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ORIGINAL PAPER

The relationship between the aging of polycarbonate characterized by SEC and the release of bisphenol A quantified by HPLC–UV

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Abstract Aging of polycarbonate (PC) and migration of bisphenol A (BPA) from PC in solutions were studied under different conditions of temperature, pH, and treatment duration. In order to investigate the relationship between the migrant and its polymer and explain the release mechanism of the BPA, the impact of different treatments on PC aging was studied by measuring molecular masses using size exclusion chromatography. The BPA which migrates in the solutions was measured using HPLC–UV. It has been found that the molecular weights of PC samples change as the conditions of treatment change. In general, the trend was to shift the Mn toward a lower average molecular weight by increasing treatment temperature, pH, and treatment duration. The findings are in concordance with the BPA concentrations in solutions. The obtained results show clearly that the levels of BPA concentrations increase with temperature, pH, and treatment duration. The BPA released does not only result from degradation mechanism originating from the treatments of the polymer, but also it results from the transport of non-polymerized monomer from the polycarbonate.

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Keywords Polycarbonate degradation · Bisphenol A migration · Non-polymerized monomer · Contaminant release · Polycarbonate aging

Introduction

Several studies have already confirmed that the release of BPA from PC baby bottles takes place, and the quantification of this migrant under different conditions has been well documented [1–5]. But the mechanism of this migration has not been sufficiently studied, is BPA the result of the material degradation mechanisms, or is it the free monomer trapped in PC because the polymerization is incomplete?

The degradation of PC leads to BPA migration. Bisphenol A has become a controversial issue because it was detected in many environmental things; water and some bottled water were analyzed by GC–MS, and the results show that the concentration of BPA detected was 17.6–324 ng/l [6]. Nam et al. [5] observed that the levels of BPA migration rapidly increase when the water temperature was over 80 °C; in addition, the average inter-chain spacing (*d*-spacing) of PC was calculated by X-ray diffraction (XRD) in order to explain the differences in migrated BPA in new PC baby bottle and 6-month-used PC baby bottles. The *d*-spacing of PC baby bottle increases with repeated use from 0.499 nm in brand-new bottles to 0.511 nm with bottles used for 6 months [5]. The results obtained in another study revealed that the BPA migration varied from 228 to 521 μg/l after being heated at 70 °C for 6 days [7].

The migration of bisphenol A from polycarbonate baby bottles has been the focal center of interest for many researchers. Brede et al. [1], for example, indicate that there are increased migration levels of bisphenol A from polycarbonate baby bottles after dishwashing, boiling, and brushing [1]. In a similar study, Maragou et al. [3] examined the migration of bisphenol A from polycarbonate baby bottles into simulants under real-use conditions: cleaning and sterilization. They have found that temperature was the crucial factor for the migration of BPA from the plastic bottles to water and this migration decreases after polymer use. A further study was carried out by Maia et al. [4] to determine the effect of detergents and temperature on the release of bisphenol A from polycarbonate baby bottles. The conclusions drawn from another study of Biedermann-Brem and Grob [8] revealed that drying was the most critical step, particularly after inadequate rinsing of bottles, when alkali detergent was "baked" to the bottle wall at elevated temperature.

BPA migration in food or beverages has been well documented [9–11]. According to Biles et al. [9], residual amounts of BPA found in PC food contact articles ranged from 7 to 58 µg/g. The effect of temperature on BPA migration from cans was also studied. The relationship between bisphenol A migration from metal cans into various food contents (glucose, sodium chloride, and vegetable oil) over, heating time, and temperature was determined, and it was found that the effect of temperature on BPA migration from cans can be more extensive than that of heating time, and the effect of container contents was also confirmed after 121 °C [10]. Biedermann-Brem, Grob [8] agree that it is due to polymer degradation, Takashi and Akio [12] say that there are two possible origins of the BPA leaching from a PC product: the migration of residual BPA and the hydrolysis of the PC itself. The results obtained in these works do not explain the migration mechanisms, these analytical methods allowed the identification and the quantification of migrants into the liquids, but the polymer properties remain unstudied.

The stability of polymers can be expressed by several parameters such as weight loss, molecular weight. Molecular weight of materials is an important physicochemical characteristic of polymers. It is well known that degradation leads to changes in molecular weight, which subsequently causes changes in material characteristics [13, 14]. Size exclusion chromatography (SEC) and gel permeation chromatography (GPC) techniques have been applied for the determination of BPA–PC characteristics [15, 16].

Changes in molecular weights can predict the changes in chain's lengths and thus the degree of degradation of polycarbonates. This study is intended to quantify the concentration of migrated BPA, to measure changes in molecular weights from a PC with different treatments of temperature, pH, and time and thus to understand the BPA migration phenomenon from plastic materials to solutions. The aim is to focus on the relationship between PC molecular weight change carried by SEC and BPA migration quantified by HPLC–UV.

Materials and methods

Materials

Baby bottles made of polycarbonate, bought from a local supermarket, are chosen to be the study samples. Bisphenol A, citric acid, chlorhydric acid, Na_2HPO_4, and NaOH from SIGMA ALDRICH Chemistry (France) and acetonitrile (HPLC grade) from PAI PANREAC were used. THF (HPLC grade) unstabilized from BIOSOLVE (The Netherland) was adopted for SEC analysis, and water was distilled and then purified via a Millipore water purification system.

Methods

The polycarbonate was prepared by cutting each baby bottle into several pieces; each one with an area of 3 cm^2. Pieces were placed in a screw tube and immersed in 25 ml of distilled water at varying temperatures and pH which was stabilized by buffers prepared as below, and then placed into a thermostatic bath at 25 and 50 h (Table 1).

Buffers preparation

pH 1.8: 20 g of acetic acid was dissolved in 200 ml of distilled water, and then 200 ml sodium hydroxide 1 M, 210 ml of chlorhydric acid 1 M and 300 ml of distilled water were added under agitation.

pH 12.1: 17.41 g of Na_2HPO_4 was dissolved in 500 ml of distilled water, and then 4.23 g of NaOH (5 M) and 500 ml of distilled water were added under agitation.

pH 6.7: 45.5 ml of acetic acid (0.5 M) was added to 309 ml of Na_2HPO_4 (0.5 M), and the volume was completed to 1 l by distilled water.

All PC samples and solutions were subjected to the following analyses:

SEC: the technique used to determine molecular weights of PC samples before and after treatments.
HPLC–UV: the technique used to quantify BPA migrating from PC samples to solutions.

Size exclusion chromatography (SEC) analysis

Molecular weight distributions of polycarbonate were obtained using SEC.

SEC measurements were measured with a Viscotek TDAmax system from Malvern Instruments that consists of an integrated solvent and sample delivery module

Table 1 Polycarbonates molecular weights determined by SEC and BPA concentrations in solutions measured by HPLC–UV after different treatments of temperature, pH, and time

Samples	Conditions			Mn (g/mol)	Mw (g/mol)	Mw/Mn	Average concentration of BPA (μg/l)	
	T (°C)	pH	*t* (h)				(1)	(2)
PC00	[a]	[a]	[a]	12,099 ± 107	28,916 ± 207	2.39	[a]	[a]
PC01	20	6.7	25	14,699 ± 105	35,277 ± 231	2.40	00[b]	00[b]
PC02	20	1.8	25	14,442 ± 98	35,094 ± 286	2.43	00[b]	00[b]
PC03	20	12.1	25	14,603 ± 80	35,047 ± 199	2.40	00[b]	00[b]
PC04	50	6.7	25	12,781 ± 111	31,569 ± 301	2.47	39 ± 1.6	12 ± 0.4
PC05	50	1.8	25	14,667 ± 113	35,787 ± 331	2.44	00[b]	00[b]
PC06	50	12.1	25	11,406 ± 101	28,058 ± 308	2.46	121 ± 1.8	27 ± 0.3
PC07	100	6.7	25	12,156 ± 97	29,903 ± 297	2.46	137 ± 2.1	28 ± 0.3
PC08	100	1.8	25	14,819 ± 88	35,565 ± 343	2.40	78 ± 1.1	18 ± 0.2
PC09	100	12.1	25	11,322 ± 74	28,305 ± 189	2.50	311 ± 2.3	33 ± 0.3
PC10	20	6.7	50	14,743 ± 89	36,562 ± 332	2.48	00[b]	00[b]
PC11	20	1.8	50	14,683 ± 91	35,532 ± 345	2.42	00[b]	00[b]
PC12	20	12.1	50	13,408 ± 109	33,520 ± 264	2.50	00[b]	00[b]
PC13	50	6.7	50	12,002 ± 71	29,404 ± 306	2.45	55 ± 0.9	19 ± 0.1
PC14	50	1.8	50	13,945 ± 96	34,025 ± 357	2.44	14 ± 0.8	06 ± 0.1
PC15	50	12.1	50	11,299 ± 83	28,021 ± 246	2.48	199 ± 1.7	35 ± 0.2
PC16	100	6.7	50	11,978 ± 107	29,945 ± 209	2.50	322 ± 2.6	41 ± 0.3
PC17	100	1.8	50	14,447 ± 121	35,395 ± 311	2.45	106 ± 2.2	22 ± 0.1
PC18	100	12.1	50	10,541 ± 99	26,563 ± 251	2.52	541 ± 3.1	57 ± 0.2

[a] Without treatment

[b] Absolute < limit of detection

(GPCmax) and a Tetra Detector Array (TDA) including a right (90°) and low (7°) angle light scattering (LS) detector (RALS/LALS), a 4-capillary differential viscometer, a differential refractive index detector (RI) and a diode array UV detector. THF was used as the mobile phase at a flow rate of 1 ml min^{-1}.

Samples were dissolved in THF until total dissolution. All polymers were injected at a concentration of 3 mg ml^{-1} after filtration through a 0.45 -µm-pore-size membrane. Volume injection was 100 µl. The separation was carried out on three Polymer Laboratory columns [3 × PLgel 5-µm Mixed C (300 × 7.5 mm)] and a guard column (PL gel 5 µm). Columns and detectors were maintained at 40 °C. The OmniSEC 4.6 software was used for data acquisition and data analysis. The molar mass and the dispersity indexes, Mw/Mn, were calculated with a calibration curve based on narrow polystyrene (PS) standards (from Polymer Laboratory), using only the refractometric detector. All PC samples treated are listed in Table 1.

High-performance liquid chromatography with UV detection (HPLC–UV)

BPA was analyzed by using HPLC (Perkin Elmer) with ultraviolet UV–Vis detector equipped with MZ analytical nucleosil C18 column (4.6 mm × 250 mm). The injection temperature was 25 °C, and the injection volume was 20 µl. The mobile phase acetonitrile–water (50/50, v/v) was eluted at flow rate of 1 ml/min (isocratic mode).

The calibration of the HPLC was made by injecting five BPA standard solutions in water. The solution concentrations were 1, 0.5, 0.1, 0.05, 0.01 mg/l. The calibration line of concentrations versus chromatographic peak areas was obtained by linear regression. The limit of detection calculated by injecting successive dilutions of BPA standard solutions was 5 µg/l. The calculated precision measurement was 2.24 % relative to standard deviation. The samples provided in Table 1 were analyzed by HPLC–UV, and to achieve this, it has followed two different steps:

(1) Analysis of the solutions for each sample after treatment conditions were repeated three times.
(2) After analysis (1), all PC pieces were washed in distilled water. After that, each piece of PC was placed in the same conditions of temperature and pH and then immersed in a bath for 1 h. The solutions were analyzed by HPLC–UV three times.

Results and discussion

SEC analysis of polycarbonate

To explain the release mechanism of the BPA, the impact of different factors on PC aging was studied by measuring molecular masses using SEC.

The molecular weights (MW) of the polycarbonate samples after different treatments and one sample undergone any treatment are shown in Table 1.

Molecular masses of PC00 sample (without treatment) are strongly low; this case explains the phenomenon transport of non-polymerized monomer from polymer to solution (during treatment). The presence of monomer and oligomer in the polymer decreases the average molecular weight, and treatments can be considered as washing/extracting operations before degradation processes. It is worth mentioning that just after the first treatments, even if the conditions are soft, the masses decrease significantly.

It is shown that the highest number average molecular weight of PC measured in all samples was 14,699 g/mol for sample treated in neutral pH at 20 °C for 25 h. The lowest was 10,541 g/mol for samples treated in basic pH at 100 °C for 50 h. So the effect of treatment condition on PC molecular weight was reported.

It is clear that the molecular weight of all PC samples decreases with increasing temperature, i.e., the molecular weight of samples treated in neutral pH for 25 h was 14,699, 12,781, and 12,156 g/mol at 20, 50, and 100 °C, respectively.

The influence of pH was also investigated. The molecular weight of PC samples reaches the highest value for PC samples treated in acid solution: 14,683, 13,945, and 14,447 g/mol at 20, 50, and 100 °C, respectively. The lowest values correspond to the samples treated in alkaline solution with 13,408, 11,299, and 10,541 g/mol at 20, 50, and 100 °C, respectively, for the same duration of treatment (50 h).

The effect of usury time or treatment duration is demonstrated in Table 1. The molecular weight of all PC samples decreases with increasing duration treatment. Despite the long time of contact, polycarbonate molecular weights continue to decrease significantly.

These results indicate that temperature, pH, and usury decrease the polymer molecular masses. It can interpret these changes in molecular weight by the transfer reactions of the intermolecular chain that after the stage of degradation. The reaction at the end of the chains generates primary radicals. The trend for the weight average values is essentially as would be expected, with a decrease in Mn with increasing duration, temperature, and pH.

BPA analysis in solutions

The values of BPA concentrations in solutions are shown in Table 1.

BPA was detectable in all samples except samples treated at 20 °C. The highest concentrations of BPA correspond to the highest temperatures, treatment duration, and pH. In step (2), the migration of BPA increased with increasing temperature, duration treatment, and pH; BPA level was 0 µg/l at 20 °C and 57 µg/l at 100 °C in basic solution.

Table 1 shows the concentration of BPA in all PC samples treated for 25–50 h at different temperatures. It is clearly shown that this concentration increases with increasing temperature for the three cases of pH in both analyses (1) and (2). The level of the release is zero or undetectable at 20 °C, medium at 50 °C, and important at 100 °C. This migration tends to be high in basic solutions and low in acid solution.

The effect of pH is also reported; it is clear from the three different pH values that the levels of migration increase as pH increases. The concentration of BPA detected after 25 h of treatment is 78, 137 and 311 µg/l in acid, neutral and basic solution, respectively. So, with regard to pH values, it concludes that the higher the pH values are, the more BPA will be released.

Furthermore, it is worth mentioning that this change in BPA migration at high temperature varies according to pH. The BPA level reaches the highest value in alkaline pH 541 µg/l at 100 °C after 50 h of treatment, and the lowest degree is marked in acidic pH 106 µg/l at 100 °C for the same duration of treatment. Concerning the results obtained from samples treated following B protocol, the same evolutions are observed, with lower concentrations.

The influence of treatment duration on PC degradation is also demonstrated in both steps of analyses (1) and (2). The level of BPA concentrations increases as the duration of treatment gets longer. That is to say, after 25 h of treatment the BPA level is 39 µg/l at 50 °C and 137 µg/l at 100 °C in neutral solutions. This level reached 55 µg/l at 50 °C and 322 µg/l at 100 °C after 50 h of treatment. The same evolution is observed for samples treated in acid and basic solutions.

The level of migrated BPA rapidly increases at high temperatures (temperatures over 80 °C), and the carbonate linkages are subjected to hydrolytic attack when temperatures rise. This is more effective in used PC than in non-used one. The hydrolysis is accelerated in alkaline pH and retarded by acid pH. Therefore, hot distilled water environment promotes the hydrolysis of PC. It is caused by hydrolysis of carbonate linkage as well as increasing *d*-spacing of PC. The *d*-spacing of PC baby bottle increased with repeated use [5].

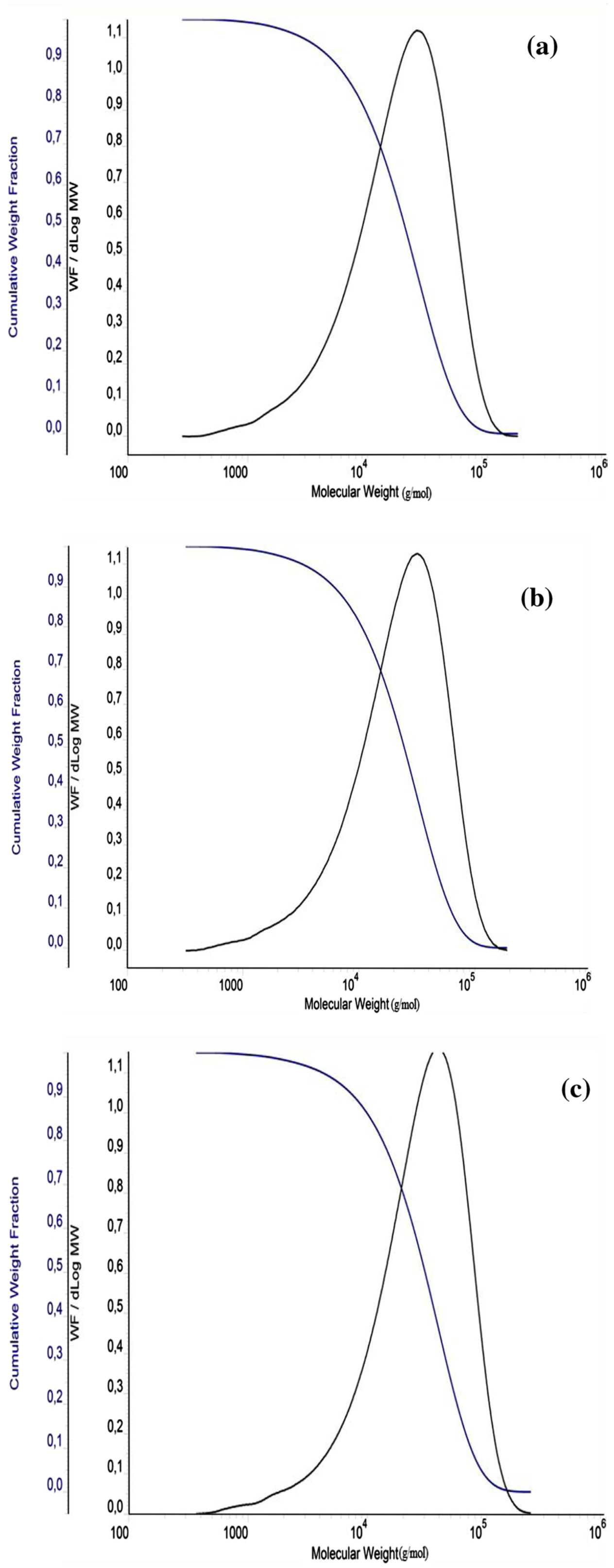

Fig. 1 Molecular weights distribution and cumulative weights fraction for PC00 (**a**), PC18 (**b**), and PC01 (**c**)

Table 2 Cumulative weights fractions at different molecular weights for three PC samples

Molecular weight (g/mol) (less than)	Cumulative weights fractions (%)		
	PC00 MW = 12,099	PC18 MW = 10,541	PC01 MW = 14,699
500	0.5	0.5	0.5
1000	1	1.5	1
5000	8	10	6
10,000	19	24	14
20,000	42	49	32.5
30,000	61	68	51
40,000	64	72	64.5
50,000	84.5	89.5	75
60,000	90	93.5	83.5
70,000	94	97	89.5
80,000	97	98.5	92.5
90,000	98	99.5	95.5
100,000	99.5	99.5	97

The cumulative mass fractions of chromatograms from Fig. 1, reported in Table 2, demonstrate the formation of more small chains with molar weights less than 5000 g/mol in the sample PC18 than in sample PC00 (a gap of 2 %) and the PC01 (a gap 4 %), and this gap increases if one considers the threshold of 10,000 g/mol (5 % compared to PC00, and 10 % compared to PC01). It is also observed that 25 % of the chains of PC01 have a molar weights >50,000 g/mol, while PC18 and PC00 have only 10.5 and 16.5 % respectively, and these results show clearly that the treatment applied on the polycarbonate in alkali solutions at high temperature decreased the average molecular weights by breaking the chains (essentially the ends of chains).

The aim of step 1 is the degradation of the PC and the extraction of BPA due to degradation and the residual one, while step 2 is only an extraction step of degradation products, because all residual monomer was extracted during step 1, and the results from step 2 showed that the PC continued to be degraded because the BPA continued to be released and this degradation is mainly due to the aging and the tiredness caused during step 1, which is shown in Table 1 that the samples with high molar weights (not degraded or are slightly degraded after step 1) do not release BPA after step 2. The fact that BPA continued to be released at different treatments and after long and short extractions shows that BPA results essentially from degradation phenomenon.

Conclusion

The relationship between the changes in the molecular weights of PC due to its degradation and the migration of BPA in solutions was reported. The current work demonstrates that temperature, pH, and usury decrease the polymer molecular masses and increase the BPA release. The level of migrated BPA increased rapidly at high temperatures and pH. This was caused by hydrolysis of carbonate linkage. The BPA detected in solutions does not only result from the diffusion mechanism of non-polymerized monomer, but the contaminant is essentially provided by the PC degradation process originating from the contact between the material and solutions.

Compliance with ethical standards

Conflict of interest All authors declares that this article has no conflict of interest.

Compliance with Ethics Requirements This article does not contain any studies with human or animal subjects.

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