NOTES

Synthesis and Characterization of Some Polyestercarbonates

Sung Sig MIN, Sang-Soo LEE,* Jong-Chan LEE, and Jae Young JHO[†]

Hyperstructured Organic Materials Research Center and School of Chemical Engineering, Seoul National University, Seoul 151–744, Korea
*Polymer Hybrids Research Center, Korea Institute of Science and Technology, Seoul 136–791, Korea

Our effort to prepare polyestercarbonates (PEC) was motivated by the need for model polymers for studying the effect of the chain topography on the properties of these polymers. PEC is a generic name representing various copolymers containing carbonate and ester units, that is, copolymers of bisphenol A polycarbonate (PC) and polyarylate (PAr).[1–3] PECs have been developed in efforts to overcome limitations of PC, which are low heat resistance and sharp ductile-brittle transition by the test conditions.[1, 2] It was reported that some PECs were better than PC in these aspects.[3]

Since we thought that the difference in the shape of chain between PC and PEC could be a factor that caused the difference in property, we tried to prepare PECs with the shapes of chain that are straighter and more kinked than that of PC. We report the synthesis of PECs containing only terephthalate units (TPEC) and only phthalate units (PPEC), respectively, the general structure of which are given in Scheme 1. Although there have been reports on TPEC,[3–6] report on the preparation of PPEC has been rare, especially for that with high molecular weight.

It was desired that, in the model polymers, the contents of carbonate and terephthalate or phthalate units be readily and systematically varied, while the distribution of the counits be kept random. Although it has been deemed that solution polycondensation is advantageous in controlling the structure of the condensation copolymers,[7, 8] we opted for interfacial procedure to prepare PECs with high molecular weight. The synthetic procedure, sequence structure, and characteristics of the polymers are reported.

EXPERIMENTAL

Materials

All the reagents were purchased from either Aldrich or JT Baker and used without further purification, unless otherwise mentioned. Phthaloyl dichloride was distilled at a reduced N_2 pressure before use. Terephthalaoyl dichloride was purified by the Soxhlet extraction with dry *n*-hexane followed by the removal of *n*-hexane at a reduced pressure. Methylene chloride (MC) was dried over 4 Å molecular sieve. Triethylamine (TEA) was refluxed with ninhydrin for 24 h, vacuum distilled, and dried over 4 Å molecular sieve. Phosgene

TPEC

PPEC
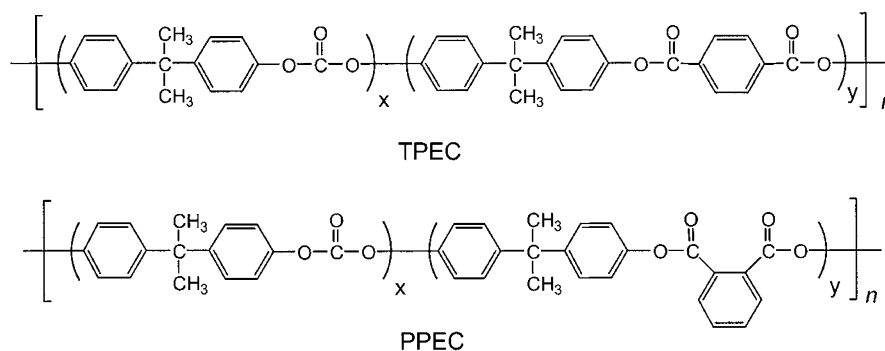
Scheme 1.

[†]To whom all correspondences should be addressed (E-mail: jyjho@snu.ac.kr).

Table I. Recipes for the synthesis of PC and PECs

Polymer	BPA	4-*tert*-Butyl phenol	Phosgene	(Tere)phthaloyl dichloride
	mol	mmol	mol	mol
PC	0.1000	0.5	0.1100	–
TPEC9	0.1000	0.5	0.0988	0.0112
TPEC6	0.1000	0.4	0.0948	0.0157
TPEC3	0.1000	0.3	0.0809	0.0296
TPEC1	0.1000	0.1	0.0505	0.0575
PPEC9	0.1000	0.4	0.0983	0.0116
PPEC6	0.1000	0.4	0.0948	0.0166
PPEC3	0.1000	0.3	0.0809	0.0291
PPEC1	0.1000	0.1	0.0505	0.0591
PPEC0	0.1000	0.0_5	–	0.1200

gas was purchased from Matheson and condensed in MC at dry ice/acetone temperature before use.

Synthesis

The synthetic procedure for PPEC1, a PEC with equimolar quantities of carbonate and phthalate units, was as follows. Bisphenol A (BPA, 22.8 g, 0.100 mol), sodium hydroxide (8.8 g, 0.220 mol), and 4-*tert*-butylphenol (15.0 mg, 0.1 mmol) dissolved in 150 mL of distilled water were mixed with 0.1 g of TEA (1.0 mmol) and 70 mL of MC. With vigorous stirring, the solution of phosgene (5.0 g, 50.5 mmol) and phthaloyl dichloride (12.0 g, 59.1 mmol) in 80 mL of MC was added for 1 h (*ca.* 1.5 mL min^{-1}) at room temperature. The reaction was stirred for an additional 4 h, during which period pH was kept between 11 and 13 by intermittently adding aqueous NaOH solution. The organic phase was separated, washed with 0.01 N aqueous HCl, washed with distilled water several times, and poured into methanol. The white precipitate was purified by several dissolution/precipitation. The other polymers were prepared by the same procedure according to the recipe given in Table I. During the preparation of PPEC3 and PPEC9, samplings at 5 min and at 1 h were conducted. The samples were obtained by washing and evaporating the solvent.

Characterization

^{1}H NMR spectra were obtained at room temperature using a Bruker AMX-500 spectrometer. Deuterated MC or deuterated chloroform/acetone (3/1 v/v) was used as the solvent. The molecular weights were measured by GPC (Waters 515) at 30°C using chloroform as the solvent/eluent. The results were calibrated with polystyrene standards. The glass transition temperatures were determined by DSC (TA 2920) at a heating rate of 20°C min^{-1} after annealing for 5 min at 250°C.

The specimens (30 × 8 × 2 mm^3) for density mea-surement were compression-molded at T_g + 70°C and slowly cooled to room temperature. The specimens were weighed in air (w_a) and in distilled water (w_w) using a Mettler density determination kit at 25.0 ± 0.1°C. Density (ρ) was calculated by the equation, $\rho = w_a \times \rho_0/(w_a - w_w)$, in which ρ_0 was the density of distilled water.

The wide-angle X-Ray diffractions (WAXD) were carried out with a MacScience M18XHF-SRA diffractometer in reflection geometry. Cu-$K\alpha$ radiation ($\lambda = 0.154$ nm) at 50 kV and 100 mA was used, and the measurements were made in the 2θ range between 5° and 35° at a scanning rate of 5° min^{-1} at room temperature.

RESULTS AND DISCUSSION

Structure of PEC

There are several methods for preparing condensation polymers and copolymers; solution, interfacial, and melt polymerization.[7, 8] Although solution or melt polycondensation method has advantages in controlling the chain structure and composition, rigorous stoichiometric control is required to obtain high molecular weight polymers. We found through the experimental efforts that this is the case for the solution copolycondensation of PPEC, resulting in the molecular weight far below 10000. We decided to employ interfacial method instead, since high molecular weight was readily achievable by virtue of the naturally balanced stoichiometry at the interface.

Although there have been studies on the interfacial copolymerization of PEC,[3–6] none of them paid attention to the structure of the resulting copolymer, especially for the sequence distribution of counits. In the present study, it was the prime concern to obtain the copolymer with known composition and random distribution of counits, and due attention were paid to structure characterization of the copolymers.

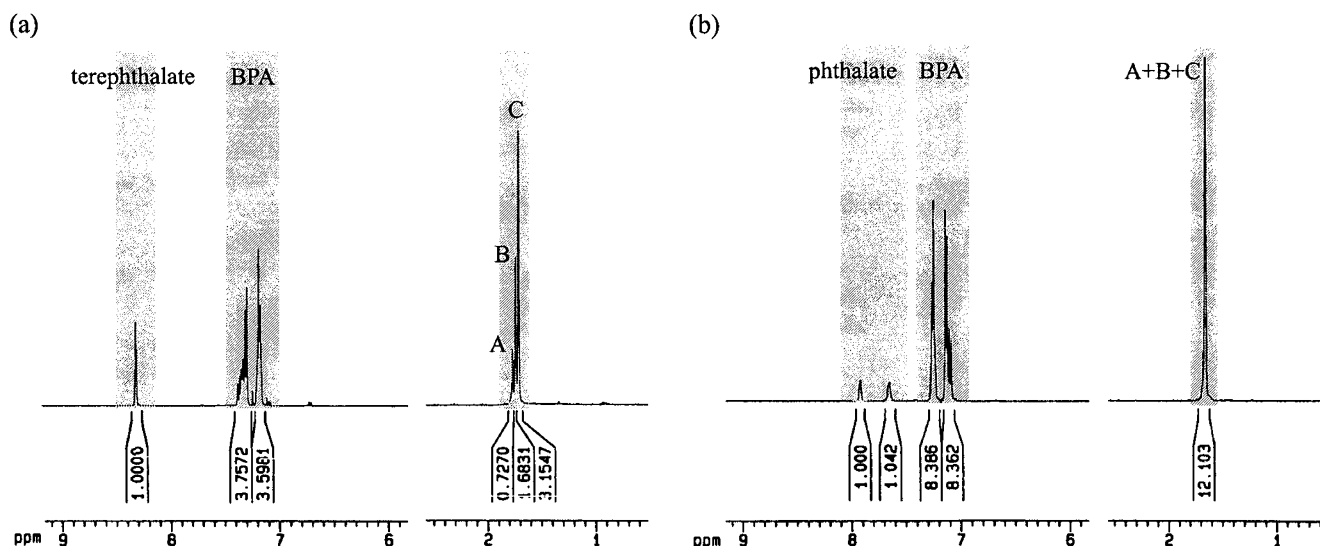It has been deemed, in interfacial copolymerization,

(a)

(b)

Figure 1. ^{1}H NMR spectra of (a) TPEC3 and (b) PPEC3.

Table II. Characteristics of PC and PECs

Code	C/P[a] in feed	C/P[a] in polymer	Yield %	M_w g mol^{-1}	M_w/M_n	T_g °C	ρ g cm^{-3}	$2\theta_{max}$ °
PC	–	–	86	54700	1.96	152	1.193	17.0
TPEC9	8.82	8.4	79	114300	1.61	157	1.195	17.1
TPEC6	6.01	6.0	77	128800	1.61	164	1.197	17.2
TPEC3	2.72	2.7	90	124800	1.70	173	1.198	17.2
TPEC1	0.91	0.9	84	163000	1.70	200	1.199	17.2
PPEC9	8.47	10.7	82	60600	2.19	153	1.197	17.1
PPEC6	5.71	5.8	87	60000	2.40	155	1.198	17.2
PPEC3	2.78	3.1	78	49400	2.09	155	1.201	17.3
PPEC1	0.85	1.0	81	161800	1.78	161	1.209	17.5
PPEC0	–	–	71	72900	1.85	159	1.219	18.6

[a] Mole ratio of carbonate units to (tere)phthalate units.
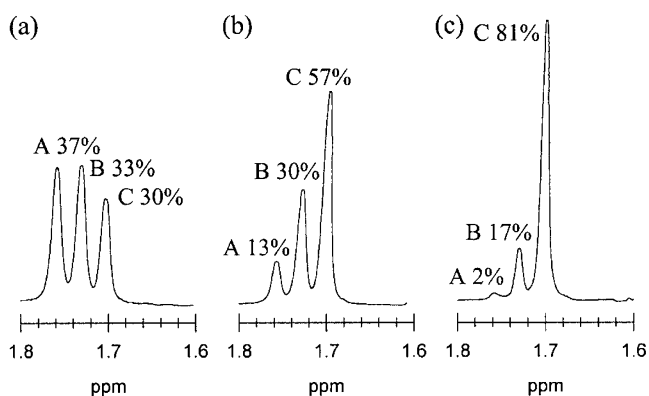
(a) (b) (c)

Figure 2. ^{1}H NMR spectra showing the isopropylidene proton peaks in (a) TPEC1, (b) TPEC3, and (c) TPEC9.

that composition and/or distribution of counits are hard to control mainly due to the difference in reactivity between the comonomers. In the present copolymerization, the reactivities in the question are those of phosgene and (tere)phthaloyl dichloride to BPA. Since the reactivity of phosgene is much higher than that of (tere)phthaloyl dichloride,[9] one would suppose that the composition of the copolymer prepared in the early stage of the reaction be different from that in the later stage, which should be much more (tere)phthalate-rich. Accordingly, the distribution of counits is supposed to be blocky rather than random or statistical.

Typical proton NMR spectra of TPEC and PPEC were shown in Figure 1. The composition of carbonate and (tere)phthalate units in the copolymers was determined by counting aromatic protons in BPA moiety and in (tere)phthalate moiety. The results in terms of carbonate/(tere)phthalate ratio (C/P) were listed in Table II. It appeared that C/P ratios in the copolymers were not much different from those in feed. It was evident that the comonomers had been reacted with BPA quantitatively and the overall or average composition of the copolymer could be controlled by feed ratio.

The sequence distribution of counits in TPEC was determined by examining the isopropylidene proton peaks of the NMR spectra. As shown in Figure 2, the isopropylidene proton peaks of BPA split in three depending on the neighboring groups; terephthalate-BPA-terephthalate (TT, peak A), carbonate-BPA- terephthalate (CT, peak B), and carbonate-BPA-carbonate (CC,

peak C). The presence of peak B with a significant intensity indicates that the copolymers not like diblock copolymers or multi block copolymers with large block lengths. If the sequence were rather blocky, the intensity of peak B would be negligible regardless of the composition.

The average sequence or block length could be calculated from the relative intensity (I_A, I_B, and I_C) of the peaks A, B, and C. The average block lengths, x in $-(CC)_x-$ and y in $-(TT)_y-$, can be written as

$$x = \frac{[TT]}{[CT]/2} = \frac{I_C}{I_B/2} \quad \text{and} \quad y = \frac{[CC]}{[CT]/2} = \frac{I_A}{I_B/2}$$

where [TT], [CT], and [CC] are the concentrations of the respective triads. The x/y determined for TPEC9 and TPEC3 were 3.80/0.87 and 9.53/0.24, respectively. The result suggests that the comonomer distribution in these copolymers is random with no long sizeable terephthalate blocks. The x/y for TPEC1 was 1.82/2.24, which means that the distribution is a little blockier than the other TPECs, having the average block length close to two.

As a parameter indicating the sequence structure of a polymer chain, degree of randomness, R, was proposed by Devaux et al.,[10] and has been used widely. The parameter is defined, based on binomial distribution, as

$$R = \frac{[CT]}{2}\left(\frac{1}{f_{\text{phosgene}}} + \frac{1}{f_{\text{terephthalate}}}\right)$$

where f is the moles of phosgene or terephthaloyl dichloride divided by the total moles of phosgene and terephthaloyl dichloride in feed. R is zero for a copolymer with long homogeneous sequence, and is unity for a statistically random copolymer. The parameters determined from NMR spectra for TPEC9, TPEC3, and TPEC1 were 0.94, 0.94, and 0.66. It clearly shows that TPEC1 is blockier than the other copolymers, which are close to a 'random' copolymer.

Although the results of average block length and degree of randomness imply that the structure of TPECs is rather random than blocky, the chance for the copolymers to have longer blocks could not be denied completely, since the values are only the averages. The average block length of, say, 3 can be obtained for the copolymer chain with the equal amount of the blocks of 5 units and that of 1 as well as for the chain with the blocks of 3 units. In other words, the presence of the same number of much longer and shorter blocks than the average can give the same average. In the present system, it is actually possible to produce tapered block structure, in which comonomers are incorporated in the chain with progressively varying block lengths due to the difference in reactivity. To clear the possibility of
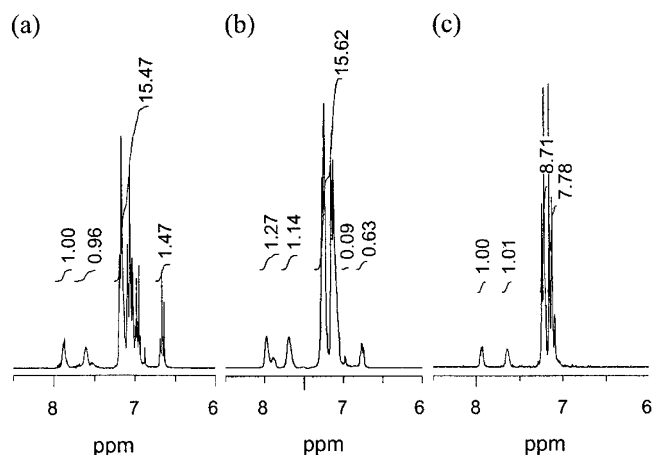
Figure 3. NMR spectra showing phenylene proton region (a) oligomer 1, (b) oligomer 2, and (c) polymer of PPEC3.

Table III. Molecular weight and ratio of carbonate to phthalate (C/P) of the samples

Sample	PPEC9		PPEC3	
	M_n	C/P	M_n	C/P
Oligomer 1	2300	8.5	2500	3.6
Oligomer 2	12800	8.8	8300	3.1
Polymer	27700	10.7	23600	3.1

C/P ratio in feed (phosgene to phthaloyl dichloride ratio) was 8.5 for PPEC9 and 2.8 for PPEC3. M_n of the polymers were determined by GPC, and M_n of the oligomers and C/P ratios were determined by ^{1}H NMR.

longer blocks in the copolymers, the structure of PPEC was examined in a different method.

Actually, the average block length or the degree of randomness of PPECs could not be determined in the same way as for TPECs, since the isopropylidene peaks did not split as shown in Figure 1b. Instead, the course of the polymerization was tracked down by comparing the molecular weight and composition of the oligomer samples taken during the reaction and those of the final copolymers. The C/P ratio of the oligomers was determined from the NMR spectra, examples of which are shown in Figure 3, in the same way as for the copolymers. The molecular weight of the oligomers was also obtained by NMR. An isopropylidene proton peak of the oligomeric PPECs appears to be composed of three peaks as shown in Figure 4. The peaks are assigned to the protons in the inside BPA units (peak A+B+C), the terminal BPA units (D), and the unreacted BPA (E), by comparing with the spectra of BPA.[11] Mathematical deconvolution of the peaks to fit Lorenzian functions were carried out,[12] and the number average degree of polymerization was calculate as 2(1 + (A+B+C)/D). The results of C/P ratio and molecular weight of the oligomers of PPEC3 and PPEC9 are summarized in Table III, in comparison with those of the polymers.

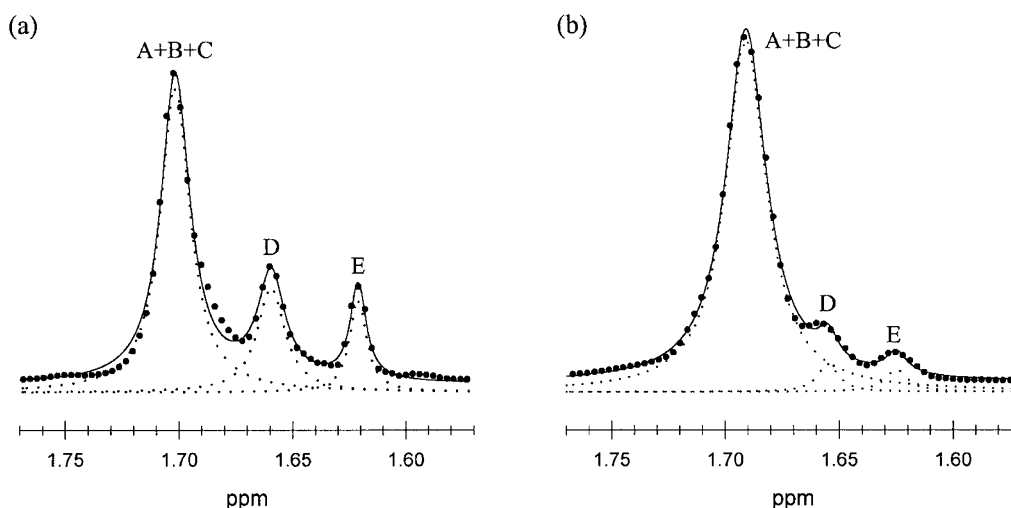The C/P ratio in the oligomer 1, sampled at 5 min

Figure 4. NMR spectra showing the isopropylidene protons peaks in (a) oligomer 1 and (b) oligomer 2 of PPEC3. The dots are taken at the actual spectra. The dashed curves represent deconvoluted Lorenzian functions. The solid curves represent the overall fit.

after the start of the polymerization, of PPEC9 is 8.5. Since the number average degree of polymerizatio n of oligomer 1 is about 10, every oligomer chain of PPEC9 is analyzed to possess one phthalate unit on the average. The ratio in the oligomer 2, taken at 1 h, is 8.8, which is similar to that of the oligomer 1. Since the oligomer 2, composed of about 50 monomer units, is supposed to contain the chains of the oligomer 1, it is thought that phthalate units were incorporated randomly along the chain. Basically, C/P ratio does not change much throughout the reaction from monomer to polymer, which indicates the constancy of the composition throughout the reaction and thus the random distribution of phthalate units in the copolymer. As the constancy of C/P ratio is observed in PPEC3 also, we deduce the random distribution of counits in this copolymer and the other PPECs.

Through the determinations of the randomness for TPEC and the analysis of the oligomers for PPEC, it is concluded that the sequence structure of these copolymers are random with sizeable long blocks. There are two points of issue to argue; one is that the random structure is suggested indirectly by analyzing oligomers, and the other is that there was no cross-examination between TPEC and PPEC. To investigate the randomness or structure of copolycondensates,[13−16] selective degradation of the polymers followed by mass spectroscopy or NMR analysis of degraded oligomers have been carried out. It is thought that this process corresponds to oligomer sampling followed by NMR analysis in the present study. Cross-examination was not thought to be necessary, since the difference in reactivity in the question that might result in blockiness is not between those of terephthaloyl and phthaloyl dichloride but is between those of phosgene and (tere)phthaloyl dichloride. The difference in reactivity

between terephthaloyl and phthaloyl dichloride is actually much smaller compared to that between phosgene and (tere)phthaloyl dichloride.[17]

The results that the copolymers are random imply that the difference in reactivity between phosgene and (tere)phthaloyl dichloride to BPA is not reflected in the sequence structure. The reason for this cannot be given at this point, a possible explanation is offered. It has been known that the reactivity in terms of rate constant of phosgene in hydrolysis or acylation is higher than aromatic acid chloride by 10 to 10^6 times.[9] In the presence of effective acid acceptor like a tertiary amine, however, the rate constant of acid chloride is enhanced greatly, as great as by 10^5 times.[9] It is thought, as a result, that the reactivity of (tere)phthaloyl dichloride, in the presence of triethylamine, was high enough to be capable to react with BPA. Although there has been no published data, it is supposed that the reactivity of phosgene should also be enhanced by triethylamine, and is higher than that of (tere)phthaloyl dichloride. However, it is thought to be possible that the reactivity of (tere)phthaloyl dichloride increased enough just to prevent the phosgene to preferentially with BPA. Although there is no experimental support to this explanation, since we did not perform the comparison of the reactivities separately, it is well known in chain copolymerization that random distribution is favored when the reactivities of two comonomers are comparable.[18]

Characteristics of PEC

The results of characterization of the copolymers are summarized in Table II. The high molecular weights of TPEC1 and PPEC1 were considered to be due to the small amount of 4-*tert*-butylphenol used, which was an end-capping agent. The reason why the molecular weight of PPEC0 was not as high as PPEC1 seemed
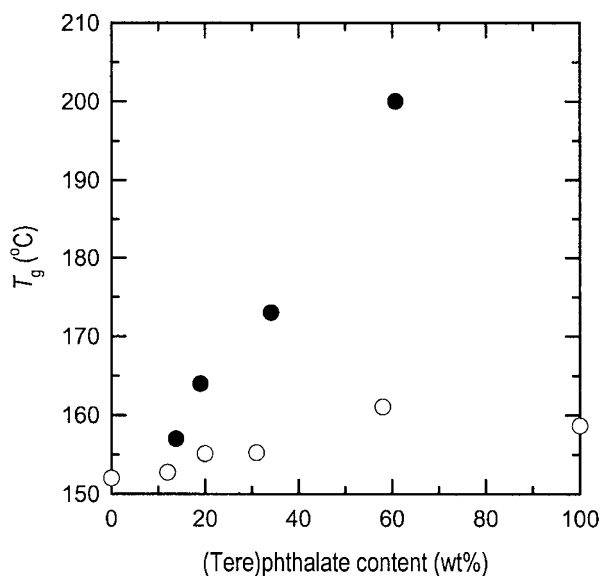
Figure 5. Glass transition temperature as a function of the terephthalate content in TPEC (filled circle) or the phthalate content in PPEC (open circle).

to be the intervention of cyclic oligomers, as has been reported previously.[19] TPEC0 could not be synthesized since it was precipitated by crystallization.[6, 7]

Glass transition temperatures (T_g) increased with increasing (tere)phthalate content as shown in Figure 5. The increase in T_g and the higher degree of increase in TPECs could be explained considering the two factors determining T_g of polymers; chain flexibility and intermolecular interaction. Incorporation of terephthalate units stiffened the TPEC chain by the conjugation over ester and phenylene groups.[20] Such a conjugation stiffening was not expected in PPEC, since the ester groups in PPEC were not in-plane with the phenylene rings. Still, however, the stiffening by the incorporation of additional aromatic moiety should be effective. Intermolecular interactions also favored the increase in T_g. Density and Bragg angle at the maximum of WAXD pattern increased with increasing (tere)phthalate content, indicating that the chains were better packed, and that inter-chain distance become shorter, respectively.[21] While the increase in T_g of PPEC might be explained by major contribution of intermolecular effect, the larger degree of increase for TPEC might be explained by the larger contribution of intramolecular chain flexibility.

There are some peculiarities in T_g of PPECs. The ascent of T_g as a function of phthalate content positively deviated from Fox equation. Moreover, T_g of PPEC1 was higher than PPEC0. This type of behavior has been reported also in a study on other polyestercarbonates,[22] while little explanation was available. Positive deviation has been observed in copolymers and blends with specific interactions such as hydrogen bonding,[23, 24]

which was not expected in the present study. We supposed that the sequence distribution might be responsible for the behavior, since it has been observed that, in the copolymers of PC, T_g was higher in the block copolymers than in the alternating copolymer.[25] Further discussion, however, seemed to be out of the scope of this study, and would be dealt elsewhere.

CONCLUSIONS

Polyestercarbonates with systematically varying content of terephthalate or phthalate units were prepared by interfacial polycondensation. Random distribution of (tere)phthalate counits was thought to be achieved, which was suggested through determining the degree of randomness and analyzing the oligomers. Glass transition temperature increased with (tere)phthalate content owing to the intramolecular stiffening effect of (tere)phthalate units and the shortened intermolecular distance.

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