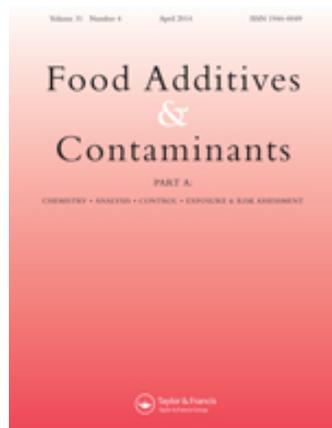


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## Food Additives & Contaminants: Part A

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tfac20>

### Updated evaluation of the migration of styrene monomer and oligomers from polystyrene food contact materials to foods and food simulants

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Accepted author version posted online: 02 Jan 2014. Published online: 25 Feb 2014.

To cite this article: Susan Genualdi, Patricia Nyman & Timothy Begley (2014) Updated evaluation of the migration of styrene monomer and oligomers from polystyrene food contact materials to foods and food simulants, Food Additives & Contaminants: Part A, 31:4, 723-733, DOI: [10.1080/19440049.2013.878040](https://doi.org/10.1080/19440049.2013.878040)

To link to this article: <http://dx.doi.org/10.1080/19440049.2013.878040>

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## Updated evaluation of the migration of styrene monomer and oligomers from polystyrene food contact materials to foods and food simulants

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(Received 23 October 2013; accepted 15 December 2013)

Due to the 2011 labelling of styrene monomer as “reasonably anticipated to be a human carcinogen” by the National Institutes of Health’s National Toxicology Program (NTP) and the controversy over whether styrene oligomers mimic the physiological effects of estrogen, an updated review of styrene monomer and oligomers in food and food contact materials (FCMs) was performed. The concentrations of styrene monomer and oligomers were determined in 24 polystyrene (PS) products and ranged from 9.3 to 3100 mg kg<sup>-1</sup> for the styrene monomer, 130–2900 mg kg<sup>-1</sup> for the sum of three styrene dimers, and 220–16,000 mg kg<sup>-1</sup> for the sum of six styrene trimers. Foods in contact with PS packaging had styrene monomer concentrations ranging from 2.6 to 163 ng g<sup>-1</sup>; dimer concentrations from the limit of quantitation (LOQ) to 4.8 ng g<sup>-1</sup> and trimer concentrations were all below the LOQ (2 ng g<sup>-1</sup>). Diffusion coefficients ( $D_p$ ) and partition coefficients ( $K$ ) were also calculated for styrene dimers and trimers. The results presented here indicate that styrene monomer concentrations in foods have not significantly changed since the 1980s and monomer concentrations in food packaging quantified in this study were all below USFDA limits. Although styrene dimers and trimers are present in higher concentrations in PS FCMs than the monomer, their migration to food is limited because of their high  $K$  values ( $4 \times 10^2$  to  $2 \times 10^6$ ) and their low diffusion coefficients in PS products. Additionally, diffusion coefficients calculated using USFDA-recommended food simulants and Arrhenius plots describing the temperature dependence of styrene dimers and trimers can be used in future calculations of dietary intake of the styrene oligomers.

**Keywords:** styrene monomer; styrene dimer; styrene trimer; food packaging; diffusion coefficients; polystyrene; migration

### Introduction

Polystyrene (PS) is widely used in the manufacture of food contact materials (FCMs), and in 2012, 50% of the domestic consumption of PS was related to food packaging and food service articles (American Chemistry Council 2013). Since 1991, the amount of PS used per year in food contact packaging and consumables increased from 2000 million to 2500 million pounds (lbs) in 1999 (Plastic Foodservice Packaging Group 2002). A recent estimate put domestic consumption at 2600 million lbs for 2012 (American Chemistry Council 2013). During the production process, the styrene monomer can become occluded in PS products and has the potential to migrate out of the FCMs and into the food. Styrene has known toxic effects on the central nervous system and neurological effects have been observed in workers continually exposed to styrene through inhalation (ASTDR’s Toxicological Profiles 2010). Although no cases have been reported on the ingestion of styrene by humans, the systemic toxicity is expected to be similar to that of inhalation (ASTDR’s Toxicological Profiles 2010). The USFDA regulates the amount of styrene monomer allowed in food grade PS at 1% by weight (10,000 mg kg<sup>-1</sup>) for contact with non-fatty foods and at 0.5% by weight (5000 mg kg<sup>-1</sup>) for contact with fatty foods of types III,

IVA, V, VIIA and IX as described in Table 1 of 21 CFR 176.170(c) (Title 21 – Food and Drugs 2013). Under the same regulation, rubber-modified PS basic polymers may not exceed 0.5% by weight of total residual styrene monomer.

Recently, in 2011, styrene was listed as “reasonably anticipated to be a human carcinogen” by the National Toxicology Panel (NTP) (DHHS 2011). Prior to this, the IARC classified styrene as “possibly carcinogenic to humans” (World Health Organization 2002). Currently, the USEPA does not have a classification for the carcinogenicity of styrene in its Integrated Risk Information System (IRIS) (EPA 1998). As a result of the NTP’s recent classification, the USFDA is updating its safety review of styrene by re-evaluating styrene concentrations in FCMs and foods contained in PS packaging.

Styrene dimers and trimers, which are also residual materials produced during polymerisation, have come under scrutiny due to conflicting reports suggesting they may or may not exhibit estrogenic activity (Ohno et al. 2001, 2003; Ohyama et al. 2001). Currently, the rate at which styrene dimers and trimers transfer from food packaging into foods is unclear. Due to their estimated low water solubilities (0.86–120 mg l<sup>-1</sup> at 25°C for the dimers and 0.0013–0.00092 mg l<sup>-1</sup> at 25°C for the trimers) (EPA 2013) compared with the

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Table 1. Concentrations ( $\text{mg kg}^{-1}$ ) of styrene monomer and oligomers in food contact materials.

Monomer ( $\text{mg kg}^{-1}$ )	Dimers ( $\text{mg kg}^{-1}$ )				Trimers ( $\text{mg kg}^{-1}$ )				Sum of trimers	Density ( $\text{g cm}^{-3}$ )		
	1,3-Diphenyl propane	2,4-Diphenyl- 1-butene	<i>trans</i> -1,2- Diphenyl cyclobutane	Sum of dimers	1,3,5-Triphenyl- cyclohexane	2,4,6-Triphenyl- 1-hexene	1e-Phenyl-4e- (1-phenylethyl)- 1,2,3,4-tetralin	1a-Phenyl-4e- (1-phenylethyl)- 1,2,3,4-tetralin			1e-Phenyl-4a- (1-phenylethyl)- 1,2,3,4-tetralin	1a-Phenyl-4a- (1-phenylethyl)- 1,2,3,4-tetralin
<i>Extruded polystyrene foam (XPS)</i>												
Ground beef tray – black foam	10.77	140.0	26.92	177.7	<LOQ	669.2	193.5	346.2	91.15	131.5	1431	0.0525
Chicken tray – foam	15.00	169.2	54.23	238.5	<LOQ	1004	567.3	984.2	234.6	309.2	3099	0.0692
Take-out container – white foam	347.3	158.3	39.71	211.4	<LOQ	847.8	357.8	686.2	160.7	262.5	2315	0.1015
<i>Expandable polystyrene (EPS)</i>												
Styrofoam cup	6.939	114.7	13.06	134.7	<LOQ	153.5	14.29	34.69	4.082	11.02	217.6	0.0623
Noodle container – white foam	47.80	123.9	13.69	143.0	<LOQ	370.7	24.29	56.31	7.619	17.98	476.9	0.0760
<i>High-impact polystyrene (HIPS)</i>												
Black coffee lid	21.36	140.5	368.2	530.0	10.00	2918	1630	2764	700.5	1119	9131	1.075
White coffee lid	299.7	158.1	404.2	579.6	<LOQ	2915	574.0	1076	258.1	366.0	5189	1.075
White coffee lid – NY	309.5	164.9	271.3	455.8	<LOQ	2302	742.6	1366	315.5	468.3	5194	1.075
White coffee lid – MD	270.7	111.15	97.69	377.3	<LOQ	1937	1545	2838	651.5	936.9	7909	1.075
Red disposable cup	361.8	<LOQ	206.3	212.5	<LOQ	692.6	1137	1992	503.8	753.3	5079	1.075
Blue disposable cup	74.89	138.1	164.6	310.4	<LOQ	1808	394.6	754.2	184.2	284.2	3425	1.075
Orange disposable cup	9.343	127.5	156.4	290.0	<LOQ	1965	370.7	702.1	159.6	255.7	3453	1.075
Red disposable bowl	518.4	178.0	291.2	503.6	<LOQ	2540	1389	2445	546.4	793.2	7714	1.075
Side sauce container	369.6	135.3	299.6	450.2	<LOQ	2174	682.4	1253	276.5	426.7	4812	1.075
Yoghurt container	485.5	172.1	432.5	620.4	<LOQ	1932	1035	1912	445.8	682.1	6007	1.075
Cookie tray	269.3	291.7	279.2	599.2	<LOQ	3491	1309	2369	548.3	864.6	8583	1.075
Chocolate candy tray	425.5	316.7	90.00	610.8	<LOQ	5652	2775	4841	1043	1432	15743	1.075
White utensil	427.7	<LOQ	451.9	451.9	<LOQ	1132	1723	2862	920.8	906.8	7545	1.075

(continued)

Table 1. Continued.

Monomer (mg kg <sup>-1</sup> )	Dimers (mg kg <sup>-1</sup> )			Trimers (mg kg <sup>-1</sup> )				Sum of trimers	Density (g cm <sup>-3</sup> )				
	1,3-Diphenyl propane	2,4-Diphenyl- 1-butene	<i>trans</i> -1,2- Diphenyl- cyclobutane	Sum of dimers	1,3,5-Triphenyl- cyclohexane	2,4,6-Triphenyl- 1-hexene	1e-Phenyl-4e- (1-phenylethyl)- 1,2,3,4-tetralin			1a-Phenyl-4e- (1-phenylethyl)- 1,2,3,4-tetralin	1a-Phenyl-4a- (1-phenylethyl)- 1,2,3,4-tetralin		
Clamshell – bakery container	219.1	17.79	343.2	21.97	382.9	<LOQ	1833	446.2	784.8	197.8	273.9	3535	1.075
Crystal utensil	2866	40.60	2045	827.4	2913	<LOQ	5116	2150	2411	1015	1557	12,250	1.075
Green reusable tumbler	648.3	6.415	84.53	79.62	170.6	<LOQ	768.2	481.5	807.9	155.8	288.7	2502	1.075
Salad tongs	735.9	12.45	216.6	311.3	540.4	<LOQ	3189	1803	3222	747.2	996.6	9957	1.075
<i>General-purpose polystyrene (GPPS)</i>	770.8	30.80	578.4	200.0	809.2	<LOQ	1601	1182	2343	524.4	800.4	6451	1.075
<i>Acrylonitrile-butadiene-styrene (ABS)</i>	3042	8.916	119.9	259.1	387.9	<LOQ	284.2	67.54	109.7	25.41	51.09	537.9	1.075

Notes: For calculations of  $C_{\text{pc}}$  (ng cm<sup>-3</sup>), the above concentrations were first converted to units of ng g<sup>-1</sup> and then multiplied by the density of the PS material. Values represent the average of triplicate measurements with % RSDs ranging from 3 to 38.

styrene monomer (310 mg l<sup>-1</sup> at 25°C) and increased molecular size (MW = 196–312 g mol<sup>-1</sup> for the dimers/trimers versus 104 g mol<sup>-1</sup> for the monomer), their diffusion coefficients are expected to be lower than that of the styrene monomer at approximately 3.0 × 10<sup>-13</sup> (Murphy et al. 1992).

Coefficients for the diffusion of styrene monomer from PS into various food simulants (corn oil, sunflower oil, water and 8–95% ethanol solutions) have been well studied (Varner & Breder 1981a; Till et al. 1982; Snyder & Breder 1983, Snyder & Breder 1985; Miltz & Rosendooddy 1985; Murphy et al. 1992; Lickly et al. 1995, 1997; Paraskevopoulou et al. 2012). A few studies have investigated the migration of styrene dimers and trimers into distilled water, heptane and 20% ethanol (Nakada et al. 2000; Choi et al. 2005). The use of heptane as a fatty food simulant is no longer recommended by the USFDA due to exaggerated effects on diffusion compared with that of a food oil. The USFDA-recommended food simulants include 95% ethanol and corn oil for fatty foods, 50% ethanol for foods containing greater than 15% alcohol by volume, and 10% ethanol for aqueous foods and foods containing less than 15% alcohol by volume (FDA 2007).

The styrene diffusion coefficient at 40°C in 95% ethanol has been established to be approximately 3.0 × 10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup> in PS products obtained directly from industry (Murphy et al. 1992). PS used in food packaging and FCMs is typically modified in some way. For example, high-impact polystyrene (HIPS) is formed through the addition of a rubbery segment to the polymer backbone, typically polybutadiene, to form a more durable product. Foamed PS products are manufactured from general-purpose, or crystal grade, PS that has been treated with a blowing agent to produce expandable polystyrene (EPS) beads. These beads can be further expanded or extruded to form various food packaging products such as foam trays, take-out containers, egg cartons and drink cups. These modifications of PS, as well as the addition of modifiers and other additives, may impact the diffusion coefficients of migrants from the food packaging.

The diffusion of the migrants from the PS packaging can be described by Fick's second law. By assuming that no partitioning barrier exists between polymer and solvent and that no concentration gradients exist in the solvent phase because it is well mixed and that the solvent phase is infinite, Fick's law can be reduced to equation (1):

$$M_t = 2C_{po}(D_p t/\pi)^{1/2} \quad (1)$$

where  $M_t$  is the total amount of migrant that has been lost from the polymer per unit square area (ng cm<sup>-2</sup>) at time  $t$

(s);  $C_{po}$  is the initial concentration of the migrant in the polymer per unit volume (ng cm<sup>-3</sup>); and  $D_p$  is the empirical diffusion coefficient in the polymer (cm<sup>2</sup> s<sup>-1</sup>). In this case, the diffusion coefficient can be determined by calculating the slope from the linear relationship between  $M_t/C_{po}$  and the square root of time.

The objectives of this study were: (1) to evaluate styrene monomer, dimer and trimer residues in several different types of FCMs; (2) to evaluate styrene monomer and oligomer concentrations in foods contained in PS packaging; and (3) to perform migration experiments to determine diffusion coefficients for the dimers and trimers using USFDA-recommended food simulants.

Results from these experiments will provide valuable data needed for updating dietary intake values for the styrene monomer and calculating dietary intake values for the styrene dimers and trimers.

## Methods

### Standards

Analytical standards were purchased from Sigma Aldrich (St. Louis, MO, USA) for the styrene monomer and deuterated  $d_8$ -styrene monomer, while the styrene oligomers were all purchased from Wako Chemical (Osaka, Japan).

### Food contact materials

PS FCMs were purchased from local supermarkets in the Washington, DC, area; for a list of products, see Table 1. A previous method (Varner & Breder 1981b) for the extraction of styrene monomer was modified and applied to the extraction of oligomers from PS FCMs. Briefly, 0.5 g of material were placed in a vial with 15 ml of ethyl acetate. The polymer was dissolved through vortexing and shaking with a digital pulse mixer (Glas-Col, Terre Haute, IN, USA) Then, 1.5 ml of methanol were added to each vial and centrifuged for 5 min at 4000 rpm. Aliquots of 1.5 ml were filtered through a 0.2- $\mu$ m PTFE syringe filter and, in some cases, also filtered through a 0.45- $\mu$ m PTFE syringe filter into a 2 ml vial. Then, 7.5  $\mu$ l of 10 000 mg kg<sup>-1</sup>  $d_8$ -styrene (98%) solution was added as an internal standard to each filtered aliquot in a 2 ml vial. The seven-point calibration curve used for quantification ranged from 4 to 3700 mg kg<sup>-1</sup>.

The recovery of this method was tested by creating a monomer and oligomer-free polymer by performing repeated extraction and precipitation steps until no migrants could be detected. This polymer was then spiked at 600 mg kg<sup>-1</sup> with the styrene monomer and oligomers and the recoveries ranged from 86% to 130%. Analysis was performed using a Gerstel cooled injection system (CIS) 4 inlet (Linthicum Heights, MD, USA) and an

Agilent 6890 gas chromatograph (GC) interfaced to a 5975 mass spectrometer (MS) (Agilent, Santa Clara, CA, USA). Injection parameters were optimised to ensure that residual PS was not producing styrene monomer and oligomers in the inlet. An initial inlet temperature of 200°C was used for a 10:1 split injection and after 20 min it was increased to 350°C at 12°C min<sup>-1</sup> and held for 10 min. The oven temperature programme initially started out at 50°C, was ramped by 15°C min<sup>-1</sup> to 310°C and followed by a 12 min hold. A Restek high-temperature column (Rxi<sup>®</sup>-5HT, 30 m × 0.25 mm i.d. × 0.25 µm film thickness) with stationary phase diphenyl dimethyl polysiloxane was used for separation. The auxiliary zone temperature was 280°C and the source and quadrupole temperatures were 250°C and 150°C, respectively.

### Food-styrene monomer

Food products analysed consisted of those in contact with PS packaging and can be found in Table 2. Additionally chewing gum was analysed because of the use of styrene butadiene in the gum base. A validated vacuum distillation-gas chromatography-mass spectrometry (VD-GC-MS) method was used for the analysis of styrene monomer in food (Nyman et al. 2013). Briefly, 2 g of food were pulverised to a powder using a Cuisinart mini-prep food processor and transferred to a round bottom flask. Internal standard (20 µl of 10 ng g<sup>-1</sup> *d*<sub>8</sub>-styrene) was added to each round bottom flask in addition to 1 ml of water. The instrumental details and parameters have been previously described (Nyman et al. 2013). Standard addition was used for the quantification of each individual food type with linear five-point calibration curves.

### Food-styrene oligomers

Extraction scheme E3 of the QuEChERS method previously used for the analysis of polycyclic aromatic

hydrocarbons in fatty fish (Forsberg et al. 2011) was used for the analysis of styrene oligomers from foods in contact with PS packaging. The final sample volume was 200 µl and 10 µl of 1 ng g<sup>-1</sup> *d*<sub>8</sub>-styrene internal standard was added to each vial. The LOQ was 2 ng g<sup>-1</sup> and corresponded to an analyte *S/N* ratio of 10:1. The eight-point calibration curve used for quantification ranged from 2 to 1000 ng g<sup>-1</sup>. Analysis was performed using an Agilent 6890 GC and 5973 MS and the same column (Rxi<sup>®</sup>-5HT) as used with the FCMs. The injection was splitless at 300°C, and the oven temperature programme had an initial temperature of 50°C, followed by a 1 min hold, a ramp rate of 15°C min<sup>-1</sup> to 340°C and a final hold for 10 min. The auxiliary zone temperature was 340°C and the source and quadrupole temperatures were 230°C and 150°C, respectively.

### Migration experiments and food simulants

Since the concentrations of styrene dimers and trimers were expected to be low, the ratio of FCM to food simulant was maximised in the two-sided migration cells. USFDA guidelines assume that 1 in<sup>2</sup> of packaging is in contact with 10 g of food (FDA 2007). In this study, 1.8–3.7 in<sup>2</sup> of packaging were placed in contact with 10 g of the food simulant in the migration cells, with the exact area dependent on the geometry of the FCM. The cells were mounted on a Glas-Col vial rotator at 20 rpm in an oven and removed starting at 2-h exposure time up to 10 days. This rotation speed has been shown to help reduce the resistance to mass transfer (Limm & Hollifield 1995). The analysis of migration solutions was performed using solid-phase micro-extraction (SPME) with a 30 µm polydimethylsiloxane (PDMS) fibre. Aliquots (2 ml) of food simulant were added to 20 ml SPME vials with 10 ml deionised water and 60 µl of 10 ng µl<sup>-1</sup> *d*<sub>8</sub>-styrene as the internal standard. The parameters for the Gerstel MPS2 (Linthicum, MD, USA) were optimised for incubation temperature (90°C), incubation

Table 2. Concentrations (ng g<sup>-1</sup>) of styrene monomer in foods (*n* = 3) held in contact with PS packaging and also chewing gum that contains styrene-butadiene as a gum base.

Food samples	Amount (ng g <sup>-1</sup> )	% RSD	Gilbert and Startin (1983) (ng g <sup>-1</sup> )	Heikes et al. (1995) (ng g <sup>-1</sup> )	Fleming-Jones and Smith (2003) (ng g <sup>-1</sup> )
Yoghurt	3.71	13	4	3.9–240	
Raw chicken	2.58	7.1	63		
Bakery croissants	44.2	3.6			
Sandwich cookies	163	2.1		216	15–165
Chocolate candies	38.8	8.9			
Noodle soup	4.33	1.9			
Raw ground beef	5.60	16	20		4–13
Chocolate chip cookies	107	10			15–111
Chewing gum #1	21.9	10.0			
Chewing gum #2	10.5	11			

time (4 min), extraction time (20 min) and desorption time (120 s). For 7 min before and after each sample, the PDMS fibre was baked out at 280°C. A pulsed split injection was used with a split ratio of 10:1 and an inlet temperature of 280°C. The initial GC oven temperature was 50°C, with a 1 min hold, followed by a ramp of 15°C min<sup>-1</sup> to 300°C and a final hold time of 5 min. A 5975T GC-MS was used for analysis with a HP-5 LTM column (30 m × 0.25 mm i.d. × 0.25 µm film thickness), and the isothermal oven was kept at 280°C, along with the auxiliary zone temperature. The MS source and quadrupole were 230°C and 150°C, respectively. The LOQ for all compounds in all food simulants was 1 ng g<sup>-1</sup>.

## Results

### *Styrene monomer and oligomers in polystyrene food contact materials*

Table 1 reports the concentrations of styrene monomer and the styrene dimers and trimers found in 24 different types of PS FCMs. Disposable food contact articles that were analysed included utensils, bowls, cups, cup lids and take-out containers, while PS food packaging in direct contact with food that was analysed included meat trays, yoghurt containers, cookie trays and chocolate candy trays. The styrene monomer concentrations quantified in this study ranged from 9.3 to 3100 mg kg<sup>-1</sup>, with a mean concentration of 340 mg kg<sup>-1</sup>. All these concentrations were below USFDA limits for styrene in food packaging materials, which is 5000 mg kg<sup>-1</sup> for fatty foods and 10 000 mg kg<sup>-1</sup> for aqueous foods (Title 21 – Food and Drugs 2013). There are currently no regulations for the styrene dimers and trimers present in FCMs. Results in Table 1 show the sum of dimer concentrations ranged from 130 to 2900 mg kg<sup>-1</sup> with an average of 500 mg kg<sup>-1</sup>, and the sum of trimer concentrations ranged from 220 to 16 000 mg kg<sup>-1</sup> with an average of 580 mg kg<sup>-1</sup>. These values compare well with previous measurements (Nakada et al. 2000) that found total dimer concentrations ranging from 170 to 420 mg kg<sup>-1</sup> and trimer concentrations ranging from 3200 to 12,000 mg kg<sup>-1</sup> in plastic containers (instant noodle bowls, plastic cups, lunch containers). The concentrations reported in Table 1 will be further used in the calculation of diffusion coefficients for the styrene dimers and trimers.

### *Styrene monomer in food*

Styrene monomer was quantified in foods in contact with PS packaging and also in chewing gums that use styrene-butadiene as a chewing gum base (Table 2). Concentrations of styrene ranged from 2.6 ng g<sup>-1</sup> in raw chicken to 163 ng g<sup>-1</sup> in sandwich cookies. Previous studies have measured styrene concentrations

in some of the same foods investigated in this study (raw chicken, fruit yoghurt, raw beef, chocolate chip cookies and sandwich cookies). These values can be found in Table 2 and represent data from studies published in 1983, 1995 and 2003 (Gilbert & Startin 1983; Heikes et al. 1995; Fleming-Jones & Smith 2003). Although the data are limited, it appears that the styrene concentrations measured in this study are consistent with those previously reported.

### *Styrene oligomers in food*

A QuEChERS method was used for the analysis of the dimers and trimers in the following seven foods: cookies, yoghurt, chocolate candy, raw chicken, raw beef, bakery croissants and noodle soup. Only one dimer, 1,3-diphenyl propane, was quantified in three of these foods (raw chicken, yoghurt, chocolate candy) with concentrations less than 5 ng g<sup>-1</sup>. This analyte is the smallest oligomer and has the highest estimated water solubility (120 mg l<sup>-1</sup>) (EPA 2013) compared with the other dimers and trimers, which all have estimated water solubilities less than 1 mg l<sup>-1</sup> (EPA 2013). The transfer of styrene dimers and trimers to hot noodle soups and noodles was previously investigated in HIPS bowls (Kawamura et al. 1998). The sum of styrene trimers was less than 63 ng g<sup>-1</sup> in all soup samples and no dimers were quantified above 5 ng g<sup>-1</sup> (the reported LOQ) (Kawamura et al. 1998). Additionally, styrene dimers and trimers were not detected above the LOQ in the plain noodles. From these limited studies, it appears that styrene dimers and trimers do not readily transfer to food, therefore additional migration testing will be carried out to further investigate this process.

### *Diffusion coefficients for styrene monomer and oligomers*

In this study, eight common PS FCMs were subjected to migration testing and evaluated for their diffusion coefficients in three different food simulants (10% ethanol, 50% ethanol and 95% ethanol). Five of the FCMs were HIPS materials, along with one XPS, one EPS and one GPPS. Since the styrene oligomers have low water solubilities, partitioning will likely slow the migration rate and reduce the quantity of migrant oligomers in foods. Therefore, only the early stage of migration, where the relationship between  $M_t/C_{po}$  and the square root of time is linear per equation (1), was used for calculating the diffusion coefficients. An example of this relationship for a blue cup (HIPS) is found in Figure 1. In this example, the linear region extends up to square root of time (s) = 415, or 48 h. Then the curve becomes curvilinear and begins to approach equilibrium. For some materials, the diffusion coefficients could not be calculated using the linear

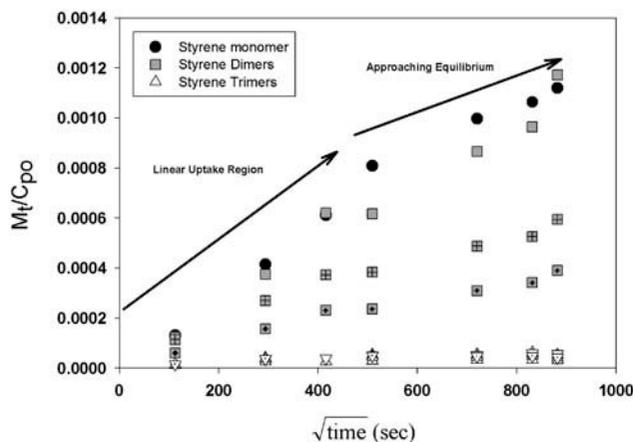


Figure 1. Uptake curves over 10 days ( $\sqrt{\text{time}} \text{ (s)} = 930$ ) for blue cup (HIPS) in 95% ethanol at 40°C. The linear uptake region extends to 48 h ( $\sqrt{\text{time}} \text{ (s)} = 415$ ), and beyond this time the dimers and trimers begin to approach or reach equilibrium.

portion of the curve either due to the migration from the polymer to the food simulant being less than the LOQ of  $1 \text{ ng g}^{-1}$ , or due to a limited linear range resulting from equilibrium being reached quickly with the food simulant. Previous studies report that styrene monomer migration is partition-limited in aqueous solvents, but not in food oil; and that little or no partitioning effect is evident in any food simulant (fatty or aqueous) over short exposure times of less than 1 day (Varner & Breder 1981a; Till et al. 1982; Snyder & Breder 1985). Therefore, diffusion coefficients for the monomer have also been estimated using equation (1) and the  $M_t$  values determined at the 24-h exposure time (Snyder & Breder 1985).

The apparent diffusion coefficients for the styrene monomer, dimers and trimers in eight different food contact articles in 95% ethanol at 40°C are presented in Table 3. When the diffusion coefficients could not be calculated using the linear relationship of  $M_t/C_{p0}$  versus the square root of time, they were calculated using equation (1) and the  $M_t$  values at the shortest exposure time (<4 h). Unlike the styrene monomer, the dimers and trimers showed partitioning effects much earlier than 24 h, in as early as 8 h. Therefore, exposures less than 8 h were necessary to estimate the apparent diffusion coefficients for the dimers and trimers. Solutions of 50% ethanol and 10% ethanol were also used in migration experiments to attempt to calculate diffusion coefficients for the dimers and trimers. The use of 50% ethanol is preferred for migration tests from PS over 95% ethanol to avoid potential exaggerated migration (FDA 2007). But since the migration of the dimers and trimers are largely partition-limited and the amounts migrating from the polymer are very low, few results were obtained with these food simulants. Therefore, only the results from the

experiments involving 95% ethanol (a worst case scenario) will be described. In 95% ethanol, the fastest diffusion appeared to take place from the foam tray (XPS), and the slowest diffusion was from the HIPS products.

Based on the concentrations quantified in 95% ethanol at equilibrium and the initial concentrations of styrene dimers and trimers in the FCMs (Table 1), partition coefficients ( $K$ ) were determined when possible (Table 4). Partition coefficients ( $K_{p,s} = C_p/C_s$ ) are defined as the concentration in the polymer  $C_p$  ( $\text{g cm}^{-3}$ ) over the concentration in the food simulant  $C_s$  ( $\text{g cm}^{-3}$ ) at equilibrium. The FCMs with the fastest diffusion rates had  $K$  values ranging from  $10^2$  to  $10^3$ , while the materials with the slower diffusion rates had  $K$  values from  $10^4$  to  $10^6$  in magnitude (Table 4). These high  $K$  values for 95% ethanol, a simulant for oily foods, indicate that styrene dimers and trimers are more likely to stay in the PS packaging material and resist transfer to oily foods. The transfer of the dimers and trimers to 50% and 10% ethanol representing fatty and aqueous foods is expected to be even lower than that to oily foods based on both their low water solubilities and quick partitioning.

In order to investigate the diffusion coefficients where partitioning was not an issue, migration experiments were also performed in corn oil. Ten-day migration experiments using a meat tray, crystal cup and blue cup were conducted at 40°C. Linear curves are presented in Figure 2 for styrene monomer in corn oil where samples were analysed using the VD-GC-MS method previously described. The analysis of styrene dimers and trimers in corn oil is more challenging due to their low volatility and will be presented at a later date. Results in Figure 2 show the migration of styrene monomer into corn oil is linear and follows Fickian diffusion over the full 10-day period. The apparent diffusion coefficients were calculated to be  $2.6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  for the foam meat tray,  $7.8 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  for the crystal cup and  $1.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  for the blue cup. The diffusion coefficient for styrene in the meat tray is comparable with previous experiments examining PS foam products with Crisco oil as a food simulant that found mean diffusion coefficients ranging from  $4.2 \times 10^{-9}$  to  $8.8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  from temperatures of 20–65°C (Lickly et al. 1995). Other experiments investigating the diffusion coefficient of styrene monomer in corn oil at 40°C used 98% pure commercial PS (Till et al. 1982) and a PS standard from Aldrich cat. #18242-7 (Snyder & Breder 1985). The diffusion coefficients in these studies were determined to be  $4.0 \times 10^{-13}$  and  $3.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , respectively.

Diffusion coefficients may be estimated based on models that have been previously described (Begley et al. 2005). Using this approach, diffusion coefficients for styrene monomer at 40°C in HIPS and GPPS were calculated to be  $4.5 \times 10^{-14}$  and  $1.6 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ,

Table 3. Apparent diffusion coefficients calculated at 40°C using 95% ethanol as a food simulant.

Name	$D_p$ (cm <sup>2</sup> s <sup>-1</sup> )									
	Yoghurt container (HIPS)	Cookie tray (HIPS)	Chocolate tray (HIPS)	Bakery clamshell container (HIPS)	Foam takeout container (XPS)	Meat tray (XPS)	Clear blue cup (HIPS)	Crystal cup (GPPS)		
Styrene	1.13E-13	1.88E-14	1.70E-14	6.54E-14	8.94E-12	1.42E-09	8.18E-12	3.11E-10		
1,3-Diphenyl propane	8.00E-17	3.14E-14	2.43E-14	3.53E-14	6.39E-12	8.95E-09	5.26E-12	6.40E-11		
2,4-Diphenyl 1-butene	6.04E-16	1.89E-15	8.01E-16	3.07E-15	1.05E-12	7.87E-09	5.11E-13	3.86E-11		
<i>trans</i> -1,2-Diphenyl cyclobutane	4.10E-15	1.21E-16	2.15E-15	4.43E-15	1.14E-12	2.31E-09	1.16E-12	6.30E-11		
1,3,5-Triphenyl-cyclohexane	n.a.									
2,4,6-Triphenyl-1-hexene	9.88E-18	7.30E-18	5.12E-18	6.93E-17	2.15E-14	4.62E-11	1.18E-14	8.31E-13		
1e-Phenyl-4e(1-phenylethyl) 1,2,3,4-tetralin	1.40E-16	6.74E-18	1.05E-17	2.41E-16	4.82E-13	3.54E-11	4.20E-14	6.40E-13		
1a-Phenyl-4e(1-phenylethyl) 1,2,3,4-tetralin	1.07E-16	5.72E-18	8.96E-18	2.24E-16	5.08E-13	4.64E-11	2.72E-14	7.70E-13		
1e-Phenyl-4a(1-phenylethyl) 1,2,3,4-tetralin	1.29E-16	1.42E-17	2.10E-17	3.10E-16	7.89E-13	6.62E-11	5.45E-14	9.23E-13		
1a-Phenyl-4a(1-phenylethyl) 1,2,3,4-tetralin	8.90E-17	8.70E-18	1.70E-17	3.04E-16	4.62E-13	7.16E-11	3.87E-14	7.53E-13		

Notes:  $D_p$  is calculated from  $M_t$  at approximately 2 h exposure.  
n.a., Not applicable (1,3,5-triphenyl-cyclohexane below LOQ in all packaging materials).

Table 4. Partition coefficients calculated from migration into 95% ethanol at 40°C ( $K = C_p/C_s$ ).

Name	$K$	Yoghurt container (HIPS)	$K$	Cookie tray (HIPS)	$K$	Chocolate tray (HIPS)	$K$	Bakery clamshell container (HIPS)	$K$	Foam takeout container (XPS)	$K$	Meat tray (XPS)	$K$	Clear blue cup (HIPS)	$K$	Crystal cup (GPPS)
Styrene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1,3-Diphenyl propane	1.1E+04	2.2E+04	2.2E+04	2.4E+04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.9E+02
2,4-Diphenyl 1-butene	4.0E+04	5.5E+04	5.5E+04	1.2E+05	1.2E+05	1.2E+05	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.9E+02
<i>trans</i> -1,2-Diphenyl cyclobutane	2.0E+04	2.7E+05	2.7E+05	7.9E+04	7.9E+04	7.9E+04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	3.3E+02
1,3,5-Triphenyl-cyclohexane	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2,4,6-Triphenyl-1-hexene	5.0E+05	1.2E+06	1.2E+06	2.0E+06	2.0E+06	2.0E+06	n.a.	n.a.	n.a.	n.a.	n.a.	3.8E+03	3.8E+03	1.3E+04	1.3E+04	3.5E+03
1e-Phenyl-4e(1-phenylethyl) 1,2,3,4-tetralin	1.8E+05	1.3E+06	1.3E+06	1.3E+06	1.3E+06	1.3E+06	3.5E+05	3.5E+05	6.4E+03	6.4E+03	6.4E+03	3.8E+03	3.8E+03	7.5E+03	7.5E+03	3.3E+03
1a-Phenyl-4e(1-phenylethyl) 1,2,3,4-tetralin	4.6E+05	1.3E+06	1.3E+06	1.4E+06	1.4E+06	1.4E+06	3.5E+05	3.5E+05	6.2E+03	6.2E+03	6.2E+03	3.8E+03	3.8E+03	9.2E+03	9.2E+03	3.6E+03
1e-Phenyl-4a(1-phenylethyl) 1,2,3,4-tetralin	2.1E+05	9.2E+05	9.2E+05	8.8E+05	8.8E+05	8.8E+05	2.8E+05	2.8E+05	5.3E+03	5.3E+03	5.3E+03	3.5E+03	3.5E+03	7.5E+03	7.5E+03	3.2E+03
1a-Phenyl-4a(1-phenylethyl) 1,2,3,4-tetralin	2.1E+05	1.1E+06	1.1E+06	1.0E+06	1.0E+06	1.0E+06	3.0E+05	3.0E+05	5.8E+03	5.8E+03	5.8E+03	3.5E+03	3.5E+03	9.2E+03	9.2E+03	3.7E+03

Note: n.a. indicates that the partition coefficient could not be calculated due to either the equilibrium not being reached or the concentration was below the LOQ in the FCM.

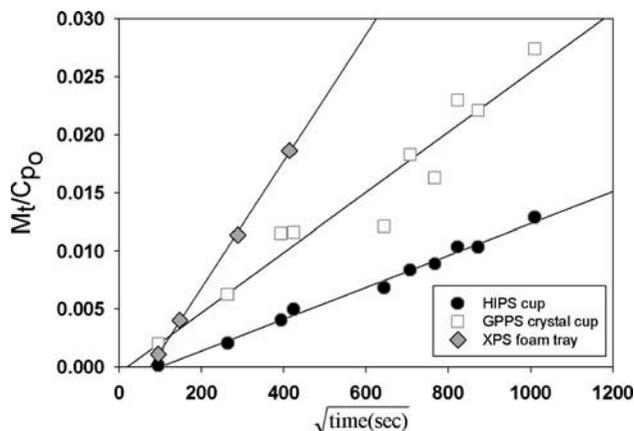


Figure 2. Diffusion of styrene monomer from PS food contact materials to corn oil over 10 days at 40°C.

respectively. These estimates are in good agreement with styrene monomer migration data for the first four samples (HIPS) in Table 3, in spite of the use of 95% ethanol. The remaining four PS packaging samples in Table 3 have much higher diffusion coefficients than modelling estimates. Two of the samples are EPS (foam takeout container) and XPS (meat tray) that are expected to be more porous than HIPS or GPPS, so their high diffusion rates are not unexpected.

The remaining two samples in Table 3 were a blue cup (HIPS) and crystal cup (GPPS) and have diffusion coefficients that are substantially higher than modelling estimates. In addition, their apparent diffusion coefficients to corn oil are also high at  $7.8 \times 10^{-10}$  and  $1.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , respectively. These high diffusion data suggest that PS morphology of these samples may be different from other HIPS and GPPS samples. The diffusion of styrene monomer has been shown to increase with increasing amounts of rubber particles in HIPS and with the use of cut edges in immersion sampling (Linszen et al. 1992). The cut edges are more pronounced with the crystal cup (GPPS) due to its brittleness compared with other PS products. Therefore, the greater diffusion observed in these two products could be related to the higher amounts

of rubber particles in the blue cup compared with the other HIPS products and more pronounced edge effects resulting from cutting the brittle crystal cup.

The temperature dependence of styrene dimers and trimers migration from the blue cup, crystal cup and foam tray was investigated by performing migration experiments at 30°C, 40°C and 50°C into 95% ethanol. Diffusion coefficients were calculated for styrene trimers at 50°C, using the  $M_t$  value at the shortest exposure time (2 h) due to rapid diffusion that leads to equilibrium being reached in less than 8 h. Linear regression equations for  $\log D_p$  versus  $1/T$  (K) are presented in Table 5 for the monomer, and for the averages of the dimers and trimers. As expected, the rate of diffusion increased with increasing temperature. These relationships are needed in calculating dietary intake values to account of the differences in diffusion rates for foods that are stored at different temperatures.

## Discussion

The re-evaluation of styrene monomer in foods and FCMs was necessary due to the recent labelling of styrene as “reasonably anticipated to be a human carcinogen” by the NTP. The results presented here indicate that styrene monomer concentrations in food have not significantly changed since the 1980s and that the styrene monomer concentrations in all the FCMs evaluated in this study were below USFDA limits. Additionally, there have been only a few studies investigating the potential migration of styrene dimers and trimers to food and none has examined their migration into USFDA-recommended food simulants. Based on the low concentrations ( $<5 \text{ ng g}^{-1}$ ) of styrene dimers and trimers quantified in food, the apparent diffusion coefficients and large partition coefficients calculated here, the migration of these compounds is expected to be low and largely partition-limited. Additionally, the results presented here can be used in future assessments of the dietary intake of styrene, and for the first time, the dietary intake of styrene dimers and trimers.

Table 5. Regression equations for the temperature dependence of styrene monomer, dimers, and trimers at 30°C, 40°C, and 50°C.

	Meat tray		Blue cup		Crystal cup	
	Slope	y-intercept	Slope	y-intercept	Slope	y-intercept
Styrene monomer	-4612	6.1	-7602	12.4	-5304	7.0
Average styrene dimers	-4015	3.2	-8603	15.4	-6579	10.8
Average styrene trimers	-4344	2.6	-7842	11.4	-8725	15.6

Note: Linear regression equations ( $\log D_p = \text{slope} (1/T) + \text{y-intercept}$ ).

## Acknowledgements

The authors would like to thank Steven Barrientos for his assistance in the lab with the styrene monomer and oligomer analysis.

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