Physicochemical Processes Involved in Migration of Bisphenol A from Polycarbonate

P. Mercea

FABES GmbH, Schragenhofstr. 35, 80992 Munich, Germany

ABSTRACT: Results of experiments, conducted by different polycarbonate (PC) producing companies, on migration of bisphenol A (BPA) from PC into different liquids, were supplied to the author for compilation, review, and discussion. The observed BPA migration levels were found to be nearly independent of the concentration of residual BPA in the PC resins. Hydrolysis of PC is the dominant mechanism responsible for the release of BPA from the polymer surface into the contacting aqueous liquid. Experiments with PC spiked with deuterated BPA revealed that diffusion-controlled migration play a minor role in the overall release of BPA from PC. The influence of a number of experimental parameters on the migration of BPA into aqueous liquids was studied. Factors found to be of importance included the temperature, pH, and ozone concentration of the liquids, as well as the surface ageing of the PC. All of the BPA migration levels obtained from experiments performed under standard conditions as given in the EU legislation and its associated guidance documents were found to be well below the EU specific migration limit of 600 µg/kg food which applies to plastics in contact with foodstuffs (EU Directive 2002/72/EC as amended). Migration is lower in oil than in the aqueous food-simulants water, 3% acetic acid, and 10 or 50% ethanol. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 579–593, 2009

Key words: bisphenol A; consumer protection; diffusion; food packaging; hydrolysis; migration; partitioning; polycarbonate

INTRODUCTION

Bisphenol A (BPA) is an industrial intermediate principally used for the manufacture of PC plastics and epoxy resins. The largest application of BPA is in the production of PC plastics. Polycarbonate plastics feature good optical clarity, high impact resistance and ductility at room temperature and below. Because of these attributes, PC is used in a wide variety of common products including digital media (e.g., CDs, DVDs), electrical and electronic equipment, glazing in the building and construction industry, automobiles, sports safety equipment, and reusable food and drink containers.

The levels of residual BPA in PC are generally below 100 mg/kg. Several studies have been published examining the potential of BPA to migrate from PC into foodstuffs or food simulating liquids.[1]

A specific migration limit (SML) has been set by the European Commission governing the safety of plastics materials used in contact with food.[2] The SML for BPA in food is 600 µg/kg food (600 parts per billion). Migration levels reported in the literature are generally well below this limit.[3] Two potential mechanisms for the release of BPA from PC into food simulants were postulated to explain the observed results in earlier migration studies[4–6]: (i) diffusion of the residual BPA from the bulk resin and (ii) hydrolysis of the plastic surface (Fig. 1).

Hydrolysis at the surface of the carbonate ester linkages in the PC backbone may occur under typical use conditions when PC is in contact with an aqueous foodstuff or during the washing or sterilization steps of polycarbonate food contact articles before use or between different use cycles.

For the overall process of BPA release from a PC sample into an aqueous contact medium the term "migration" is probably not the proper one—hydrolysis is a chemical reaction while migration is related to diffusion in and from the bulk of the polymer. However, in the field of food packaging, "migration" is usually used to name the overall process of substance release/transfer from the packaging into the food. In the same respect will "migration" be used in this work.

Whereas BPA migration from PC into foodstuffs has been well studied,[1,3–5] little has been reported on the relative contributions of the above two BPA release processes into foodstuffs under conditions representative of actual use.

A comprehensive number of previously unpublished experiments regarding migration of BPA from

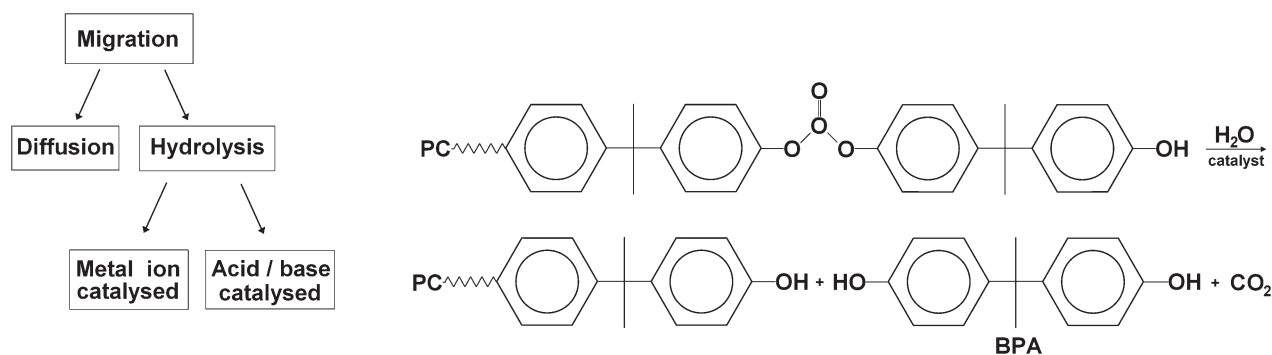*Correspondence to:* P. Mercea (petermercea@gmail.com).

Figure 1   Mechanisms for BPA release (migration) from PC samples in contact with aqueous food simulants.

PC materials has been presented to the author by the PC producers. The aim of this article is to summarize and discuss the results of these experimental data. A special emphasis is given to the migration of BPA from commercial PC containers and bottles into drinking water.

EXPERIMENTAL

The investigations presented here were designed to study the influence of the following variables on the release (migration) of BPA from PC samples into liquid food simulants:

   molding and annealing conditions of the PC sample preparation,
   residual levels of BPA and water in the PC resin,
   type of liquid medium used as food simulant,
   storage time and temperature of the PC sample-food simulant system,
   ozone level, mineral content (Na^+, Mg^{2+}, Ca^{2+}), and pH of the water stored in the PC containers/bottles,
   washing conditions and container/bottle age and
   polymer degradation level at the inner surface of the water containers/bottles.

Polycarbonate sample preparation

Two categories of PC samples were used in the investigations. The first one comprises PC films cast from methylene chloride solutions as well as injection-molded platelets and test bars. These samples are not used in their actual form in commercial food packaging. The second category consists of commercial blow-molded PC water storage containers (large containers of about 5 gallons ($\sim$ 19 L) and smaller bottles of about 0.3–2 L), Figure 2.

   A summary of the PC samples investigated is given in Table I. The PC density of all these samples was taken as $\rho_P = 1.2$ g/cm^3.

   Because the samples listed in Table I originate from different companies there are inherent differen-

ces in how the PC resins were manufactured and thus slight differences in their physicochemical properties. Therefore the data reviewed here should represent a good cross section of samples from the PC food-contact market.

   Some of the PC samples were spiked with deuterated BPA, d_{16}-BPA, Table I. The thin PC Films of 65–80 µm thickness were drawn from PC solutions in methylene chloride (10–15%) spiked with d_{16}-BPA. Therefore it was assumed that d_{16}-BPA was homogeneously distributed in the matrix of these samples, which contained up to 200 ppm of d_{16}-BPA besides trace levels of residual BPA (4–5 ppm).

   With the PC Bottle 2 the residual BPA was first removed from the ground resin by a chemical washing process. Then d_{16}-BPA was added to the regrind, which was subsequently extruded, pelletized, and blow-molded into small bottles. The data shown in Table I indicate that a trace of residual BPA of about 2 ppm remained in PC Bottle 2.

   BPA and d_{16}-BPA have slightly differing molecular masses, $m_{BPA} = 228$ g/mol and $m_{d16\text{-}BPA} = 244$ g/mol,
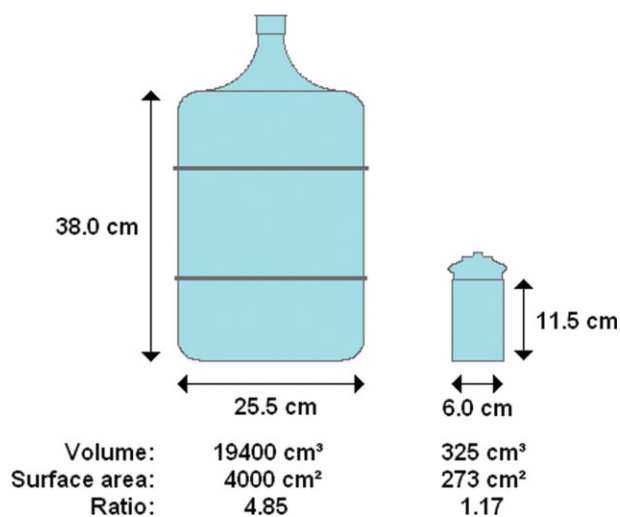

Figure 2   Approximate shape and sizes of PC Container 3 and Bottles 1 and 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Polycarbonate (PC) Samples Investigated

Type of PC sample	Thickness, d_p (µm)	Residual BPA (ppm)	Added d_{16}-BPA (ppm)
PC Film	65, 70, 75, and 80	4.0 or 5.0	50, 100, or 200
PC Plate 1	2,000	5.0	50
PC Plate 2	4,000	2.5	–
PC Plate 3	2,000 and 4,000	4.0, 5.0, or 9.0	–
PC Bars	4,000	9.0 or 9.3	–
PC Discs	3,175	10 to 15[a]	–
PC Container 1	1,200	2.5 or 2.6	–
PC Container 2	1,700	7.0 to 11.0	–
PC Container 3[b]	1,250	5, 12, 25, 26, or 70	–
PC Bottle 1	1,000	5, 12, or 25	–
PC Bottle 2	1,000	2.1	6.0

[a] Estimated.
[b] Aged and collected from the field.

respectively, and thus can be easily discriminated by mass spectrometry (MS) and/or using special high performance liquid chromatography (HPLC)techniques and mass spectrometry detection.

To find a correlation between the level of BPA migration into water and changes at the inner surface of PC containers over time, experiments were conducted with aged Containers 3 obtained from a bottling facility. The 24 PC Containers 3, as shown by the time stamp on their bottom, were 3, 5, and 7 years old, respectively. They were washed, rinsed, and filled with deionized (DI) water and then stored at 49°C for 30 days. After that time the amount of BPA in the DI water was analyzed. Then the containers were emptied and divided into two groups based on age and observed migration for different inner surface treatments. Containers of one group were washed with 100 mL of methanol while the others were subjected to an acid wash with 100 mL of 0.02M methanesulfonic acid. Then the containers were rinsed and filled with DI water and stored again for 1 month at 49°C. Subsequently the amount of BPA in the bottled DI water was determined. Similar migration experiments were performed with the PC Container 2 where the ageing was simulated by subjecting the containers to multiple cleaning/washing steps before the water bottling.

From PC Container 3, six cutout samples were prepared to determine inner surface changes due to their ageing. Their surfaces were derivatized with bromine vapor to quantify the phenolic OH end groups.

To evaluate the effect of regrinding of aged PC bottles on BPA migration PC Container 3 from previous experiments were reground and melt-formed into small bottles. In parallel, under the same processing conditions, new bottles were molded from virgin resin. Both types of bottles were filled with mineral water, stored at constant temperature, and afterwards the amount of BPA in the bottled water was determined

Contact media and migration conditions

The migration experiments with the PC films, plates, discs, and bars listed in Table I were performed by immersing the samples in vials containing different liquids—see Table II—and then monitoring the level of BPA and/or d_{16}-BPA in these media. The tests were performed at constant temperature.

The migration of BPA from the commercial PC containers and bottles was investigated by storing at constant temperatures water (different types) in them, see Table II. The loss of BPA and d_{16}-BPA from the outer surface of these PC samples to the surrounding atmosphere, by a diffusion-evaporation process, can be considered as negligible because the vapor pressure of BPA in air is very low, $p_{BPA} \sim 2 \times 10^{-7}$ mmHg at 20°C.

The water used in the PC Container 2 was purified via reverse osmosis, remineralized and sterilized in an ozonator. The ozone, O_3, concentration in this prepared ozonized mineral water was about 0.25 g/L.

The possible effect of ageing of PC on BPA migration was investigated by performing migration tests with PC Container 2 that had been subjected to multiple washing steps before water bottling. The washing procedure started by rinsing the containers with water and then washing them with a detergent solution at 60°C. Afterwards the containers were rinsed without heating with ozonized process water (0.4 mg O_3/L) followed by rinsing with ozonized mineral water. The residence time of the solutions in the containers in each washing step was about 10 s. Containers were washed 1, 25, or 50 times before being bottled with ozonized mineral water.

TABLE II
Migration Experiment Conditions

Type of sample	Contact medium	Contact conditions	
		Time (h)	Temperature (°C)
PC Films	LiChrosolv® H_2O 3% Acetic Acid	218–720	40, 60, or 80
PC Plate 1	LiChrosolv® H_2O	168	60
PC Plate 2	LiChrosolv® H_2O	4–368	40, 60, or 80
PC Plate 3	LiChrosolv® H_2O	672	40
PC Plate 3	Rhenser water	5,128	21–25
PC Bar	3% Acetic acid 10% Ethanol 50% Ethanol Olive oil	2 and 240, respectively	70 and 40, respectively
PC Bar	3% Acetic acid 10% Ethanol Olive oil	4 4 0.5	Total reflux Total reflux 121
PC Discs	Water 3% Acetic acid 10% Ethanol	720 0.5 + 240 0.5 + 240	40 100 + 40 100 + 40
PC Container 1	Milipore/Merck H_2O Rhenser water	5,128	21–25
PC Container 2	Mineral water	up to 4536	20–25
PC Container 3 PC Bottle 1	Several qualitative parameters like annealing, molding conditions, moisture levels, washing conditions, storage times and temperature, and water types		
PC Bottle 2	Deionized water	1,296	22, 38, or 54

A series of experiments was conducted to investigate a total of eight variables/parameters potentially influencing the migration of BPA from the PC Container 3. These parameters can be separated into three groups following the process of making and filling the containers.

1. Material and processing parameters: residual amount of BPA (low and high) and moisture in the PC resin (low and high) as well as molding conditions (normal and abusive) and final treatment by annealing (yes–no) during the manufacturing process.
2. Washing parameters: washing done at 60°C with sodium metasilicate (SMS) as detergent and chlorine (Cl_2), 60 or 100 ppm, or ozone (O_3), 0.34 or 0.26 ppm as sanitizing agent.
3. Storage and water quality parameters: different qualities of water (pH of 5, 7, or 9 and O_3 levels of 0.2 and 0.6 ppm, respectively) and storage time and temperature (25 or 48°C).

The investigation of the effect of these test conditions in all their combinations and levels on the BPA migration process would have required 576 experiments with the PC Container 3. By using a fractional factorial experimental design, this number was reduced to 219 experiments which simulated the combined effect of 8 molding combinations × 3 washing combinations × 8 storage conditions = 192 experiments. Additionally 27 selected combinations of containers and conditions were investigated as replicates for a good estimation of error to determine the standard deviation of the results.

To move from the investigation of large PC Container 3, which was resource intensive, smaller sized laboratory-scale PC Bottles 1 and 2 were manufactured. A full factorial design of experiments, to simulate the combined effect of 3 BPA residual levels (5, 12, and 26 ppm) × 2 pH levels (5.4 and 6.5) × 3 storage temperatures (21, 39, and respectively, 54°C) × 3 washing conditions (equivalent to 1, 3, or 5 years of filled use), was performed additionally with the PC Container 3 and Bottles 1 and 2. From a total of 72 experiments 18 were selected as replicates for an estimation of the standard deviation of the results. The entire experiment was executed twice, one using the PC Container 3 and then the laboratory scale PC Bottles 1 and 2.

To test the influence of the water quality parameters on the BPA migration process PC Container 3 and Bottles 1 and 2 were also filled with different types of mineral water, see Table III.

PC films and plates, see Table I, that were prepared from resin containing d_{16}-BPA to evaluate BPA migration mechanisms were exposed to LiChrosolv® analytical grade water and 3% acetic

TABLE III
Types of water used in the experiments with the PC Container 3
and PC Bottles 1 and 2

Water description	Container type	pH	Ozone level (ppm)
Bottled at: Bottling Plant 1			
Ozarka distilled water	PC Container 3	6.5	0.34
Ozarka distilled water	PC Container 3	5.4	n.d.
	PC Bottles 1 and 2		
Utopia spring water	PC Container 3	7.7	0.34
Oasis drinking water	PC Container 3	6.5	n.d.
	PC Bottle 2		
Bottled at: Bottling Plant 2			
Zephyrhills spring water	PC Container 3	7.7	0.26
Zephyrhills spring water	PC Container 3	7.7	0.56

acid at various temperatures, and were sampled over time to determine migration of residual BPA and d_{16}-BPA.

PC Bottle 2 that were prepared from resin containing d_{16}-BPA were exposed to deionized water at a constant temperature for 54 days. The migration of BPA and d_{16}-BPA was measured and the ratio of both determined.

Investigations were designed to study the effects of the alkali ions content of water (mineralization) and degradation of the PC on BPA migration.

To find out if there is a "back-diffusion" of BPA from water into PC, two types of water (Rhenser and Millipore/Merck), bottled in PC Container 2, were spiked with 20 ppb of d_{16}-BPA. Then the level of d_{16}-BPA remaining in the bottled waters was monitored over 214 days at room temperature.

In the regrind study, both the small bottles made from reground aged PC Container 3 and those made from virgin resin were subjected to washing, filling with mineral water and storage at elevated temperature. After 30 days the concentration of BPA in water was measured and compared.

Analytical methods and procedures

In a number of experiments involving migration of BPA from PC containers into water, samples were concentrated and injected directly into the analytical instrument without any further treatment. However, it was not possible to determine the level of BPA and d_{16}-BPA in the PC resins and in the other contact media used in these investigations (3% acetic acid, 10 and 50% ethanol, and olive oil) with this approach. Therefore, for these cases, alternate sample preparation procedures were developed.

Several analytical techniques were used for the different parameters. Residual BPA in the PC matrix was measured using HPLC with fluorescence detection after dissolving the polymer in dichloromethane and subsequent precipitation of the polymer with methanol. BPA levels in the aqueous food (simu-

lants) were determined with high-performance liquid chromatography (HPLC) with fluorescence detection (Em 230 nm/Ex 305 nm). Without any further enrichment a limit of detection of about 0.5–1 ppb BPA in water and 3% acetic acid was obtained.

For the simultaneous analysis of BPA and d_{16}-BPA in the PC resins and in the liquid contact media, gas chromatography coupled with mass spectrometric detection, GC/MS, was used. A limit of detection of 0.01 ppb was obtained.

To determine the degradation of PC Container 3 subjected to ageing/storage, an analysis of their inner surface was performed by using two experimental methods.

First the phenolic OH endgroups of PC were quantified by X-ray fluorescence spectroscopy (XPS). For this purpose, parts from the aged PC containers were cut out and the respective surface derivatized with bromine. The OH concentration in the samples can then be computed by multiplying from the Br atom percentage found with the XPS technique.

For measuring the molecular weight of PC samples, gel permeation chromatography (GPC) with UV detection at 254 nm was used. The interior surface samples were obtained by placing a piece of metal tubing on the surface of the sample and compressing the sample and tube in a vice to form a seal. Chloroform was added to the tube and allowed to remain for about 10 s. Afterwards the solvent was analyzed.

RESULTS AND DISCUSSION

Migration of BPA from PC samples into a liquid contact medium

The experimental results shown in Figures 3–6 are evidence of the dependence of BPA migration on time, t, temperature, T, and pH level. Concerning Figure 4 one must emphasize that pH = 10.1 is already far out of the relevant food realm. At lower pH values the scattering range is enhanced because of the low migration values. On can see that an
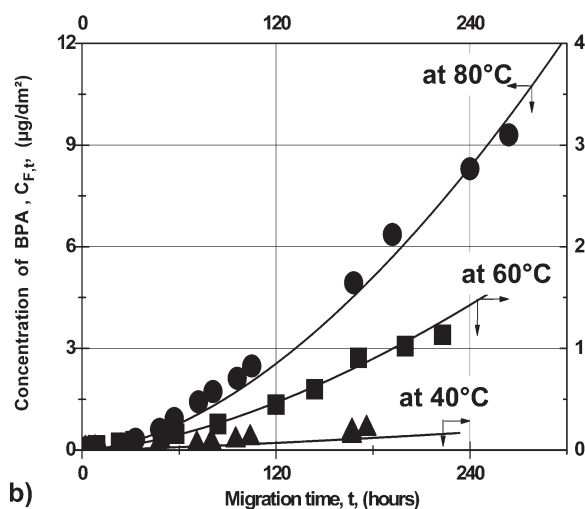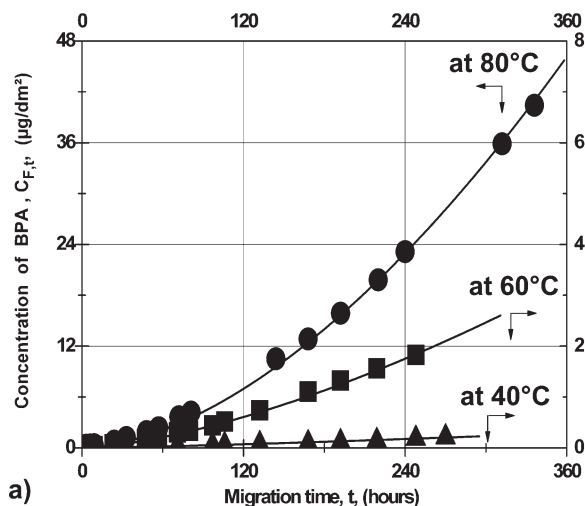
a)

b)

Figure 3 Time dependence of isothermal BPA migration, in μg/dm² units, from PC films into LiChrosolv® analytical grade water (a) and 3% acetic acid (b).
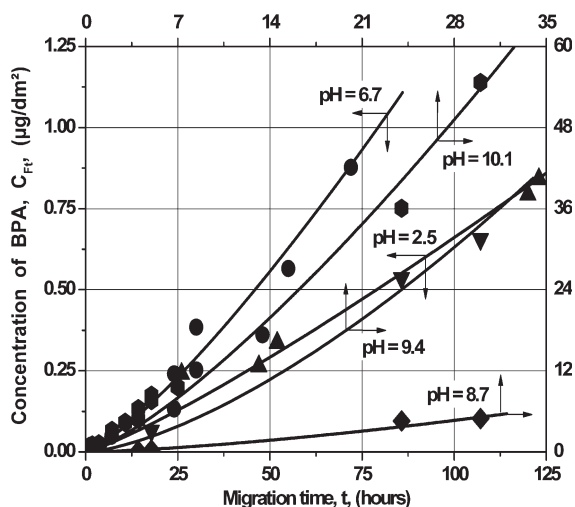

Figure 4 Dependence on pH of BPA migration, in μg/dm² units, from small PC platelets into demineralized water at 60°C.

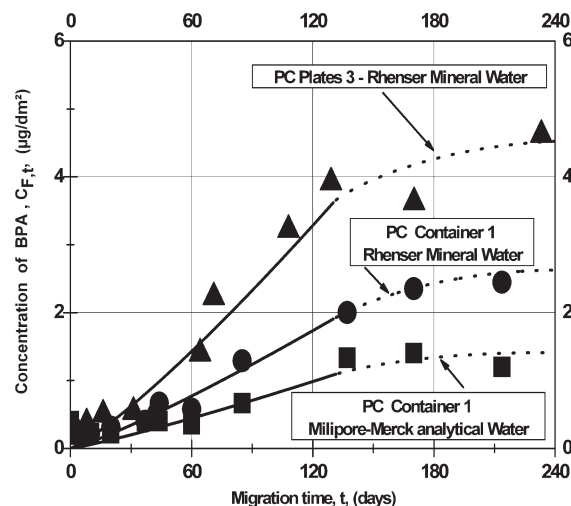**Figure 5** Migration of BPA, in μg/dm² units, from PC plates and containers made from the same PC resin into different qualities of water at 20°C.

increase of pH determines a steep increase of the BPA concentration, $C_{F,t}$, in water. For example, for a migration time $t = 24$ h, a shift of pH from 2.5 to 10.1 raises the migration level from about 0.13 to about 40 μg/dm². Although a log $C_{F,t}$ versus pH plot of these results is close to linear, due to the scatter of the experimental results, it is difficult to derive an equation related to the chemistry assumed to be responsible for these results.

From Figures 3–5 one can see that for a certain time, t, after starting the migration experiments, the slopes of the BPA migration curves steadily increase.

Similar results were obtained in all experiments performed with aqueous contact media. For a Fickian diffusion of BPA from the bulk of the PC
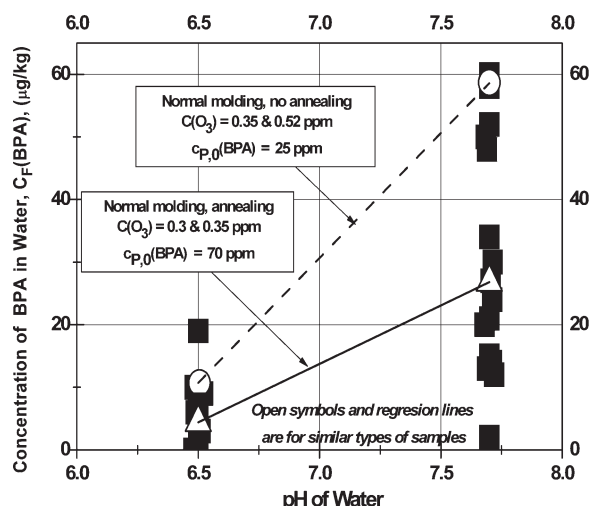

Figure 6 Dependence of BPA migration, in μg/kg units, from PC Container 3 on pH of water, 30 days at 48°C.

samples the migration curves should have shown a steadily decreasing slope from the very beginning of the experiments. Thus, the shape of the migration curves from Figures 3–5, supports the hypothesis that not Fickian diffusion from the bulk but hydrolysis at the surface of the PC samples is the main source of BPA release into an aqueous medium. In Figure 5 one can see that for longer runs, after a certain time, the migration curve shows a decreasing rate of BPA release from the PC samples. This can be attributed to the (i) inhibition of PC surface hydrolysis with time and (ii) absorption of BPA by the PC samples when its concentration in the liquid exceeds a certain value. The shape of the dotted portion of the curves from Figure 5 suggests this trend. The scatter and limited number of results at "longer times" did not allow the development of a model to quantify $C_{F,t}$ for the whole duration of these longer runs.

The results shown in Figure 5 refer to samples which were produced using the same PC resin. One can see here that there is a difference in migration level between the blow-molded PC Container 1 and the PC Plate 3. This may be assigned to differences in concentrations of open PC chain ends (OH) on the surface of the PC samples probably caused by the different process-inherent characteristics of surface forming. From Figure 5 one can also see that the BPA migration into water is dependant on the nature of the water filled into the PC containers. The commercial Rhenser mineral water and Millipore/Merck analytical water are known to differ in pH values and mineral content. This suggests that one or both of these parameters influence the PC surface hydrolysis process.

To check the hypothesis of PC backbone hydrolysis at the interface with the aqueous medium two additional measurements were done to determine surface changes of the PC Container 3. The first one quantified the phenolic OH end groups by using X-ray fluorescence spectroscopy (XPS). The second measured the molecular weight of a surface sample in comparison to a bulk sample to determine degradation, see Table IV. The GPC analysis revealed that the inside surface of all bottles was degraded relative to the bulk which is consistent with the proposed mechanism of PC hydrolysis at the contact surface with the aqueous medium.

Figure 6 shows the results for two sets of 20 PC Container 3 filled for 30 days with water with pH 6.5 and 7.7, respectively. The general finding is that rising the pH level of water in one and the same type of container leads to an increased migration (in Fig. 6 this is highlighted by two straight lines corresponding to two pairs of identical containers). This is consistent with the findings already reported above in Figure 4.

TABLE IV
Molecular weight analysis of the aged PC Container 3

Bottle age (years)	Sample	Molecular weight in bulk (g/mol)	Molecular weight of surface layer (g/mol)	Concentration of OH-end groups (ppm)
3	1a	61,620	53,293	3,180
	1b	60,856	43,492	3,816
5	3a	63,835	36,622	6,360
	3b	61,688	48,238	2,544
7	5a	63,417	42,133	4,452
	5b	67,722	39,835	3,816

In Figures 3–5 the sections of isothermal migration curves which exhibit an increasing slope were fitted quite well by using a simple empirical equation:

$$c_{F,t}(\text{BPA}) = B_P(\text{BPA})t^{\beta} \qquad (1)$$

This was found to be valid for all time-dependent migration experiments (TDM), presented by the PC producing companies for this review. Table V summarizes the B_P(BPA)s and βs obtained by fitting with eq. (1) all TDMs for which at least five experimental results were reported for the considered portion of the migration curve.

Qualitatively the results shown in Table V suggest that the parameter B_P(BPA) depends on the temperature T, the special PC sample/contact medium-system (e.g., the type of PC, ingredients in the aqueous medium) as well as the characteristics of the PC sample/medium interface (e.g., roughness). However, due to the limited number of experimental results it is not yet possible to derive quantitative conclusions in this respect. On the other hand, the data from Table V seem to show that the parameter B_P(BPA) is not dependent on the thickness d_p of the PC samples or their residual BPA content.

From Table V one can estimate for PC Plates 3 an activation energy, E_a, for the process responsible for the release of BPA into water. For migration times shorter than 15 days one obtains $E_a \sim 128$ kJ/mol.

Plotting from Table V the β versus the temperature T, Figure 7, one can see that they generally increase with T. This trend is more obvious when plotting the mean values ⟨β⟩ and could be interpreted as an applicability of the Arrhenius law to the hydrolysis of the PC samples.

In terms of the commercial manufacture of bottles or containers from polycarbonate resin, normally via blow-molding or injection-blow-molding, it is important to understand the impact of production variables, such as molding conditions and the content of moisture and residual BPA in the resin on the migration of BPA when the containers are used to hold water. The results obtained in this work

TABLE V
Parameters for the migration of BPA from PC samples into different qualities of water and 3% acetic acid

Polycarbonate sample				Contact medium					
				Reverse osmosis Rhenser or Mineral water		H$_2$O Lichrosolv Millipore or Demineralized water		3% Acetic acid	
Type	Thickness (μm)	Conc. $C_{P,0}$ (BPA) (ppm)	Temp. (°C)	B_P(BPA) (μg/dm^2 h) × 10^4	β	B_P(BPA) (μg/dm^2 h) × 10^4	β	B_P(BPA) (μg/dm^2 h) × 10^4	β
PC Container 1	1,200	2.5	20	1.5	1.15	–	–	–	–
	1,200	2.5		–	–	1.7	1.15	–	–
	1,200	2.6		2.7	1.17	–	–	–	–
	1,200	2.6		–	–	0.95	1.145	–	–
PC Container 2	1,700	7.0		2.5	1.34	–	–	–	–
	1,700	7.0		2.35	1.33	–	–	–	–
	1,700	7.0		1.8	1.36	–	–	–	–
PC Plate 2	2,000	2.5		4.37	1.2	–	–	–	–
PC Films	65	5	40	–	–	4.0 (pH = 6–6.5)	1.3	–	–
	70	4		–	–	1.0 (pH = 6–6.5)	1.3	0.9	1.26
	80	5		–	–	3.1 (pH = 6–6.5)	1.3	–	–
	80	4		–	–	3.4 (pH= 6–6.5)	1.3	0.89	1.3
	80	4		–	–	1.4 (pH= 6–6.5)	1.3	0.5	1.34
	80	4		–	–	1.5 (pH= 6–6.5)	1.3	0.65	1.31
PC Plate 3	2,000	5		–	–	1.75	1.42	–	–
	2,000	9		–	–	5.5	1.25	–	–
	2,000	9		–	–	5.3	1.27	–	–
PC Disc	3,157	–		1.35	1.23	–	–	–	–
PC Container 3	1,250	70	48	17.5 (pH = 6.5)	1.41	–	–	–	–
	1,250	70		87.1 (pH = 7.7)	1.43	–	–	–	–
PC Films	70	4	60	–	–	4.3 (pH = 6–6.5)	1.65	1.65	1.6
	75	5		–	–	2.8 (pH = 6–6.5)	1.65	2.1	1.61
	75	5		–	–	2.15 (pH = 6–6.5)	1.615	1.55	1.6
	80	4		–	–	2.9 (pH = 6–6.5)	1.52	1.8	1.62
	80	4		–	–	4.1 (pH = 6–6.5)	1.53	1.05	1.61
	80	4		–	–	4.7 (pH = 6–6.5)	1.54	1.1	1.63
PC Plate 1	2,000	5		–	–	3.0	1.59		
	2,000	5		–	–	6.0	1.45	–	–
PC Plate 3	2,000	5		–	–	6.4	1.4	–	–
	2,000	4		–	–	5.1	1.52	–	–
	2,000	5		–	–	11.0	1.56	–	–
PC Platelets	2,000	4		–	–	28.8 (pH = 2.5)	1.18	–	–
	2,000	4		–	–	38.7 (pH = 6.7)	1.27	–	–
	2,000	4		–	–	384.6 (pH = 8.7)	1.44	–	–
	2,000	4		–	–	2043.4 (pH = 9.4)	1.50	–	–
	2,000	4		–	–	6250.4 (pH = 10.1)	1.31	–	–
PC Films	75	4	80	–	–	18.5 (pH = 6–6.5)	1,72	–	–
	75	5		–	–	15.0 (pH = 6–6.5)	1.56	–	–
	75	5		–	–	–	–	7.1	1.71
	75	5		–	–	–	–	8.0	1.57
	75	5		–	–	–	–	8.35	1.68
	80	4		–	–	–	–	7.3	1.76
	80	4		–	–	–	–	7.5	1.64
PC Plate 3	2,000	4		–	–	95.0	1.725	–	–

indicate that the blow-molding and subsequent annealing process, as well as the BPA and residual moisture content of the PC resin processed had little, if any, effect on the extent of BPA migration from the containers into the bottled water. The scatter of the experimental results with PC Container 3 (used containers which were reground and reprocesses to new ones) was attributed mainly to the fluctuations of the container parameters resulting from the manufacturing process as well as to the normal variability observed with analytical measurements of a migration experiment. Also different conditions of washing the new bottles after production did not cause significant differences in BPA migration behavior.
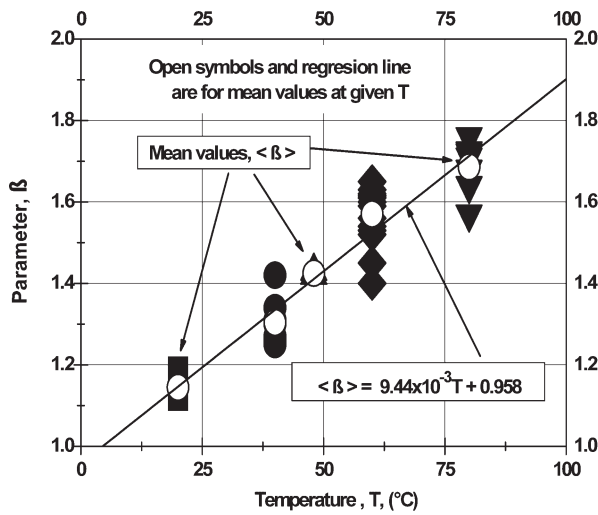
Figure 7 Temperature dependence of the parameter, β.

The influence of the washing conditions was assessed by looking at the analysis of variance (ANOVA) of the migration results obtained. No regression was performed since the three different washing conditions do not represent a continuous variable. The ANOVA showed that the differences due to the different washing conditions used are just outside of statistical significance (95% confidence interval).

These experiments underscore that BPA migration into the water must be attributed primarily to hydrolytic degradation of PC rather than to Fickian diffusion of BPA from the matrix of the polymer. Otherwise an increase of the residual content $C_{P,0}(BPA)$ from about 25 to 70 ppm would have caused about a threefold increase of the BPA level, $C_{F,t}(BPA)$, in water.[7] However, such a behavior was
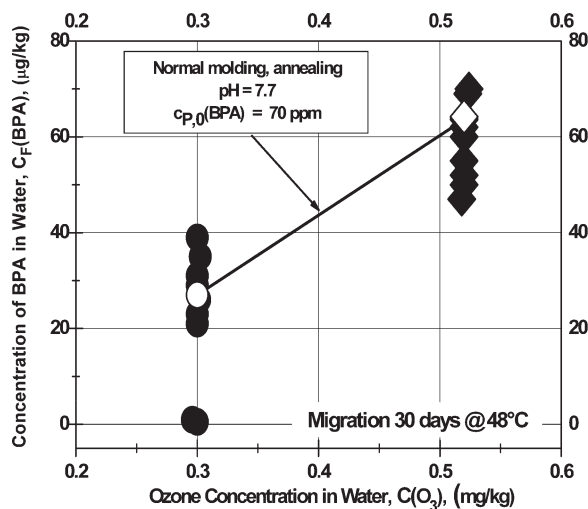

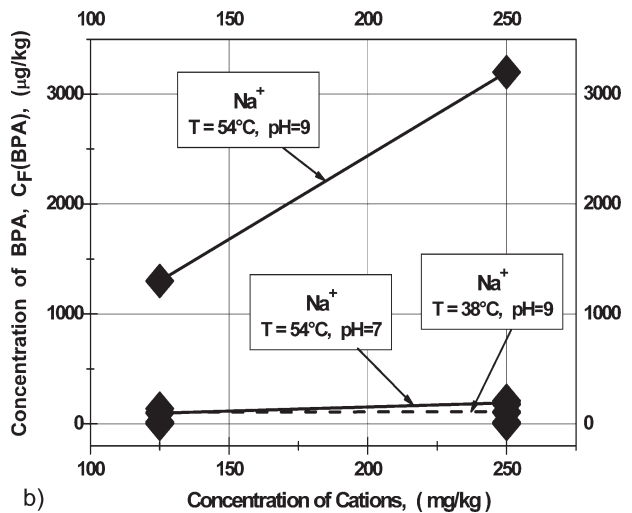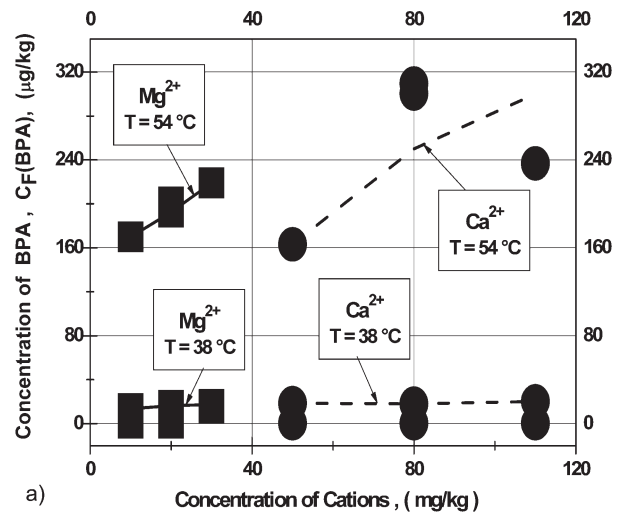**Figure 8** Effect of ozone (O_3) content of bottled water on the migration of BPA, in µg/kg, units, from PC Container 3.

Figure 9 Effect of cations on migration of BPA, in µg/kg units, from PC Bottles 2 into mineralized water.

not found in any of the experiments reported in this review.

Figure 8 shows the results for two sets of 10 PC Container 3 filled for 30 days with water with an ozone concentration of about 300 and 520 ppb, respectively. The general finding is that rising the ozone concentration of water leads to an increased migration (in Fig. 8 this is highlighted for one pair of identical containers filled with the same type of water). Ozonized water is sometimes used in the container washing process before refilling.

Additional experiments were conducted with the PC Bottles 2 to observe the influence of common mineral content of bottled waters on the PC hydrolysis process by adding neutral salts of Na^+, Ca^{2+}, and Mg^{2+} cations. A number of 42 experiments plus 12 replicates were performed at three levels of T, pH, and cation concentration, respectively. The results in Figure 9 show that at elevated temperatures an increased mineral concentration of the
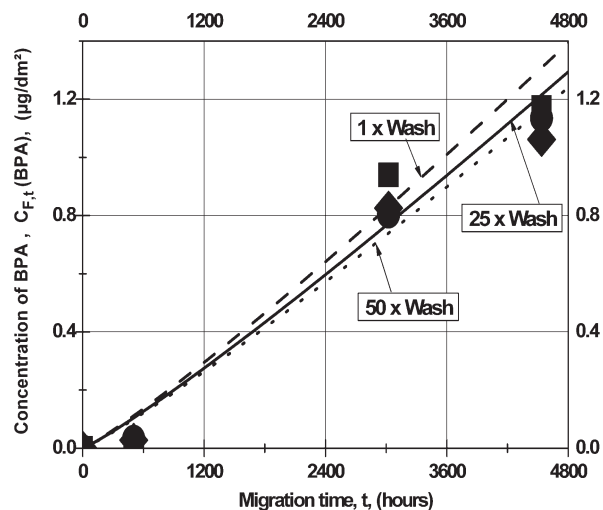
Figure 10 Effect of PC Container 2 washing on the migration of BPA, in $\mu g/dm^2$ units, into water.

water leads to an increased BPA migration. With Na+ this effect is accentuated by a higher pH, too. However, at room temperature and/or typical drinking water pH levels these interactions seem to be very small. This may suggest that under these later conditions the PC hydrolysis is not catalyzed by any of the cations investigated.

Another factor which was thought to have an influence on the BPA migration from a PC container into water is the number of washing cycles during the container cleaning process before bottling the water in it. To test this hypothesis a series of PC Container 2 were subjected to up to 50 such cycles (see "Contact Media and Migration Conditions" section). The results of this investigation show that, within the limits of the experimental errors, the washing process of PC water containers and cycling this process did not cause a significant change of BPA migration into the water, see Figure 10.

Similar results were also obtained with the PC Container 3. Also the washing conditions—different washing temperatures, detergents, and sanitizers (Cl_2 or O_3) used—were found to be outside of statistical significance on the subsequent migration of BPA from the PC containers into the bottled water and thus on the PC surface hydrolysis.

The influence of the PC container age on the migration of BPA into the bottled waters was checked by means of an additional series of experiments with 3-, 5-, and 7-year-old PC Container 3, Figure 11. With these aged containers it was not possible to control previous molding and washing parameters.

The results shown in Figure 11 seem to indicate that at room temperature there is little or no effect on the BPA migration from Container 3 due to their

age. However, at a higher storage temperature, $T = 48°C$, migration from the 5 and 7 years old containers increased. This effect seems to be further enhanced by a higher pH level of the bottled water. Other experimental results indicated that the age of Container 3 in interaction with higher temperatures and rising water ozone levels leads to an increased BPA migration level, too.

From Table IV it is obvious that a degradation of the inner surface of the PC Container 3 and a concomitant increase of the number of open PC chain ends during the ageing process took place. Because of that one can assume that hydrolysis rates of aged PC surfaces in a migration experiment with aqueous media will be enhanced in comparison with a smooth new PC surface.

Further experiments were conducted with contact media other than drinking water to better cover the influence of different natures of food on the migration of BPA from PC being in contact with these media. Some of the results obtained are summarized in Table VI.

From Table VI one can see that the migration in water-ethanol mixtures is higher than in pure water. A reason for this could be that, with increasing ethanol content, the solubility of BPA in water-ethanol mixtures increases which determines a different partitioning/kinetic partitioning of BPA between PC and liquid.

It is obvious that, under similar experimental conditions, the lowest level of BPA migration from PC is linked with olive oil. This is surely attributable to the facts that such a nonaqueous nonpolar liquid can neither hydrolyze polycarbonate nor solve BPA well.
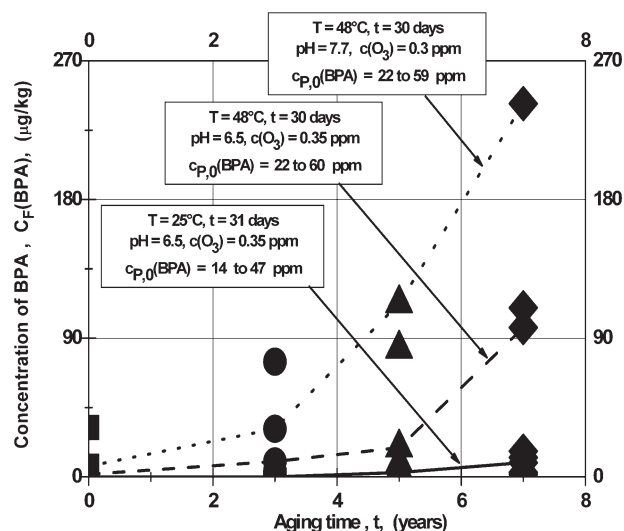

Figure 11 Effect of PC Container 3 aging on the migration of BPA, in $\mu g/kg$ units, into water.

TABLE VI
Migration of BPA from PC samples into various food simulants

Type of sample	Contact medium	Migration level (µg/dm²)				
		10 days at 40°C	2 h at 70°C	4 h at Reflux	0.5 h at 121°C	0.5 h at 100°C followed by 10 days at 40°C
PC Films	H₂O LiChrosolv®	0.13	–	–	0.08	–
d_p = 80 µm	3% Acetic acid	0.41	–	–		–
$C_{P,0}$ (BPA) = 4.0ppm						
PC Bars	3% Acetic acid	0.20	0.28	0.85	–	–
Diameter = 4 mm	10% Ethanol	0.30	0.19	0.87	–	–
$C_{P,0}$ (BPA) = 9.3ppm	50% Ethanol	0.45	0.26	–	–	–
	Olive oil	0.09	0.14	–	–	–
PC Plates	H₂O LiChrosolv®	–	–	0.08	–	–
d_p = 2 mm	50% Ethanol	–	–	0.22	–	–
$C_{P,0}$ (BPA) = 5.0 ppm						
PC Disc	Water	0.20	–	–	–	–
d_p = 3.157 mm	10% Ethanol	–	–	–	–	0.091
	3% Acetic acid	–	–	–	–	0.108

Migration of deuterated-BPA from and into a PC sample being in contact with an aqueous medium

To assess the contribution of the BPA mass diffusion from the bulk of polycarbonate to the overall release of BPA into the contacting liquid medium experiments were conducted with samples, to the PC matrix of which, small amounts of deuterated BPA (d₁₆-BPA) were added.

For one the diffusion of d₁₆-BPA from the PC matrix into a liquid contact medium was investigated by TDM experiments with cat films. Some of the results obtained are presented in Figure 12. Comparing the migration levels of BPA and d₁₆-BPA in Figures 3 and 12 one can see that the BPA concentration in water originating from PC surface hydrolysis (makes up the majority of the BPA in Fig. 3) did in all cases much surpass the concentration of d₁₆-BPA originating from diffusion from the spiked PC samples (Fig. 12), and this was despite the fact that in the spiked PC Films the concentration of residual BPA was at least one order of magnitude smaller than that of d₁₆-BPA. This indicates that PC surface hydrolysis in aqueous media is a BPA generating process that contributes much more to the migration of BPA than the diffusion of any residual BPA from the bulk of PC. Similar results were obtained from investigations made with PC Bottle 2 (see Table VII).

The migration curves given in Figure 12 have the classical shape typical for a diffusion-controlled, partition limited migration process. This form differs from the shape of the migration curves shown in Figures 3–5 and discussed in "Migration of BPA from PC Samples into a Liquid Contact Medium" section. The results from Figure 12 were fitted with theoretical curves in which the adjustable parameters were the diffusion coefficient, D_p, of the d₁₆-BPA molecules in the matrix of the PC samples and their partitioning coefficient, $K_{P,F}$, at the polymer-contact medium interface ($K_{P,F}$ denotes the ratio of the equilibrium concentrations of the migrant in the polymer and the contact medium). It is assumed that the migration of d₁₆-BPA from the polymeric sample of a given thickness, d_p, into a finite volume of the contact medium, V_F, obeys Fick's laws, and that D_p is independent of the migrant concentration in the PC matrix. To fit the experimental results starting values for the adjustable parameters were chosen and by successive iterations the curve fitting program delivered a pair of D_p and $K_{P,F}$ values, for which the least squares error to the experimental points was minimum. Using this procedure for all time-dependent d₁₆-BPA migration experiments the D_ps and $K_{P,F}$s summarized in Table VII were obtained.

The small molecular mass difference of 228–244 g/mol would not be expected to cause a sizeable difference between the D_ps of BPA and d₁₆-BPA (see Refs. [8] and [9] for the effect of isotopic mass differences on diffusion in polymers). Thus one can assume that in the same PC resin and under similar experimental conditions, the diffusion coefficients of BPA and d₁₆-BPA are about equal.

At ambient temperatures diffusion in liquids proceeds at a pace of about 10^{-5} cm²/s.[10] In elastomers small molecules with a molecular mass of 150–250 g/mol exhibit diffusion coefficients in the range of 5×10^{-9} to 1×10^{-11} cm²/s[11–16] and about 5×10^{-10} to 1×10^{-11} cm²/s in polyolefines (polyethylene, polypropylene).[17] Therefore, the results in Table VII point out that the diffusion coefficient of BPA in the PC matrix is up to more than six orders of
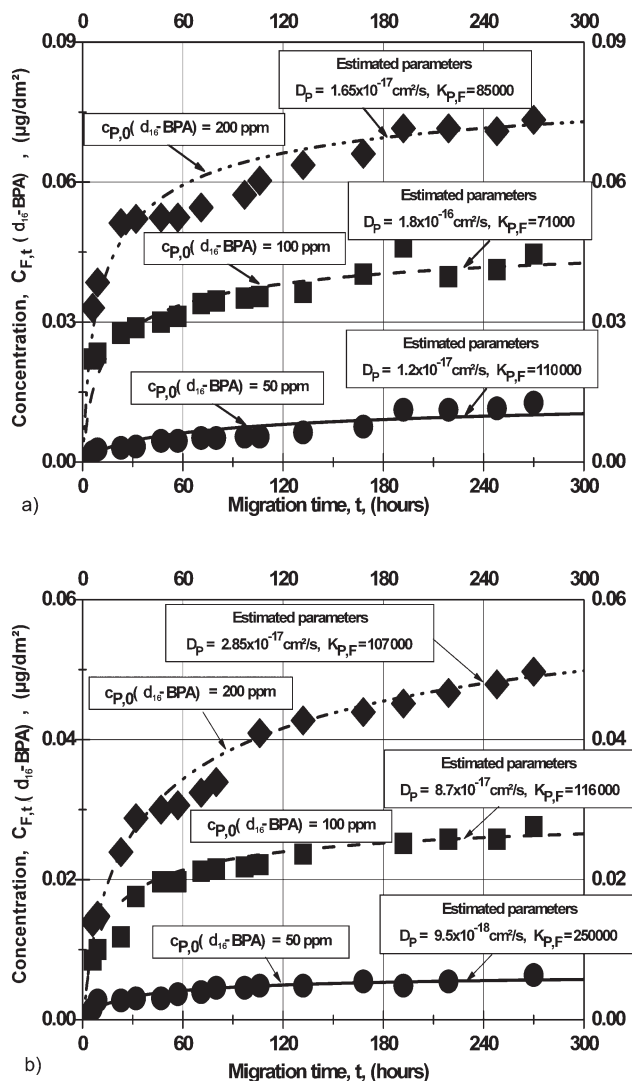
Figure 12 Time-dependent migration of d_{16}-BPA, in $\mu g/dm^2$ units, from PC films into LiChrosolv® analytical grade water at 60°C (a) and 3% acetic acid at 40°C (b).

ing of d_{16}-BPA between the polymer and the aqueous contact medium. This should be valid for BPA too and means in fact that BPA solves much better in the polymer matrix than in an aqueous liquid phase. A high $K_{P,F}$ leads to small equilibrium concentrations of BPA $C_{F,t}(BPA)$ in the contact medium. From a practical point of view, a high $K_{P,F}$ value acts in a diffusion-driven migration process as a thermodynamic brake at the plastic/medium interface.

On the other side, a high $K_{P,F}$ could determine a surface-to-bulk "back migration" of BPA from the aqueous medium into the PC sample. This process can be estimated for example from Figure 5 for the PC Container 1. At 20°C, for contact times exceeding 120 days, the concentration of BPA in the bottled water is about 3 ppb (as a result mainly of the hydrolysis of PC). Assuming that at this temperature the D_p for BPA in PC is about 10^{-18} cm²/s and $K_{P,F}$ about 150,000 (see Table VII) one can compute the "back migration" of BPA from water to the PC containers.[18] The BPA concentration profiles resulting from this process are shown in Figure 13 in a very narrow region around the PC-Water boundary.

From here one can see that, in a thin "boundary layer" of the PC samples (about 0.2 μm thick), the mean concentration of the "back migrated" BPA would be quite high, about 200 ppm.

This process of "back migration" of BPA from water into a PC sample was checked in another experiment, too. PC Container 1 was filled with Millipore analytical and Rhenser commercial mineral water, respectively, to which 20 ppb of d_{16}-BPA was added. The containers were stored at room temperature for up to 214 days and the d_{16}-BPA content of the bottled water monitored from time to time. Although the scatter of the experimental results was rather high, they show that for times exceeding 30 days the mean d_{16}-BPA concentration in the bottled waters is about 16% smaller than its initial value. Calculating, with the parameters given above, the migration of d_{16}-BPA from water to the PC Container 1 yielded an average decrease of d_{16}-BPA concentration in water of about 12%, for migration times between 30 and 214 days. Taking into account all sources of errors these two results agree quite well to sustain "back diffusion" of BPA from water into PC as would be expected.

Table VIII shows the results of the migration experiments with the PC Bottle 2 spiked with small amounts of deuterated BPA. The table lists for each bottle the initial concentrations of nondeuterated and deuterated BPA and the corresponding concentrations in the water after 54 days of exposure of exposure at 54°C. In addition, the average ratio of the initial concentrations c(BPA)/c(d16-BPA) in the

magnitude smaller than found for similar sized molecules in most nonglassy polymers used in food packaging. This means that a diffusion-driven migration of BPA from the bulk of a PC sample at typical consumer use conditions proceeds at a very low pace.

In Table VII one can see that, for the 80-μm-thick PC films, the increase of d_{16}-BPA concentration from about 50 to 100 or 200 ppm generally causes a sizeable increase of the migrant's diffusion coefficient. This could be an indication that, below a certain threshold concentration, the d_{16}-BPA molecules are solved in the PC matrix predominantly in sites of stronger bonding. However, the limited number of experimental results available does not allow a more comprehensive analysis/discussion of this topic.

Concerning the partitioning coefficients, $K_{P,F}$, one should note that there is a strongly shifted partition-

TABLE VII
Diffusion and partitioning coefficients for the migration of d_{16}-BPA from PC films into water and 3% acetic acid

	Polycarbonate sample			Contact medium H$_2$O LiChrosolv®		Contact medium 3% Acetic acid	
Type	Thickness (μm)	Concentration, $C_{P,0}$(d_{16}-BPA) (ppm)	Temperature (°C)	Diffusion coefficient, D_P (cm^2/s) × 10^{18}	Partitioning coefficient, $K_{P,F}$	Diffusion coefficient, D_P (cm^2/s) × 10^{18}	Partitioning coefficient, $K_{P,F}$
PC Film	70	50	40	2.00	195,000	4.75	285,000
	80	50		1.35	297,500	9.50	250,000
	80	100		42.5	107,500	82.0	116,000
	80	200		25.0	115,000	28.5	107,000
PC Film	70	50	60	40.0	98,500	82.5	64,000
	75	100		250.0	55,000	25.0	120,000
	75	200		190.0	48,000	400.0	54,000
	80	50		12.0	110,000	95.0	75,000
	80	100		180.0	71,000	260.0	73,000
	80	200		165.0	85,000	77.0	105,000
PC Film	75	100	80	775.0	8,350	940.0	5,250
	75	200		950.0	6,100	875.0	22,000
	80	100		–	–	400.0	3,250
	80	200		–	–	260.0	12,500

sample resin and of migrant concentrations in the bottled waters after 54 days of exposure is given.

The BPA/d_{16}-BPA ratio in the water, at any time, should be about the same as the initial ratio in the polymer if migration is only governed by diffusion from the bulk of the PC samples (within the limits of the experimental errors). However, due to the much higher concentration of BPA in water than what would have resulted only from the diffusion from the bulk of the PC bottles, the ratio c(BPA)/ c(d_{16}-BPA) in water is many orders of magnitude higher than that in the polymer. Thus the above results also support the hypothesis that hydrolysis of the polycarbonate at the interface between the

plastic and the aqueous foodstuff is the main source of BPA in the bottled water.

The process of manufacturing spiked PC Bottle 2 by mixing small quantities of d_{16}-BPA into the PC resin and subsequently extruding, pelletizing, and blow-molding the bottles, can be suspected to lead to a nonuniform distribution of the d_{16}-BPA in the bulk of the polymer matrix. Such effects were mentioned for example for slipping agents mixed into polypropylene.[19] How d_{16}-BPA was distributed in the matrix of the spiked PC Bottle 2 was not investigated in the present work. But even if one assumes that, the added d_{16}-BPA was not distributed
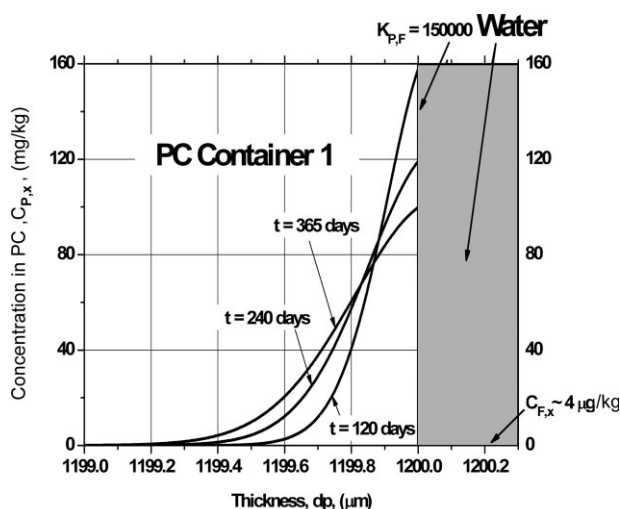

Figure 13 ''Back-migration'' BPA concentration profiles in PC.

TABLE VIII
Migration of BPA and d_{16}-BPA from PC Bottle 2 into deionized water at 54°C

PC Bottle 2 Sample No	Initial mean concentration in resin $c_{P,0}$ (mg/kg)		Migrant concentration in water after 54 days at 54°C $c_{F,t}$ (mg/kg)	
	BPA	d_{16}-BPA	BPA	d_{16}-BPA
1	2.2	5.6	119	<0.001
2	2.0	6.0	105	<0.001
3	2.6	5.7	–	–
4	2.2	6.0	109	<0.001
5	2.0	5.4	133	<0.001
6	2.3	6.6	117	<0.001
7	1.7	6.1	149	<0.001
8	2.4	6.0	106	<0.001
9	2.0	5.9	102	<0.001
10	1.8	6.3	–	–
Average	2.1	6.0	118	<0.001
$\frac{c(BPA)}{c(d_{16}-BPA)}$	0.35		>118,000	

uniformly in the PC resin, the shear quantity of the migration results obtained with the PC Bottle 2 can not possibly be expected. After 54 days of contact at 54°C between PC and water the overall d_{16}-BPA concentration in all water samples was below the 0.001 ppm detection limit of the analytical method used. At room temperature this migration process would proceed even slower making it hard to quantify the d_{16}-BPA content of the bottled water for much longer times.

Statistical analysis of BPA migration

The comprehensive set of data obtained from the investigation of the PC Container 3 was analyzed from a statistical point of view, too. For this each level in the experimental design was analyzed separately. The analysis of variance (ANOVA) and the response surface regression show that five migration parameters are significant in describing the observed BPA levels in water:

experimental temperature, T,
pH level of water,
ozone concentration in water,
interaction of T and pH, and
interaction of ozone concentration and T.

The regression coefficient ($r^2 = 0.981$) and residual error show that these parameters explain more than 98% of the observed variability. Any additional variables introduced at this level did not add any more value to the analysis and therefore lead to a reduction in the correlation coefficient. The PC Container 3 were large commercial bottles taken from a standard production line of a commercial molder. Smaller bottles (PC Bottles 1 and 2) were used to take into consideration the limited space available in the lab-scale experimental set-up. A comparison was made to see if migration results obtained with large commercial bottles were comparable with the ones for lab produced smaller bottles. It was found that they behave similarly. The BPA levels measured in the water from PC Bottles 1 and 2 were more scattered, ranging from non detection to 38 ppb. This can be explained by the change of surface to volume ratio which is about four times higher for the small bottles than for the large water containers. The overall experimental average values also changed by a factor of about 4. The three main migration parameters mentioned above accounted in this case for only about 68% of the variability of the measured BPA migration levels. Because of the increased variability in the small scale experiment only a qualitative comparison with the large scale can be established.

Comparison of BPA migration data with regulatory requirements

A series of samples have been tested to verify compliance of BPA migration from PC with the EU specific migration limit (SML) of 600 μg/kg food (or 100 μg/dm²), applicable to plastics in contact with foodstuffs, as described in EU Directive 2002/72/EC as amended. Testing conditions have been selected according to the rules laid down in EU Directive 97/48/EC. The results are displayed in Table VIII and all data were found to be well below the specific migration limit. Details on the legislation of the European Union (EU) for food contact materials are given in Ref. 20.

CONCLUSIONS

Migration experiments with a large number and variety of laboratory PC test specimens or commercial PC water containers used for the bottling of drinking water were performed. Therefore, one can state that the results obtained represent a good cross section of PC products used in the food-contact market. Migration experiments performed with samples spiked with deuterated BPA revealed that diffusion controlled migration has only a minor contribution to the release of BPA from polycarbonate articles into aqueous liquids. The experimental data sustain the assumption that responsible for this process is the hydrolysis of the polycarbonate polymer chains at the interface with the aqueous media. Over the range of experiments conducted the levels of BPA migration measured into contacting aqueous media were found to be essentially independent of the residual concentration in the polycarbonate (2–70 ppm).

An attempt was made to quantify this process with a simple empirical equation. However, this equation is valid only for the initial stage of the BPA release from the PC samples into the aqueous medium. For longer times, inhibition of PC surface hydrolysis and absorption of BPA by the PC sample itself were assumed to lead to a steady decrease (and eventually a stopping) of the rate of BPA migration.

The d_{16}-BPA/BPA diffusion coefficients in the PC matrix calculated from the TDM experiments are orders of magnitude lower than those for polyolefine polymers (low and high density polyethylene and respectively, polypropylene) widely used in food packaging.

The much higher solubility of BPA in the PC matrix as compared to that in water could be responsible for a "back-migration" of the BPA released from the polymer as a result of the hydrolysis. However, because of the very low D_ps of BPA in PC, the rate

of this process is very slow and at room temperature it affects only a very thin layer below the surface of the PC sample.

All migration levels obtained from experiments performed under standard conditions as described in the EU legislation and the associated guidance documents were found to be well below the EU specific migration limit (SML) of 600 μg/kg food, which applies to plastics in contact with foodstuffs, as described in EU Directive 2002/72/EC as amended.

For lack of hydrolytic activity and being a bad solvent for BPA, migration is lower in oil, when compared to migration into aqueous food simulating solvents (water, 3% acetic acid, 10% ethanol, and 50% ethanol).

In addition to the exposure temperature, the following variables were shown to have an effect on the BPA migration from polycarbonate in contact with water:

1. pH of the water: higher pH levels lead to higher migration levels. At room temperature, the presence of cations in the bottled water seem to have no influence on the migration levels, from which it is concluded that they do not catalyze the polycarbonate hydrolysis reaction.
2. Ozone concentration of water: an increased O_3 concentration in the bottled drinking water determines, under identical contact conditions, a higher BPA concentration in the liquid.
3. Surface ageing of the polycarbonate material: at elevated temperatures higher migration levels of BPA are observed in migration experiments with PC water containers which have been in commercial use for 3–7 years. Spectroscopic and a molecular weight analysis of the polycarbonate surface showed that BPA and low molecular weight species accumulate at the surface resulting in increased BPA level during the migration testing.

Molding conditions, applied during the manufacturing of the PC water containers, appear to have no significant effect on the migration levels.

Regrinding and remolding of aged PC containers results in regenerated surfaces, BPA migration from remolded aged polycarbonate samples is comparable to new bottles.

References

1. The EU risk assessment on BPA (full report). Available at: http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/ REPORT/bisphenolareport325.pdf.
2. European Commission. Directorate Food Contact Materials, EU Directive 2002/72/EC and Its Amendments, Brussels 2002 and Practical Guide; European Commission: Brussels, 2004.
3. The Opinion of the European Food Safety Authority on the Re-assessment of Bisphenol A (abstract). Available at: http://www.efsa.europa.eu/etc/medialib/efsa/science/afc/afc_opinions/bisphenol_a.Par.0001.File.dat/afc_op_ej428_bpa_op_en.pdf. Published online on January 29, 2007.
4. Brede, C.; Fjeldal, P.; Skjevrak, I.; Herikstad, H. Food Addit Contam 2003, 20, 684.
5. Ehlert, K. A.; Beumer, C. W. E.; Groot, M. C. E. Food Addit Contam 2008, 25, 904.
6. Biles, J. E.; McNeal, T. P.; Begley, T. H.; Holliefield H. C. J Agric Food Chem 1997, 45, 3540.
7. Crank, J. In The Mathematics of Diffusion, 2nd ed.; Claredon Press: Oxford, 1990; p 44.
8. Frisch, H. L.; Rogers, C. E. J Chem Phys 1964, 40, 2293.
9. Mercea, P.; Tosa, V. Isotopenpraxis 1985, 21, 413.
10. Cussler, E. L. Diffusion: Mass Transfer in Fluid Systems, 2nd ed.; Cambridge University Press: London, 1997.
11. Aminabhavi, T. M.; Munnolli, R. S. Polym Int 1993, 32, 61.
12. Aminabhavi, T. M.; Munnolli, R. S. Polym Int 1995, 36, 353.
13. Kariduraganavar, M. Y.; Kulkarni, S. B.; Aminabhavi, T. M. J Appl Polym Sci 2003, 88, 840.
14. Kariduraganavar, M. Y.; Kulkarni, S. B.; Aminabhavi, T. M. J Appl Polym Sci 2003, 89, 3201.
15. Kariduraganavar, M. Y.; Kulkarni, S. B.; Aminabhavi, T. M. J Appl Polym Sci 2003, 90, 3100.
16. Dubey, V.; Gupta, A. K.; Maiti, S. N.; Rao, N. B. S. N. J Appl Polym Sci 2000, 77 2472.
17. Mercea, P. In Plastic Packaging; Piringer, O.-G., Banner, A. L., Eds.; Wiley-VCH: Weinheim, 2008; p 525.
18. Mercea, P.; Piringer, O.; Tosa, V.; Petrescu, L. MIGRATEST© EXP, Software for Migration Estimation; FABES GmbH: Munich, 2008.
19. Quijada-Garrido, I.; Barrales-Rienda, J. M.; Frutos, G. Macromolecules 1996, 29, 7164.
20. Food Safety—Chemical Safety of Food-Food Contact-EU Legislation. Available at: http://ec.europa.eu/food/food/chemical safety/foodcontact/eu_legisl_en.htm.