

Migration of Acrylonitrile from Styrene/Acrylonitrile Copolymers into Food-Simulating Liquids

Tim D. Lickly,* Daniel A. Markham, and Marvin E. McDonald

Health and Environmental Sciences, The Dow Chemical Company, 1803 Building, Midland, Michigan 48674

Correlating residual polymer concentration in polymers to the monomer migration into food simulants has been of interest for many years. Most repeated-use food-contacting articles go through multistage temperature exposures during their lifetime; therefore, the effect of varying temperature of the polymer on the migration of the monomer is of great importance in estimating the exposure of consumers to the monomer via food in contact with the polymer, in addition to the knowledge of the migration at a single temperature as has been the focus of previous studies on other polymer/monomer combinations. Studies on the migration of acrylonitrile (AN) from two styrene/acrylonitrile copolymers (SAN), one with a high melt flow which is sold into repeated-use food-contact applications and one with an extremely low melt flow, show that a linear relationship exists between the amount of AN migrating from the SAN polymers into water and the square root of the time of exposure for both polymers. No difference (within estimated experimental error) was observed when the apparent diffusion coefficients obtained for the two polymers at a given temperature were compared. The data also show that a linear relationship exists between the logarithm of the AN diffusion coefficients calculated from experimental data using a simple Fickian diffusion model and the inverse of the absolute temperature of exposure. Data obtained for a two-stage temperature exposure agreed with the results obtained from an analytical solution which had previously been developed to predict the amount of monomer migrating during a multistage temperature exposure.

INTRODUCTION

Correlating residual monomer concentration in a food-contact article with monomer migration into foods or food simulants has been of wide interest to both industry and governmental regulating bodies for many years (Gilbert, 1976; Koros and Hopfenberg, 1979; Reid et al., 1980; Till et al., 1987; Schwöpe and Reid, 1988). Studies have been completed on the migration of styrene monomer and additives from polystyrenes (Till et al., 1982; Miltz and Rosen-Doody, 1984; Snyder and Breder, 1985; Schwöpe et al., 1987; Murphy et al., 1991) and acrylonitrile (AN) migration from polyacrylonitriles (Brown et al., 1978; Stampa and Imhof, 1979; Tatsuno et al., 1980; Lickly et al., 1991; Markelov et al., 1992), which have focused on both the migration of the monomers and the ability to predict the migration of the monomers to food and food simulants under time/temperature conditions other than those tested. Styrene/acrylonitrile resins (SAN) are used in many repeated-use food contact applications; therefore, there is interest in understanding the migration of AN from SAN materials. Experimental work which has been previously carried out and reported for AN migration from polyacrylonitriles did not include any variations in temperature during the course of the exposure of a polymeric article or the effects of the initial storage time/temperature prior to exposure. Ayres et al. (1983) clearly showed the effects of variable storage times on the ability to predict monomer migration in polymers, which was further expanded on by Markelov et al. (1992). The work reported herein extends the database on the migration of AN from SAN resins and utilizes the concepts previously used for modeling the migration of monomers. This work also addresses a simple approach to determining the effect of a fluctuation of exposure temperature or the effect of an initial storage time prior to exposure on the migration of AN from an AN-containing article.

MATERIALS AND METHODS

Preparation of the Polymer. Test specimens consisted of 2-in. diameter by $\frac{1}{8}$ in. thick injection-molded polymer disks. This configuration was selected to simulate the surface of typical end-use products. Two commercial SAN polymers (produced by The Dow Chemical Co.) were examined with residual AN levels of about 35 and 85 ppm, which is typical for residual levels in repeated-use SAN food-contact articles. The polymer selected for the majority of the studies is sold into food-contact applications by Dow and has a high melt flow for processability. The other polymer studied has the lowest melt flow of all of the Dow commercial SAN polymers. These two polymers were selected to cover the extremes of melt-flow characteristics for the Dow commercial SAN polymers. Previous work had shown the importance of using freshly molded samples (Ayres et al., 1983; Lickly et al., 1991; Markelov et al., 1992); therefore, the polymer disks were stored in intimate contact with one another at freezing temperatures from the time the disk molding was complete until the start of the migration studies, which was less than 24 h after molding.

Residual AN was determined on a ground composite sample of each polymer at the time of the migration study. Again, care was taken to minimize loss of AN during grinding by freezing the disks in liquid nitrogen and purging the grinder with liquid nitrogen while the polymer was ground. These analyses were accomplished by dissolving 0.5 g of ground polymer disk in 5 mL of *o*-dichlorobenzene in a sealed vial and analyzing the vapor space above the solution by headspace gas chromatography. Quantitation was by standard addition.

Food-Simulating Liquid. Water was selected as the food simulant because water was assumed not to interact with AN copolymers, AN is extremely soluble in water, and many aqueous foods are stored in articles made from AN copolymers. Also, no significant difference has been observed between the migration of AN from AN copolymers into water, 3-4% acetic acid, and 8-10% ethanol (Stampa and Imhof, 1979; Tatsuno et al., 1980; Yoshida et al., 1980; Lickly et al., 1991), and the migration of AN into water has been shown to be equal to or greater than the migration into heptane and food oils (Stampa and Imhof, 1979; Tatsuno et al., 1980). Thus, water was expected to be a solvent

* Author to whom correspondence should be addressed.

which would yield a prediction of the maximum concentration of AN that could migrate into any foods in contact with the polymer.

The water used was obtained from a Millipore Corp. Milli-Q water purification system.

Experimental Procedures. I. Diffusion Coefficient Determinations. Five replicate migration samples were prepared for each polymer at each temperature. Each replicate consisted of 11 polymer disks placed into an 8-oz "canning" jar with a cross-shaped spacer made from 1/8 in. diameter glass rod placed between each disk and several on top of the stack to keep the disks from contacting each other yet ensure complete submersion in the water. Water (150 mL, preheated to the appropriate temperature as necessary) was added to each jar, and each jar was sealed with a canning jar lid containing a butyl rubber gasket, which was lined with a thin layer of aluminum foil. Stability experiments were run over the temperature range studied to assure no loss (<5%) of AN occurred throughout the duration of the study.

Temperatures/times of exposure for these determinations were 70 °F (21 °C) for 10 days, 120 °F (49 °C) for 3 days, and 180 °F (82 °C) for 24 h. Samples of one polymer were molded from the same lot of resin at two different time periods 6 weeks apart, and the migration at 70 °F was determined after each molding to determine the reproducibility of these experiments. The 70 °F migration samples were placed on a bench top at room temperature, and the temperature of the area was monitored during the exposure period. All other migration samples were placed in convection ovens set at the appropriate temperature.

The migration samples that were heated to 180 °F were placed into a freezer and chilled for 30 min after the 24-h exposure period, and then an aliquot from each was transferred to a 4-mL liquid chromatograph (LC) autosampler vial. The LC vials were sealed with poly(tetrafluoroethylene)-lined self-sealing septa. Analytical samples from the migration sampled held at other temperatures were taken directly after exposure.

II. Repeated-Use Determination. Five replicate migration samples were set for one polymer using the same canning jar configuration as was used in the diffusion coefficient determination experiments. The jars were filled with preheated Milli-Q water and exposed for six consecutive 1-h exposures, decanting the water and refilling the jars with fresh preheated water after each hour of exposure, saving a sample for analysis between each exposure.

In a preliminary experiment a temperature profile was obtained using the same migration sample configuration except that a glass cover with a septum port, through which a thermocouple probe was inserted, replaced the canning jar lid. The thermocouple extended into the center of the polymer stack via a hole drilled in the center of each disk. The septum port was then sealed. A volume of 150 mL of 180 °F preheated water was added to the jar, the jar was sealed, and a temperature reading was taken. It was found that the temperature obtained was 158 °F. Therefore, the convection oven was set at 158 °F, and the following exposure procedure was used. The temperature profile sample was allowed to come to room temperature (~70 °F), filled with 180 °F preheated water, and placed in a convection oven for 60 min. The sample was then removed from the oven and placed into a freezer to cool for 15 min. The temperature profile sample was carried through two cycles, and the temperature was found to range from 147 to 158 °F during the 60 min in the oven and dropped to about 100 °F while in the freezer.

The same procedure that was used for the temperature profile experiment was followed for the six consecutive 1-h migration sample exposures, with 180 °F preheated water being added to the migration samples, and the migration samples were placed in the 158 °F oven. At the end of each hour of exposure, the migration samples were transferred to a freezer and allowed to cool for 15 min. After cooling, an aliquot of the water was transferred to a 4-mL LC vial, the remainder of the water was decanted from each jar, and fresh preheated water was added to the jar. Each jar was then placed back in the oven for the next hour of exposure.

III. Repeated-Use Determination with Temperature Fluctuation. Five replicate migration samples were set for one polymer using the same canning jar configuration as was used in

the diffusion coefficient determination experiments. The jars were filled with preheated Milli-Q water and exposed for six consecutive 1-h exposures at 122 °F following the procedure that was described under Repeated-Use Determination, with the exception that after each hour of exposure at 122 °F the analytical sample was removed from the exposure vessel *without* the 15-min cooling period in the freezer. After the sixth 1-h analytical sample was obtained, fresh preheated water was added and the jars were placed on a New Brunswick Scientific Gyrotory shaker (200 rpm) in an oven set at 122 °F. After 17 h, the migration samples were removed from the oven and aliquots were taken for LC analysis. The water was decanted from the jars, the jars and polymer disks were then rinsed twice with Milli-Q water to prevent carry-over, and fresh preheated water was added to the jar.

After one additional 1-h exposure at 122 °F, aliquots were obtained for analysis. The exposure temperature was then increased to 158 °F, and fresh preheated water was added. Four additional 1-h samples were obtained at this temperature, following the same procedures as were used at the start during the 122 °F exposure period. Again, no cooling time was used between removing the migration samples from the oven and taking the analytical samples.

Sample Analysis. Samples, blanks, and standards were analyzed using reversed-phase high-performance liquid chromatography (HPLC). Analysis was accomplished using the following parameters: detector, LDC spectroMonitor III at 205 nm; column, Du Pont Zorbax ODS 4.6 mm × 25 cm; eluent, methanol-water (20:80); flow rate, 1 mL/min; injection volume, 200 μL; guard column, Guard-Pak (C-18). A detection limit of about 5 ng/mL (2 ng/cm²) was estimated. The response of AN standards was shown to be linear over the entire range of results reported.

RESULTS AND DISCUSSION

I. Diffusion Coefficient Determinations. The theory of the process of migration of residual monomers or additives from polymeric food-packaging materials following Fick's laws has been dealt with extensively in the past (Berens and Hopfenberg, 1977; Koros and Hopfenberg, 1979; Reid et al., 1980; Till et al., 1982, 1987; Vrentas and Duda, 1986). The simple equation

$$M_1 = (2C_0/\sqrt{\pi})\sqrt{D_1t_1} \quad (1)$$

where M_1 is the amount migrating in ng/cm², C_0 is the starting concentration of component of interest in polymer in ng/cm³, D_1 is the apparent diffusion coefficient in cm²/s, and t_1 is the time of exposure in seconds, can be used to determine the apparent diffusion coefficient of a monomer in a polymer when the following assumptions are true: (1) there is no resistance to mass transfer of the migrant between the polymer surface and the food or food simulant, (2) there is no penetration of the food-packaging polymer by the food or food simulant, (3) the migrant is homogeneously distributed in the polymeric material at the start of the study, (4) the polymeric material does not become depleted of the component under study during the experiment (less than 50–60% migration), and (5) the amount of food or food simulant is large such that partitioning (equilibrium) effects do not limit the migration from the polymer. The previously reported work on the migration of AN from ABS copolymers (Lickly et al., 1991) supported the concept that Fickian diffusion theory is followed for AN migration from AN-containing copolymers, as had previously been suggested (Ayres et al., 1983); therefore, eq 1 has been used for all diffusion coefficient calculations. The validity of these assumptions for the SAN experiments reported herein is discussed at the end of this section.

Using eq 1 to calculate the apparent diffusion coefficients from the migration data obtained for the diffusion coefficient determination experiments yielded values of

Table I. Residual Acrylonitrile Levels, Acrylonitrile Migration Levels, and Calculated Diffusion Coefficients for the Migration of Acrylonitrile from Styrene/Acrylonitrile Polymers into Water

acrylonitrile concn in polymer, $\mu\text{g}/\text{cm}^3$	temp, $^{\circ}\text{F}$	time of exposure, s	acrylonitrile migration		exptl procedure ^b	diffusion coeff, cm^2/s
			ng/mL^a	ng/cm^2		
83.8 ± 3.4^c	70	8.64×10^5	557.5 ± 14.0	166 ± 4.2	I	3.6×10^{-12}
36.1 ± 1.8	70	8.64×10^5	295.1 ± 4.9	87.8 ± 1.5	I	5.4×10^{-12}
34.6 ± 1.8	70	8.64×10^5	307.7 ± 5.6	91.6 ± 1.7	I	6.4×10^{-12}
34.6 ± 1.8	120	2.59×10^5	503.9 ± 8.0	150 ± 2.4	I	5.7×10^{-11}
40.1 ± 0.8	122	8.64×10^4	349	104	III	6.1×10^{-11}
37.7 ± 1.3	158	2.16×10^4	406	121	II	3.7×10^{-10}
34.6 ± 1.8	180	8.64×10^4	1075 ± 51.5	320 ± 15.3	I	7.8×10^{-10}

^a ng of AN/mL observed at the exposure ratio of 1 in.² of polymer/1.92 mL of water ($0.30 \text{ mL}/\text{cm}^2$). ^b The experimental procedure identifies which experiment was used to generate the data—either (I) diffusion coefficient determinations, (II) repeated-use determination, or (III) repeated-use determination with temperature fluctuation (see text). ^c All confidence intervals (\pm values) are 1 standard deviation of replicate sample values. For residual AN values either four or five samples were analyzed. For AN migration values five samples were analyzed.

3.6×10^{-12} , 5.4×10^{-12} and $6.4 \times 10^{-12} \text{ cm}^2/\text{s}$ at 70°F ; $5.7 \times 10^{-11} \text{ cm}^2/\text{s}$ at 120°F ; and $7.8 \times 10^{-10} \text{ cm}^2/\text{s}$ at 180°F (Table I). The experiment in which the same lot of polymer was molded at two different times 6 weeks apart and a migration study at 70°F for 10 days was initiated within 24 h of molding the samples showed excellent reproducibility, with the diffusion coefficient determined initially as $5.4 \times 10^{-12} \text{ cm}^2/\text{s}$, and a diffusion coefficient of $6.4 \times 10^{-12} \text{ cm}^2/\text{s}$ was determined for the samples molded and exposed 6 weeks later.

Diffusion coefficients were also obtained by summing the migration data obtained from the six 1-h exposures at 158°F for the repeated-use determination experiment and for the accumulated 24 h of data at 122°F for the repeated-use determination with temperature fluctuation experiment. The apparent diffusion coefficients from these data yielded values of $6.1 \times 10^{-11} \text{ cm}^2/\text{s}$ at 122°F and $3.7 \times 10^{-10} \text{ cm}^2/\text{s}$ at 158°F , consistent with the values obtained from the diffusion coefficient determination experiments (Table I).

The SAN polymer with the high melt flow which is sold into food-contact applications was used in two of the 70°F exposures, the 120°F exposure, and the 180°F exposure from the diffusion coefficient determination experiment and was also used for the repeated-use determination experiment. The polymer with the low melt flow was used for one 70°F exposure from the diffusion coefficient determination experiment and for the repeated-use determination experiment with temperature fluctuation experiment. A comparison of the apparent diffusion coefficients for the high melt flow copolymer at 70 (5.4×10^{-12} and $6.4 \times 10^{-12} \text{ cm}^2/\text{s}$) and 120°F ($5.7 \times 10^{-11} \text{ cm}^2/\text{s}$) to the apparent diffusion coefficients for the low melt flow copolymer at 70 ($3.6 \times 10^{-12} \text{ cm}^2/\text{s}$) and 122°F from the repeated-use determination experiment ($6.1 \times 10^{-11} \text{ cm}^2/\text{s}$) shows no difference at a given temperature, within the combined experimental errors of all measurements.

When the diffusion coefficients for all exposures reported in Table I are plotted in an Arrhenius form, a linear relationship between the inverse of the absolute temperature and the logarithm of the calculated diffusion coefficient for AN from the two SAN polymers is apparent. This line appears to closely parallel the line previously obtained (Lickly et al., 1991) for the migration of AN from ABS data over the temperature ranges studied (Figure 1). Fitting both sets of data (ABS and SAN) yielded regression equations ($\log D_p = -3932*(1/T) + 2.46$, $r^2 = 0.998$ for ABS; $\log D_p = -3769*(1/T) + 1.503$, $r^2 = 0.992$ for SAN), from which activation energies of 18.0 and 17.3 kcal/mol were obtained for AN diffusion through ABS and SAN, respectively. The activation energies were similar to those previously reported for AN diffusion through other ABS and SAN polymers (Markelov et al., 1992) and for vinyl

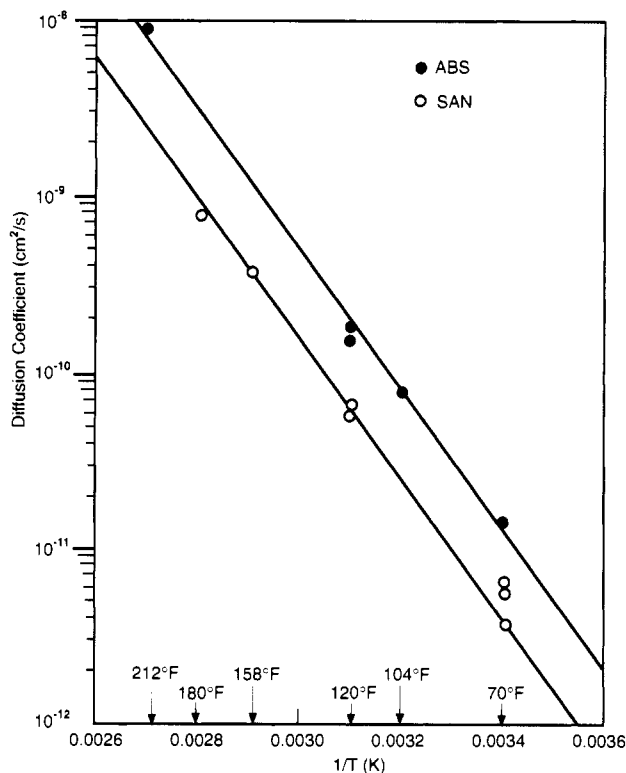


Figure 1. Effect of temperature on the diffusion of acrylonitrile from ABS [data from Lickly et al. (1991)] and SAN polymers into water.

chloride monomer diffusion in poly(vinyl chloride) (Berens and Hopfenberg, 1977).

II. Repeated-Use Determination. The results of the repeated-use determination experiments reinforce the observation that the migration of AN from SAN into water follows Fick's laws. Examining eq 1, one can see the amount of AN migrating from a polymer under a given set of conditions should be proportional to the square root of the time of exposure. The results of the repeated-use experiments demonstrate that a linear relationship existed between the amount of AN that migrated and the square root of the time of exposure from "freshly molded" plaques with no prior heat history (Figures 2 and 3). One consideration to note is that it was assumed in this experiment that no migration occurred during the 15 min that the sample was in the freezer cooling between the heating period and sampling, even though it is obvious that some minimal migration would have occurred.

It is noted that the line of best fit through the points does not bisect the origin (0,0) of either graph. One possible explanation for this is while the water was at the appropriate temperature when placed in the sample jar,

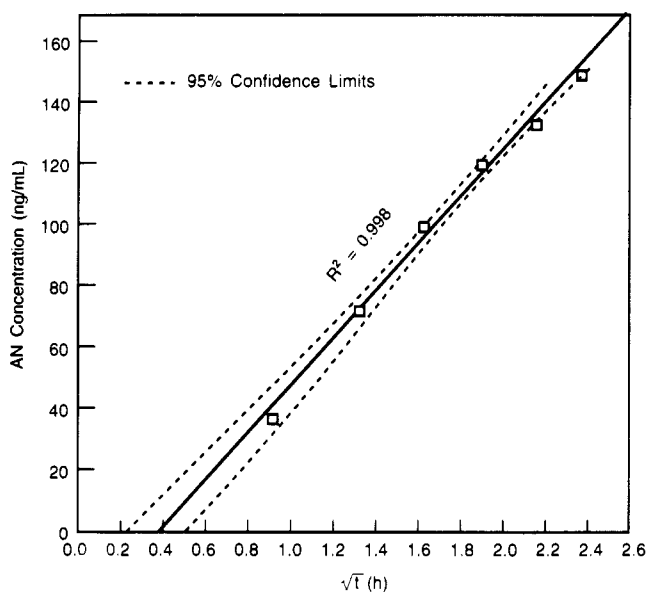


Figure 2. Cumulative amount of acrylonitrile migrating from a SAN polymer into water at 158 °F.

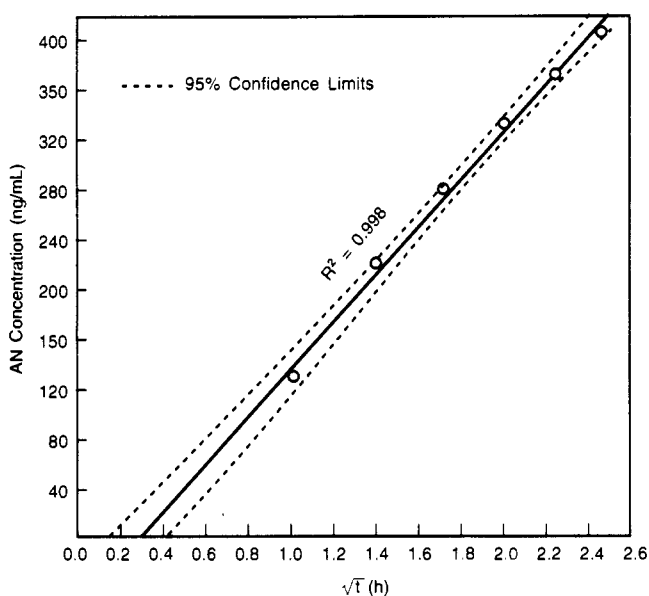


Figure 3. Cumulative amount of acrylonitrile migrating from a SAN polymer into water at 122 °F.

the polymer itself had to initially heat up from room temperature, which would yield lower than expected migration. A second more probable explanation is while the polymer was exposed soon after molding (within 24 h) and care was taken to "store" the molded plaques at freezing temperatures in intimate contact with one another between molding and exposure, enough migration of AN could have occurred during the cooling of the polymer after molding to affect the uniformity of distribution of the AN in the polymer such that AN was not homogeneously distributed at the start of the exposure period, as has been pointed out with other experiments (Ayres et al., 1983; Stanley and Alger, 1989; Markelov et al., 1992). Equation 1 was used, nevertheless, as it yields a reasonable estimation of the diffusion coefficient for the purposes of estimating migration into food simulants as reported in these experiments.

III. Repeated-Use Determination with Temperature Fluctuation. In most applications a SAN polymeric article is not molded and immediately put into use at a constant temperature. Frequently, days to months elapse

before food is in contact with the article, and then the temperature to which the article is exposed fluctuates over the course of its lifetime. One such example would be a beverage container application (coffee cup) in which the article is molded, then it is in the distribution chain for an extended length of time, and finally it arrives at the consumer. At this point it may be put into use at one temperature (hot or cold), washed at an elevated temperature, and then stored at room temperature until the next use. Using predictions obtained from freshly molded samples would dramatically exaggerate the consumer exposure to the component of interest in the case of volatile monomers such as acrylonitrile, as has been previously noted (Ayres et al., 1983). Two approaches could be taken to obtain some estimate of consumer exposure. One would be to attempt to simulate this sequence of events and actually make measurements at the time of interest. Since many different articles are used with an unimaginable number of variations of conditions of use, it would be much easier to estimate the migration using the apparent diffusion coefficients and applying any time or temperature information as appropriate.

This experiment was designed to demonstrate the effect of temperature shifts during the course of exposure on the amount of AN migrating from an article. This is a simplified approach to the migration that is anticipated from food-contact articles such as repeated-use food containers, where the article is exposed to a variation in temperatures during its lifetime. The previous experiment (II) showed the results from a freshly molded article exposed to 158 °F water. In the temperature fluctuation experiment the polymeric sample was first exposed to water at 122 °F for 24 h, and then the temperature was increased and the exposure was continued at 158 °F for 4 h. Recently an approach has been presented (McDonald, 1992) which deals with estimating the migration of a low molecular weight component from a polymeric article for a multistage diffusion process consisting of steps at different temperatures. A brief, qualitative description of that approach follows.

Consider a thin polymer sheet in which the migrant is homogeneously distributed initially. In a multistage diffusion process where the different steps are at different temperatures, it is assumed that the temperature changes are instantaneous. The concentration at the surface of the sheet is assumed to be zero. The initial condition for any step after the first is the concentration profile that exists from the previous step. These assumptions permit a simple equation to be derived which describes the amount of material that diffuses from the sheet in the particular step in question. The assumption of instantaneous temperature change is reasonable considering the fact that the temperature change occurs many orders of magnitude more quickly in the polymer than the concentration changes. This is because the thermal diffusivity is much larger than the mass diffusion coefficient in most practical cases.

The resulting equation for the amount of material that migrates during the n th step is, for cases where less than 50–60% of the material has migrated from the polymer

$$M_n = \frac{2C_0}{\sqrt{\pi}} \left[\sqrt{\sum_{i=1}^n D_i t_i} - \sqrt{\sum_{i=1}^{n-1} D_i t_i} \right] \quad (2)$$

where M_n is the amount migrating in ng/cm² during the n th temperature step, D_i is the diffusion coefficient in cm²/s for the i th temperature step, and t_i is the time of

Table II. Comparison of Measured Acrylonitrile Migration Levels and Theoretical Predictions for SAN Polymer in Repeated-Use Experiments (with and without Temperature Fluctuations)^a

time, h	actual expt at 122 °F, ng/mL	theor calcn at 122 °F, ^c ng/mL	no exposure at 122 °F		
1	41 ^b	67			
2	37	28			
3	28	21			
4	21	18			
5	17	16			
6	17	14			
7-23	176	157			
24	11	7			
	↓	↓			
time, h	exposure temp increase to 158 °F, ng/mL	theor when exposure temp increase to 158 °F, ^c ng/mL	time, h	actual expt 158 °F (4 h), ng/mL	theor calcn started at 158 °F, ^c ng/mL
25	30	39	(1)	129	163
26	24	35	(2)	88	70
27	25	32	(3)	63	52
28	20	30	(4)	50	45

^a Polymer exposure was 3.35 cm²/mL, residual AN in polymer was 37.7 μg/cm³. Values listed to left of brackets are the observed concentrations for the incremental time period. Values to right of brackets are mathematical summary of observed increments. ^b Data reported are the single hour measurements with the exception of the 7-23-h period where the sample was continuously exposed without change of simulant. ^c Diffusion coefficients used for theoretical calculations: 122 °F, 6.1 × 10⁻¹¹ cm²/s; 158 °F, 3.7 × 10⁻¹⁰ cm²/s.

exposure in seconds for the *i*th temperature step. More details may be obtained from the original paper when it is issued.

For the repeated-use with temperature fluctuation experiment outlined above, eq 1 would predict the migration during the first time/temperature step (122 °F). For the second time/temperature step (158 °F), the theoretical migration can be calculated following eq 3 (which is derived from eq 2)

$$M_2 = (2C_0/\sqrt{\pi})[\sqrt{D_1t_1 + D_2t_2} - \sqrt{D_1t_1}] \quad (3)$$

where all variables from eq 1 apply to the first time/temperature step and M_2 is the amount migrating in ng/cm² during the second temperature step, D_2 is the diffusion constant in cm²/s for the second temperature step, and t_2 is the time of exposure in seconds at the second temperature.

Table II presents the results obtained from this experiment and compares these results to the results from the analytical solution based on eq 3. Also included are the results from the repeated-use determination experiment at 158 °F and the results obtained for the calculation of the expected migration from freshly molded polymer (no prior heat history). All theoretical calculations use the diffusion coefficients listed in Table I.

The significance of the prior heat history to the actual migration is clearly shown from these data, with only about one-third of the migration observed for a 4-h 158 °F exposure after a 24-h exposure at 122 °F as was observed for a 4-h 158 °F exposure with no prior heat history. These data also show excellent agreement was obtained between modeling of the expected concentrations at different time points during a single step and a two-step temperature exposure using the diffusion equations previously given and the actual measured data for these exposures.

IV. Validity of Assumptions. Some of the diffusion assumptions, of course, are not exactly true. But it can be shown that even though some of the assumptions are not exactly true, there is little or no apparent effect, thus validating the use of the assumptions for this work and thus the reason for labeling the diffusion coefficients calculated as either "apparent" or "calculated". Other assumptions are simply validated by experimental design, as described below.

While there must be some resistance to mass transfer in all of the experimental designs where the concentration

of a component is allowed to increase in the simulant, a comparison of the data from the 120 and 122 °F experiments shows that the effect is negligible for these experiments. The 120 °F exposure was 3 days in duration with no agitation of the sample. The 122 °F exposure data were the sum of the concentrations of the hourly exposures for 6 h straight, where there was fresh solvent every hour, and the concentration from that sample, which was then agitated continuously for the next 17 h with no solvent change (Table II). The close agreement of the two diffusion coefficients at 120 and 122 °F, determined from these two different experimental exposure procedures ranging from a procedure where there was no mixing for 72 h to a procedure where there was essentially continuous mixing over a 22-h period, indicates that there was little effect due to the resistance to mass transfer for these experiments. The SAN polymers are considered to not be penetrated by water; therefore, we expect no increased migration due to polymer/simulant interaction. The migrant, obviously, is not homogeneously distributed in the polymeric material at the start of the study, as during cooling after molding some AN would have migrated from the surface region of the polymeric plaques, as has been discussed by previously (Ayres et al., 1983; Stanley and Alger, 1989). For the experiments reported herein, though, immediately upon cooling the samples were stacked together in intimate contact, wrapped in an oxygen-free barrier wrap, and placed in a freezer until the exposures were started, which was within 1 day of molding. When samples were taken from the freezer for exposure, only samples from the middle of the stack were used, which would maintain as near homogeneity as possible. The polymer samples were not depleted of AN under any of the exposure conditions, with the highest migration observed being for the 180 °F exposure, where less than 10% of the total AN in the polymer migrated into solution. Finally, from examining the data from Figures 2 and 3, one can see no equilibrium partitioning occurred over the course of these two experiments. Then, comparing the data generated for all of the diffusion coefficients from all experiments (Figure 1), it appears the data are self-consistent, indicating that the equilibrium partitioning did not occur in any of the experiments. Thus, the validity of all assumptions, and the subsequent use of the Fickian diffusion model, appears to be appropriate.

Conclusions. New data on the migration of AN from SAN copolymers used in repeated-use food-contact applications have been presented and appear to follow Fickian diffusion principles. A linear relationship was observed between the apparent diffusion coefficients obtained using a simple diffusion model and the inverse of the absolute temperature of exposure over temperatures ranging from 70 to 180 °F. The activation energy for AN diffusion through the SAN polymer studied was similar to activation energies previously obtained for AN diffusion through ABS polymers and other SAN polymers. The importance of considering the history of the sample prior to definitive migration studies was experimentally demonstrated, and a simple mathematical model was presented to deal with multistage diffusional processes consisting of steps at different temperatures.

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