 2, and they are somewhat inferior in thermal resistance to TBP–PC.



Structure 1 Structure 2 Structure 3

It is considered that the interaction between the end-cap groups of neighboring PC molecules would lead to higher impact resistance PCs since such an interaction works to make the molecular weight of the PCs apparently higher. In this study, in anticipation of improving the impact resistance of PCs through the interaction of the end groups, end-capping agents having polar groups or aromatic rings with a large number of π electrons 10 were selected. However, as shown in Table 1 (Runs 10–18), the PCs end-capped with polar groups are inferior in impact resistance. This may be explained by the decrease in the free volume of the end structure of the polymer chain, which is caused by the interaction among the end groups. Accordingly, crazing occurs more easily than shear deformation at low temperatures.

To evaluate the molecular mobility of the PCs, dynamic mechanical spectra were measured. E'' (loss modulus) of the end-capped PCs (Runs 1–3, 16) are shown in Fig. 2. The peak area is known to be proportional to the molecular mobility [9,10]. Compared to TBP–PC, the molecular mobility of TOP–PC and CP–PC was large and that of 1-N–PC was small. Based on these results, it is presumed that the improvement in impact resistance of TOP–PC and CP–PC is attributable to the energy dissipation.

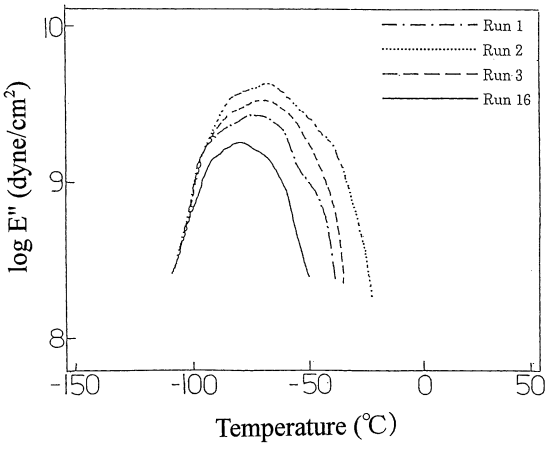


Fig. 2. Dynamic mechanical spectra E'' of end-capped PCs.

Table 2
Properties of end-capped PCs

Run	End-capping agent	M_v	Flow value ($\times 10^{-2}$ ml/s)	Izod impact value (%)			
				23°C	0°C	− 5°C	− 10°C
20	TBP	18,900	13.0	100	70	30	0
21	TOP	18,500	12.2	100	100	60	50
22	CP	19,100	11.5	100	100	80	40
23	TBP	19,900	9.1	100	90	30	10
24	TOP	20,500	8.2	100	100	100	90
25	CP	20,400	8.6	100	100	90	70

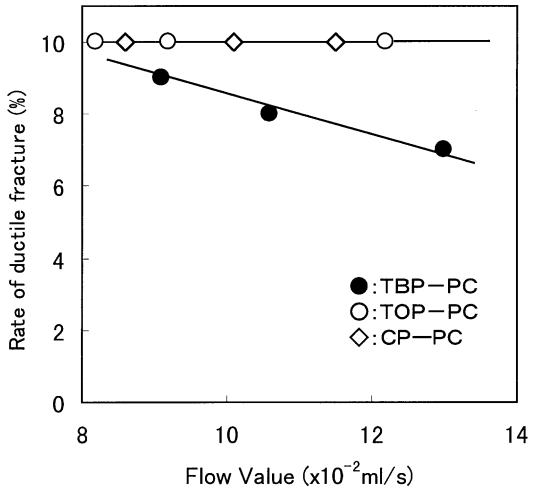


Fig. 3. Relationship of flow value and rate of ductile fracture.

3.4. Relationship between fluidity and impact resistance

Using the PC end-capped with TBP, TOP–PC and CP–PC, the relationship between fluidity and impact resistance was investigated. PCs having different molecular weights were prepared by changing the molar quantity of end-capping phenols. The results are summarized in Table 2. Fig. 3 shows the relationship between the flow values and the rate of ductile fracture from the Izod impact test at 0°C. When the M_v of TBP–PC was decreased, the flow value increased while the rate of ductile fracture decreased. On the contrary, in the case of TOP–PC and CP–PC, the flow value increased with the decrease in M_v while the rate of ductile fracture was maintained. Thus, it can be said that the PCs end-capped with TOP or CP are superior, in balance of fluidity, thermal resistance and impact resistance, to commercially available PCs end-capped with TBP.

References

[1] Schnell H. Chemistry and physics of polycarbonate. New York: Interscience, 1964.
[2] Freitag D, Fengler G, Morbitzer L. Angew Chem Int Ed Engl 1991;30:1598–610.
[3] Lu B, Chung TC. Macromolecules 1999;32:2525–33.
[4] Hillmyer MA, Schmidt SC, Marohn SL. Polym Prepr 1999;40:441.
[5] Yoshida E, Nakamura M. Polym J 1998;30:915–20.
[6] Ranucci E, Ferruti P. Macromolecules 1991;24:3747–52.
[7] Marousek V, Svoboda P, Kralicek J. Angew Makromol Chem 1990;178:85–93.
[8] Makimura Y, Yoshida E, Kitao T. Polym J 1997;29:128–33.
[9] Read BE. Proc Fifth Int Congr Rheol 1970;4:71.
[10] Nakayama K, Furumiya A, Okamoto T, Yagi K, Kaito A, Choe CR, Wu L, Zhang G, Xiu L, Liu D, Masuda T, Nakajima A. Pure Appl Chem 1991;63:1793–804.