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Thermally induced redistribution and degradation of bisphenol-A polycarbonate fractions in open and closed systems

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Abstract

Thermally induced chain-scission and redistribution reactions in as-polymerized and fractionated bisphenol-A polycarbonate (PC) materials made by melt-transesterification and interfacial polymerization were studied at temperatures between 200 and 300 °C in open systems, where volatile reaction products are continuously removed, and in closed systems, where these products are retained. Under the applied conditions, PC made via interfacial polymerization shows no measurable susceptibility towards redistribution. This is the result of an extremely low concentration of hydroxyl end-groups. Upon similar thermal treatment, PC made by melt-transesterification undergoes fast redistribution which leads to post-condensation in open systems and strong changes of molecular weight distributions (MWDs) for fractions in all cases. Redistribution effects were visualized through changes in the MWD of mixed fractions. The initial stages of redistribution were simulated using a Monte Carlo method based on a random sampling technique. From comparison between experimental and simulation results, it can be concluded that approximately half a percent of all carbonate linkages is involved in a redistribution reaction per minute at 250 °C for the studied samples. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Bisphenol-A; Melt-polymerization

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1. Introduction

Bisphenol-A based polycarbonate (BPA-PC) is a widely used thermoplastic engineering resin possessing unique properties such as high transparency, high impact strength, broad temperature resistance and an excellent dimensional stability [1]. Currently, BPA-PC is produced on an industrial scale either by interfacial phosgenation or melt-transesterification processes [2]. In the interfacial process, an aqueous solution containing BPA and an organic solvent containing phosgene are mixed whereupon polycarbonate is formed at the interface of the two immiscible phases. In the melt-transesterification process, BPA and diphenyl carbonate (DPC) are reacted as pure components under reduced pressure and at high temperatures. Very small amounts of basic catalysts are always added to accelerate the reaction and the proper choice of catalyst is essential for polymer quality. Advantages of the melt-transesterification technology over the interfacial process are the absence of large volumes of organic solvents and highly toxic phosgene. Moreover, the final resin contains a much lower level of residual contaminants. In contrast, the elevated temperatures used during the melt-polymerization process may lead to side reactions resulting in the formation of branching products [3]. In addition, interfacially and melt-polymerized PC show two significant structural differences:

(i) Interfacial PC is normally fully end-capped (usually with phenyl or 4-alkyl phenyl carbonate end-groups). By contrast, melt-polymerized PC contains a significant residual concentration of uncapped end-groups (bisphenol monocarbonate) [3].
(ii) Due to fast redistribution reactions occurring during polymerization (see below), melt-polymerized PC is characterized by a 'thermodynamic' most probable Flory molecular weight distribution (MWD) whereas interfacial polymerization is kinetically controlled, leading to a different (although similar) distribution [2].

1.1. Thermal behaviour of BPA-PC

The thermal behaviour of polycarbonate materials has

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been the subject of several studies [4–20], most of these covering aspects of degradation at very high temperatures. Degradation pathways of PC made by interfacial phosgenation and melt-transesterification processes are different due to microstructural dissimilarities (i.e. concentration of hydroxyl end-groups and potentially branching structures) as well as traces of residual inorganic contaminants. These differences are especially distinct at moderate temperatures up to approximately 350 °C. At higher temperatures, degradation takes place via either radical [15,16] or intramolecular ester-exchange [17–19] pathways which are essentially process-independent.

The thermal degradation of melt-polymerized PC is a finely balanced competition between scission and crosslinking processes. The dominating mode of degradation depends mainly on whether or not certain volatile products, mainly water and phenols, are removed from the degrading polymer. It was reported by various authors [5–14] that the continuous removal of volatile products from melt-polymerized PC leads to chain extension as a result of condensation reactions. Upon prolonged thermal treatment also branching and crosslinking occur. On the other hand, when PC is heated in a sealed system, volatile products are retained and scission reactions predominate resulting in viscosity reduction [5–12,14].

Except for susceptibility to hydrolysis, PC made by interfacial phosgenation is thermally stable up to approximately 300 °C [1]. Below this temperature, crosslinking and scission reactions occur to a very limited extent only due to the low concentration of hydroxyl end-groups [2].

1.2. Redistribution in condensation polymers

Redistribution processes were first described by Flory for polyester materials [21]. They lead to a state of equilibrium in which the concentration of reactive species remains constant, i.e. there is no net change in the number of chemical linkages and the number average molecular weight (M_n) is unaffected. Redistribution reactions, however, can affect the MWD. Two molecules with equal chain length can react and form one long and one short chain while a long and a short chain can form two molecules of intermediate size.

Redistribution in condensation polymers can take place in two ways: (i) between an end-group and an in-chain ester moiety and (ii) by ester interchange (carbonate interchange in case of PC). Uncatalysed ester interchange reactions in general proceed at an extremely slow rate [21]. Both redistribution mechanisms are schematically shown for BPA-PC in Fig. 1.

As stated before, polycarbonate made via the melt transesterification process has a most probable thermodynamic MWD. This means that under normal melt processing conditions, redistribution takes place but does not lead to a significant change in MWD.

For interfacially polymerized PC, full chain-end capping usually prevents redistribution via hydroxyl end-groups and only the (very slow) carbonate interchange can take place.

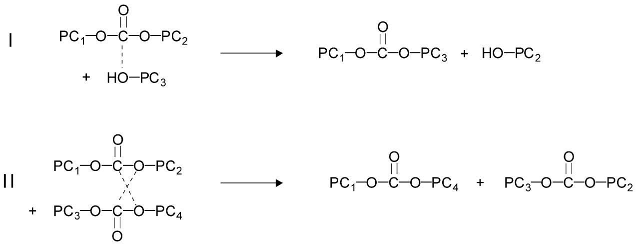

Fig. 1. Redistribution reactions for BPA-PC, (I) involving an end-group and (II) carbonate interchange.

The objective of this paper is to understand and compare thermally induced MWD changes for PC materials made via melt-transesterification and interfacial phosgenation processes. The applied experimental methods are based on the use of narrowly dispersed fractions and of a Monte Carlo simulation model to describe the initial stages of redistribution. In a systematic study, the influence of open and closed systems on the thermal processes has been assessed. Redistribution effects in the investigated PCs are visualized by monitoring changes in the MWD upon thermal treatment of mixed fractions. Experiments are carried out at moderate temperatures in the range between 200 and 300 °C thus minimizing the effects of competing thermal reactions.

2. Experimental

2.1. Samples

PC1 and PC2 are lab-synthesized polycarbonate samples made by a melt-transesterification process from BPA and diphenyl carbonate using literature-described procedures [22,23]. PC3 is a commercial sample obtained by interfacial phosgenation. The polymer which is fully end-capped by phenyl carbonate end-groups has been kindly supplied by General Electric.

2.2. Fractionation

Polycarbonate samples are preparatively fractionated using the continuous polymer fractionation (CPF) method. Fractions are obtained from methylene chloride–diethylene glycol solvent/anti-solvent mixtures. In CPF, an extracting agent extracts low molecular weight material from a concentrated polymer solution. The extracted low MW material forms the sol fraction while the remaining higher MW material forms the gel fraction. As CPF is a continuous process, fractions of preparative size are obtained in a relatively fast and convenient way. The fractionation procedure is described in detail in a previous paper [24].

2.3. Thermal experiments

Thermal tests are carried out in a Perkin Elmer Pyris 1 DSC apparatus using aluminium sample cups containing holes and completely sealed cups. Fraction mixtures are prepared by dissolving the combined fractions in methylene chloride at a concentration of 5 w/v% followed by evaporation of the solvent. A uniform polymer film is obtained which is cut to a suitable size for DSC experiments. Prior to DSC measurements, PC samples are dried overnight at 120 °C under vacuum. After DSC treatment, the samples are collected and prepared for size exclusion chromatography (SEC) and NMR analysis.

2.4. Monte Carlo simulation

A program based on Monte Carlo sampling principles has been written in Visual Basic to simulate redistribution processes occurring in PC materials. In a number of cycles, chains, which are randomly collected from the MWD, are successively split and re-combined. Each simulation experiment is carried out with a total of 10 million monomers. The simulation procedure is described in more detail in Section 3.

2.5. Analytical

2.5.1. Size exclusion chromatography

Polycarbonate samples in methylene chloride (0.1 w/v%) are injected into a Waters SEC system coupled to a UV absorbance detector. Two PL-gel 5μ 300 × 7.5 mm columns with pores sizes of 10^3 and 10^5 Å are used in series with methylene chloride as mobile phase. The eluted polymer is detected at 254 nm. Calibration is performed against a series of polycarbonate standards with known absolute molecular weights.

2.5.2. NMR

Proton-NMR measurements are run on a Bruker Avance 400 spectrometer. A pulse width of 90° (10 μs), relaxation time of 4 s and acquisition time of 2.6 s are used. Samples are dissolved in D-chloroform at a concentration of 5–10 w/v%. 1024 free induction decays (FIDs) are collected for analysis of the fractions. Modified units are quantified by integrating the absorbances at 8.01 ppm (phenyl salicylate structure, PhSAL) and 8.14 ppm (phenyl salicylate phenyl carbonate structure, PhSALPhC) against the total absorbance of aromatic protons in the region between 6.5 and 7.6 ppm. The hydroxyl end-group concentration of the samples is similarly determined by integrating the absorbance at 6.62 ppm against the total absorbance of aromatic protons.

2.5.3. Determination of water content

The concentration of residual water in the PC samples is determined using a Brabender Aquatrac apparatus. PC samples and calcium hydride are added to a sealed vessel which is evacuated and then heated to 140 °C for several hours. Under these conditions, water is released from the polymer and specifically reacts with the calcium hydride to yield calcium hydroxide and hydrogen gas. The gas pressure is proportional to the water content in the samples.

3. Results and discussion

3.1. Fractionation of PCs and characterization of fractions

PC samples were fractionated into fractions of different molecular weight using the CPF method. Molecular weights were measured by SEC-UV. Concentrations of hydroxyl end-groups and modified units were determined using proton-NMR. Characterization results are shown in Table 1. Only PC1 and PC2 contain modified units; details on the analytical characterization of these samples can be found in a previous paper [24].

3.2. Thermal treatment in open and closed systems

Polycarbonate samples (un-fractionated polymers, individual fractions and combined fractions) were subjected to thermal treatment in a DSC device using cups with holes and completely sealed cups, hereafter referred to as an 'open system' and a 'closed system', respectively. Upon thermal treatment in an open system, the evolved volatile products are continuously removed by a nitrogen flow while in a closed system these products are retained.

The thermal experiments were carried out at temperatures ranging from 200 to 300 °C for different periods of time (1–30 min). Throughout this paper, thermal treatment for 15 min at 250 °C has been used as a reference experiment to compare the thermal behaviour of the various samples. Under these conditions, MWD changes induced by the different degradation processes can be monitored with sufficient accuracy while the PC microstructure, i.e. the concentration of modified units in PC1 and PC2 remains unaffected as confirmed by NMR.

Evolution of the MWD can be qualitatively monitored through the relative change in molecular weight

$$\Delta\mathrm{MW} = \left[\frac{(\mathrm{MW_t} - \mathrm{MW_0})}{\mathrm{MW_0}}\right] \tag{1}$$

where MW represents M_w as well as M_n, and $\mathrm{MW_0}$ and $\mathrm{MW_t}$ are molecular weights before and after thermal treatment, respectively. Table 2 shows the relative change in the number and weight average molecular weights for polymers PC1–PC3 and derived fractions upon thermal treatment for 15 min at 250 °C in open and closed systems.

The extent of chain-scission as a result of thermal treatment is quantitatively measured by the level of

Table 1
Characterization data for PC1, PC2 and PC3

	Sample	SEC-UV			Proton-NMR	
		M_w (g/mol)	M_n (g/mol)	D	Modified units[a] (ppm)	Hydroxyl end-groups (ppm)
PC1	Total	21,700	9520	2.28	1250	570
	PC1F1	11,400	6590	1.73	760	1050
	PC1F2	17,700	11,570	1.53	1220	675
	PC1F3	31,900	24,100	1.32	1870	250
PC2	Total	23,700	9210	2.57	5260	1185
	PC2F1	11,900	6330	1.87	3715	1855
	PC2F2	22,100	14,120	1.57	5355	780
	PC2F3	28,900	19,090	1.51	5765	610
	PC2F4	39,200	24,950	1.57	7045	455
PC3	Total	23,200	9270	2.50	–	<20
	PC3F1	13,200	6110	2.16	–	<20
	PC3F2	23,600	15,150	1.56	–	<20
	PC3F3	37,700	26,550	1.42	–	<20

[a] Total amount of phenyl salicylate and phenyl salicylate phenyl carbonate modified units. For details, see Ref. [24].

degradation (LOD) expressed through the following relation

$$\mathrm{LOD} = \left[\frac{1}{M_{\mathrm{n_t}}} - \frac{1}{M_{\mathrm{n_0}}} \right] \mathrm{mol/g} \qquad (2)$$

where $M_{\mathrm{n_0}}$ and $M_{\mathrm{n_t}}$ are the number average molecular weights before and after thermal treatment, respectively. The LOD in open and closed systems is shown in Fig. 2 for PC1–PC3 and respective fractions. The given standard deviation values are based on a 5% experimental relative error for the SEC-MW measurement.

In order to visualize redistribution effects, fractions with the highest and lowest MW were mixed in a 1:1 (w/w%) ratio and subjected to thermal treatment in open and closed systems. The MWD of the unheated fraction mixture is bimodal. Upon redistribution, the SEC peak shape will gradually change from a bimodal to a monomodal distribution until the most probable Flory distribution is reached, as evidenced by a polydispersity (D) of 2.

Table 2
Relative change in M_w and M_n upon thermal treatment at 250 °C for 15 min in open and closed systems

Sample	Open system		Closed system	
	ΔM_w (%)[a]	ΔM_n (%)[a]	ΔM_w (%)[a]	ΔM_n (%)[a]
PC1	+4	+3	−1	−1
PC1F1	+15	+1	−2	−6
PC1F2	+11	−4	−1	−8
PC1F3	+26	−12	−5	−13
PC1F1 + 2 + 3[b]	+9	+4	−1	−1
PC2	+9	+4	−5	−3
PC2F1	+16	+1	−3	−6
PC2F2	+17	−4	−7	−16
PC2F3	+50	−11	−6	−23
PC2F4	+25	−18	−7	−23
PC2F1 + 2 + 3 + 4[b]	+8	+8	−5	−5
PC3	0	0	−1	−2
PC3F1	+1	+1	−2	−4
PC3F2	+2	0	−1	−2
PC3F3	−1	0	−3	−6

[a] Calculated using Eq. (1).

[b] Re-mix samples: mixing ratio corresponds with fraction size as yielded by the fractionation process.

3.3. Thermal treatment of BPA-PC made via interfacial phosgenation

PC3 and corresponding fractions are fully end-capped

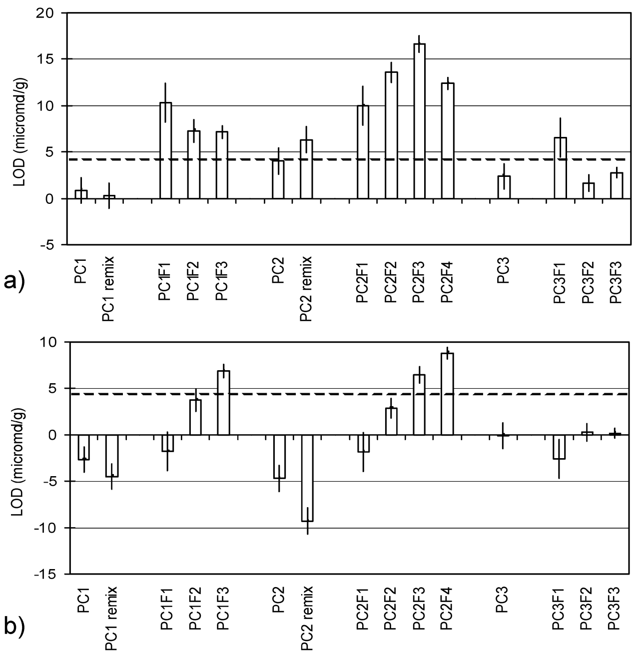

Fig. 2. LOD for PC1, PC2 and PC3 upon thermal treatment for 15 min at 250 °C in (a) closed and (b) open systems. Vertical markers crossing the top of each bar indicate standard deviations of the measurements. The dotted horizontal line indicates a LOD value corresponding to hydrolysis induced by 80 ppm water.

(Table 1). For these polymers, Table 2 and Fig. 2 show that both M_w and M_n remain nearly constant upon thermal treatment for 15 min at 250 °C in open and closed systems. Hence, no significant post-condensation or degradation has taken place under these conditions. LOD values are very low and of the same order of magnitude in open and closed systems. Similar results are obtained for experiments performed under all other conditions used in this study, i.e. virtually no change in molecular weight and a minimal LOD.

When a 1:1 (w/w%) mixture of PC3 fractions 1 and 3 is subjected to thermal treatment in open and closed systems, the bimodal MWD is unaffected under all experimental conditions, indicating that no significant redistribution has taken place. Due to the very low hydroxyl end-groups concentration of PC3, redistribution can only take place via the slow carbonate interchange route which, if occurring at all, does not modify the MWD under the used conditions.

3.4. Thermal treatment of BPA-PC made via melt-transesterification

3.4.1. Closed systems

M_w and M_n for the un-fractionated and re-mixed samples remain approximately constant within experimental error (of about 5%) upon thermal treatment for 15 min at 250 °C (Table 2). The re-mixed samples are obtained by mixing the fractions in a ratio corresponding to their size as yielded by the fractionation process and essentially are re-composed versions of the initial polymers. The nearly constant M_w and M_n values indicate that no significant post-condensation nor degradation has taken place. In a closed system, volatile products formed by redistribution (in particular diphenyl carbonate) are retained, resulting in the establishment of an equilibrium. As a result, the thermodynamic distribution remains unaffected. The situation is different for the fractions which start from out of equilibrium distributions. As can be derived from Table 2, the MWD broadens upon thermal treatment as the distributions move back toward their equilibrium. LOD figures confirm the quasi absence of degradation for PC1 and PC2 un-fractionated and re-mixed samples (Fig. 2(a)). The marginal ΔM_n and LOD values observed are compatible with the assumption of hydrolysis caused by trapped residual water, as also postulated by Davis and Golden [8,10]. It was experimentally observed by us that water cannot be completely removed from the samples, not even by applying severe drying conditions, i.e. overnight drying at 120 °C and by applying vacuum. Under these conditions, residual water contents between 30 and 80 ppm were measured for all samples. Prolonged drying had no reducing effect on the residual water content. In Fig. 2, the dotted horizontal line indicates a LOD value corresponding with a level of hydrolysis induced by 80 ppm water. From this, it can be derived that hydrolysis from residual water can account for the observed effects in case of PC3 and (for the essential part) for un-fractionated and re-mixed PC1 and PC2 melt-polymerized samples.

For PC1 and PC2 individual fractions, LOD appears to be higher than the hydrolysis threshold and ΔM_n higher than the measurement error (Table 2 and Fig. 2(a)). For PC1 fractions, the difference is marginal considering that the error bar on measured M_n is probably underestimated (a 5% relative error is somewhat optimistic for M_n). For PC2 fractions on the other hand, the increase is clearly significant. The origin of this effect remains an open question.

3.4.2. Open systems

Upon thermal treatment for 15 min at 250 °C, ΔM_w and ΔM_n of un-fractionated and re-mixed PC1 and PC2 samples show similar positive trends as a result of post-condensation since the volatile reaction products are now continuously removed by the gas flow. Because the samples already possess a starting MWD very close to the most probable Flory distribution, their polydispersity is not affected.

By contrast, individual fractions show much stronger and diverging trends. ΔM_w is strongly positive whereas ΔM_n can be negative or positive but shows a systematic trend toward higher values for lower starting M_n. The LOD is similarly reduced or offset with decreasing molecular weight of the fractions (Fig. 2(b)). These changes result from a competition between chain-scission and redistribution-driven post-condensation. Because the starting distributions are far from equilibrium and narrow, polydispersity rapidly increases toward its equilibrium value of 2, explaining the diverging trends for ΔM_w and ΔM_n. The high hydroxyl end-group concentration for low molecular weight fractions causes redistribution reactions with concurrent M_n increase to occur at a very fast rate thus off-setting the molecular weight lowering effect of hydrolysis (and possibly other unknown) reactions. High-MW fractions contain lower amounts of hydroxyl end-groups. As a result, redistribution reactions take place at a relatively slower rate and chain-scission predominates.

Fig. 3 shows how the LOD in an open system depends on hydroxyl end-group concentration for PC1 and PC2

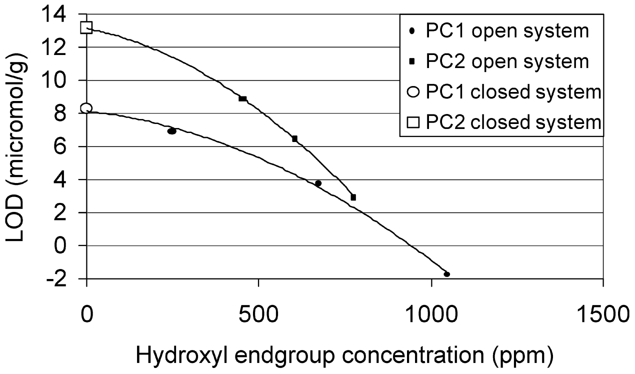

Fig. 3. LOD as a function of hydroxyl end-group concentration for PC1 and PC2 upon thermal treatment for 15 min at 250 °C. Closed symbols are used for individual fractions in open systems. Open symbols represent the average LOD for all fractions in closed systems.

fractions. Extrapolation of each curve to a zero hydroxyl concentration represents a virtual PC material with no reactive end-groups. As the graph shows, the extrapolated LOD at this point is very close to the experimentally determined average LOD for PC1 and PC2 fractions heated in a closed system (Fig. 2). This can be explained as follows. A PC sample with no hydroxyl end-groups, when heated in an open system, would be susceptible to chain-scission only, since redistribution processes would be extremely slow (direct carbonate interchange only). This is similar to the situation for a closed system where hydrolysis is also the predominant degradation mechanism and redistribution has no net effect on M_n.

These results imply that redistribution and chain-scission processes are independent of each other. In closed systems, redistribution has no net effect on LOD while in open systems it (partly) compensates the loss of MW. We can only speculate about the small difference between the extrapolated values for PC1 and PC2 (8 and 13 μmol/g, respectively). As we mainly ascribe the LOD in closed systems to hydrolysis, it probably arises from a small systematic difference between the residual water content in PC1 and PC2. This might in turn be due to minor differences in residual catalyst concentration. Since the latter is too low to measure accurately, we cannot verify this assumption.

3.4.3. Redistribution of mixed fractions

The lowest and highest MW fractions of PC1 and PC2, respectively, were mixed and subjected to thermal treatment in open and closed systems in order to visualize and quantify redistribution. Experimental results for PC2 are shown in Fig. 4 for short times at 225 °C. The original bimodal MWD of the fraction mixture gradually shifts to a unimodal peak. Most of the visible shift occurs within the first minutes, suggesting a very fast redistribution rate. Results for PC1 (not shown) are similar.

In a redistribution process, polymer chains split and recombine continuously, resulting in a visible MWD change until the most probable Flory distribution is reached. A Monte Carlo model was implemented to simulate this. In a number of simulation cycles an ‘attacker’ chain attacks at a random monomer of a ‘victim’ chain and two chains with new individual lengths are formed while the combined length remains unchanged. To provide a correct picture of the process kinetics, care has to be exercised to give the correct statistical weights to the attackers and victims. Since our results confirm that redistribution proceeds through reaction of phenolic end-groups on carbonates, and since these end-groups are randomly distributed (see Table 1 and Ref. [24]), the attacker chain has to be randomly selected from the distribution of all chains, i.e. the number average MWD. On the other hand, the victim monomer has to be selected from the distribution of all monomers, i.e. the weight average MWD. The total number of chains and, hence, M_n has to remain constant which allows for an internal check of the simulation. A total number of monomers of ten million and a number of molecular weight slices of 50 (equally spaced on a logarithmic scale) were found to be adequate for following the initial stages of redistribution correctly.

Fig. 5 shows the simulated MWD of a 1:1 (w/w%) mixture of fractions 1 and 4 of PC2 for an increasing number of simulation cycles. Input data for this simulation is the MWD of the initial fraction mix as obtained from SEC-UV measurements. As with the experiments, the bimodal MWD of the fraction mixture rapidly changes to a unimodal peak, which remains unchanged when a polydispersity of 2 has been reached, i.e. the Flory distribution.

An exact matching of the experimental and simulated MWD was found to be only feasible in case of open systems

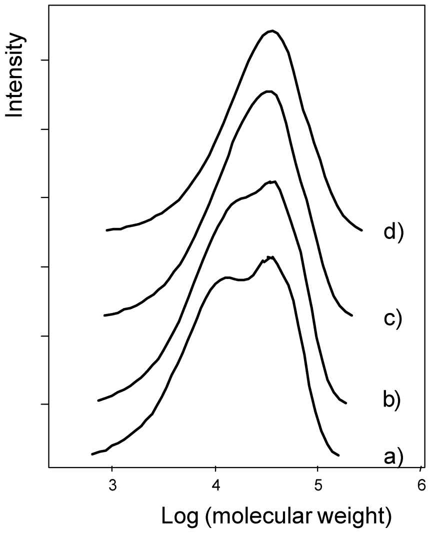

Fig. 4. MWD for a 1:1 (w/w%) mixture of PC2 fractions 1 and 4 heated at 225 °C in an open system, (a) $t = 0$ min, (b) $t = 1$ min, (c) $t = 3$ min and (d) $t = 6$ min.

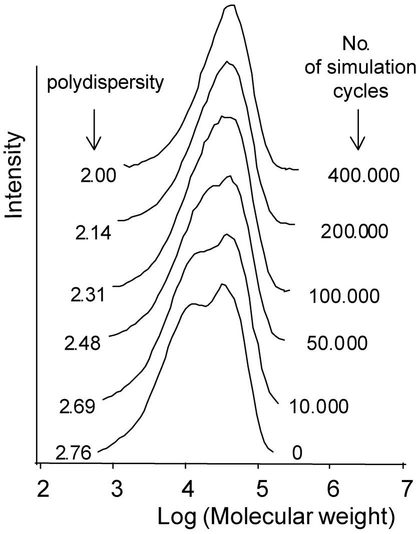

Fig. 5. Simulated MWD for a 1:1 (w/w%) mixture of PC2 fractions 1 and 4 at an increasing number of simulation cycles.

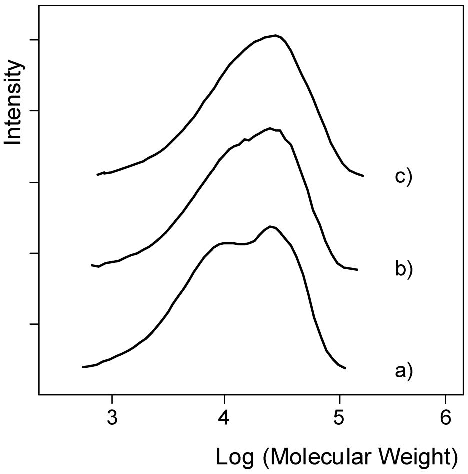

Fig. 6. MWD for a 1:1 (w/w%) mixture of PC1 fractions 1 and 3, (a) initial fraction mix, (b) experimental: thermal treatment at 250 °C for 1 min in an open system and (c) simulation: 50,000 cycles.

for short heating times up to 6 min and temperatures not higher than 250 °C. Under harsher conditions, post-condensation and hydrolysis reactions obscure the effects of pure redistribution. For closed systems, even at very short heating times, hydrolysis and redistribution reactions compete to such an extent that exact matching is not possible. A more complex simulation would be required to describe the competing processes.

In Fig. 6, the simulated MWD after 50,000 cycles for the PC1 fractions mixture is reported. It best matches the experimental data after about one minute.

An approximate redistribution rate can therefore be obtained by comparing the experimental results with the simulation data: 50,000 redistribution reactions for a total of ten million monomers correspond to about one minute reaction. Hence, as a rough estimate, approximately half a percent of all carbonate groups react per minute at 250 °C. This conclusion is valid for PC1 as well as PC2 within the experimental error, which seems logical considering the comparable levels of hydroxyl end-group concentrations (within a factor 2).

4. Conclusions

Whereas melt and interfacially polymerized PC show similar susceptibility toward hydrolysis, their post-condensation/redistribution rate in the melt is completely different.

Under the conditions used in this study, BPA-polycarbonate made via interfacial phosgenation undergoes no measurable post-condensation and redistribution in open and closed systems. This is due to the extremely low concentration of hydroxyl end-groups in these samples.

The thermal behaviour of PC made by melt transesterification is characterized by a complex combination of redistribution, post-condensation and hydrolysis reactions taking place simultaneously. This is the result of a significant concentration of hydroxyl end-groups which play a predominant role in thermally induced processes occurring at temperatures up to 300 °C. In open systems, the three processes take place simultaneously, while in closed systems post-condensation reactions are prevented.

The first stages of redistribution in an open system, when competition between the various thermal processes is still limited, can be simulated using a Monte Carlo model. At 250 °C, approximately 0.5% of all carbonate groups are involved in a redistribution exchange reaction per minute for the systems studied.

Acknowledgments

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