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Chemistry of the Interactions of Acetaldehyde Scavengers for Poly(ethylene terephthalate)

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ABSTRACT: The acetaldehyde (AA) scavenging mechanisms of anthranilamide, metaxylenediamine (MXDA), and alpha-cyclodextrin were investigated through a combination of proton nuclear magnetic resonance (^{1}H-NMR) and mass spectrometry techniques. AA was found to react with the amide and amine groups of anthranilamide to produce a two-ring structure with water as a byproduct. MXDA possesses two terminal, primary amines that make it difunctional. The aldehyde group of AA reacts with each primary amine to create an imine group and water. The imine groups were found to act as chromophores, supporting the results of previous work with poly (ethylene terephthalate). The AA scavenging mechanism for alpha-cyclodextrin was determined through concentration dependent NMR experiments. As the concentration of alpha-cyclodextrin was increased, the chemical shifts of AA's protons increased until a saturation point was reached at a molar ratio of one to one. This indicates that each alpha-cyclodextrin accommodates one AA molecule through hydrogen bonding and a size-enclosure mechanism. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4191–4200, 2013

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INTRODUCTION

The generation of acetaldehyde (AA) in poly(ethylene terephthalate) (PET) has been broadly studied.[1–3] Investigations have included the mechanisms, by which AA is formed, its affect upon various foodstuffs, and ways to minimize its presence in PET. One approach for reducing detectable levels of AA has been the addition of AA scavengers to PET resins and formed articles. These scavengers do not suppress PET degradation. They are instead designed to interact with any AA that is generated during processing and thus reduce or eliminate the diffusion of AA from manufactured containers.[4]

There are at least three reported mechanisms, by which AA is scavenged. One type of scavenger reduces the appearance of AA through chemical reaction and formation of a physical bond with the scavenger to create at least one new product.[5] A second type of scavenger limits the diffusion of AA by forming an inclusion complex with the volatile, organic compound. This occurs when AA penetrates the internal cavity of the scavenging agent and is held in place by secondary chemical bonding.[6] The third type of AA scavenger includes catalysts, which reduce AA concentrations in PET by converting AA into another chemical species.[7–9] The conversion of AA into another chemical, such as acetic acid, reduces its volatility and any effects on flavor of the packaged food or beverage.

Evaluations of various AA scavengers for use with PET have focused mainly on their ability to reduce the detection of AA [5–9]. The scavenging mechanisms; however, have rarely been explored and/or verified. Bandi, et al.[10] studied the mechanism of color formation when PET is melt-blended with polyamides; particularly poly(m-xylylene adipamide) (MXD6). They determined that as a result of reactions between the amine end groups of MXD6 and the aldehyde groups of AA, imine group chromophores were formed. While MXD6 is typically added to PET to reduce its permeability, this reaction indicates that MXD6 is also an AA scavenger. Other forms of literature, such as patents, do not explicitly describe these scavenging mechanisms; only the benefits of their usage. Previous work in our laboratory concentrated on melt blending and preparation of PET with various concentrations of anthranilamide, metaxylenediamine (MXDA), and alpha-cyclodextrin AA scavengers.[11] Scavenging abilities of these blends were closely monitored as were the scavengers' effects on the physical properties of PET. The purpose of the current work is to identify and compare the AA scavenging mechanisms of the anthranilamide, MXDA, and alpha-cyclodextrin.

EXPERIMENTAL

Materials

The AA scavenger, anthranilamide was purchased from Sigma-Aldrich (St. Louis, MO), MXDA was donated by Mitsubishi Gas

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Chemical America (Tokyo, Japan) and alpha-cyclodextrin was supplied by the Wacker Chemical Corporation (Adrian, MI). AA was purchased from Sigma-Aldrich (St. Louis, MO), whereas both deuterium oxide (D_2O) and deuterated chloroform ($CDCl_3$) were purchased from Cambridge Isotope Laboratories (Andover, MA).

Nuclear Magnetic Resonance Spectroscopy

One-dimensional ^1H and ^1H–^1H COSY nuclear magnetic resonance (NMR) experiments were conducted using a Varian Inova 600 MHz NMR spectrometer (Palo Alto, CA), located in the Instrumentation Center of the University of Toledo. Measurements were performed at ambient temperature and used the appropriate deuterated solvent as an internal standard. $CDCl_3$ was used to study the AA scavenging mechanisms of both anthranilamide and MXDA; whereas D_2O was used for alpha-cyclodextrin studies. Evaluations of the AA scavenging systems began by obtaining a reference NMR spectrum for each material, dissolved in the appropriate solvent. Measured amounts of both AA and AA scavenger were then separately dissolved using the same deuterated solvent. These solutions were then combined into one tube and analyzed. Multiple samples, of varying concentrations, were prepared to study the AA scavenging mechanism of alpha-cyclodextrin. ACD/H-NMR advanced prediction, processing and interpretation software and ChemSketch® software programs were used for prediction, simulation, and drawing of ^1H-NMR spectra and chemical structures.

Mass Spectrometry

Mass spectrometry experiments were conducted to compliment and verify the NMR analysis. The Hewlett-Packard (Palo Alto, CA) Esquire Ion Trap (Billerica, MA) liquid chromatography/mass spectrometer, located in the University of Toledo Instrumentation Center, was equipped with electrospray ionization (ESI) and an ion trap. Samples of 10–15 mg were dissolved in chloroform and injected directly into the mass spectrometer. To aid the ionization process, a small aliquot of methanol was added to each solution.

RESULTS AND DISCUSSION

Anthranilamide AA Scavenging Mechanism

Investigations of the AA scavenging reaction between anthranilamide and AA included ^1H-NMR characterization of the individual unreacted components. Figure 1(a) shows the structure of AA and its ^1H-NMR spectrum, while dissolved in $CDCl_3$. An integration factor is shown under each prominent signal, indicating the number of protons represented by that peak. From left to right, the 1–3 ratio correlates with the ratio of one hydrogen atom in AA's aldehyde (O═CH) group to the three hydrogen atoms located in its methyl (CH_3) group. Peak assignments, locations, and integration factors are summarized in Table I.

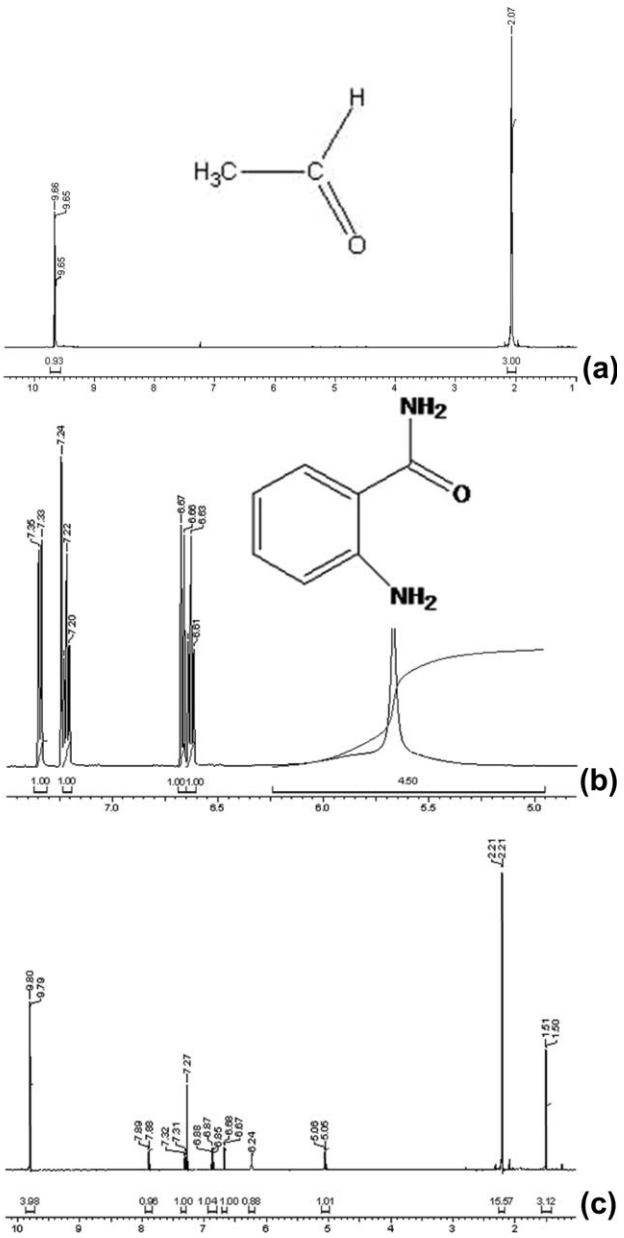

Figure 1. ^1H-NMR spectra in $CDCl_3$ of (a) AA, (b) anthranilamide, and (c) the reaction products of anthranilamide and AA after 2 days at 60°C.

Table I. Peak Assignments for the ^1H-NMR Spectrum of AA in $CDCl_3$

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
2.07	Doublet	3	AA	CH_3
7.24	Singlet	-	Chloroform-d	
9.65	Quartet	1	AA	O═CH

Table II. Peak Assignments for the ^{1}H-NMR Spectrum of Anthranilamide in $CDCl_3$

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
5.67	Singlet	4.5	Anthranilamide	NH_2 and O=CNH_2
6.63	Triplet	1	Anthranilamide	CH
6.67	Doublet	1	Anthranilamide	CH
7.20	Triplet	1	Anthranilamide	CH
7.24	Singlet	-	Chloroform-d	
7.34	Doublet	1	Anthranilamide	CH

Table III. Peak Assignments for the ^{1}H-NMR Spectrum of the Reaction Between Anthranilamide and AA, in $CDCl_3$, After Heating for 2 Days at 60°C

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
1.50	Doublet	3	Reaction product	CH_3
2.21	Doublet	15.5	AA	CH_3
5.06	Quartet	1	Reaction product	Undetermined
6.24	Singlet	1	Reaction product	Undetermined
6.68	Doublet	1	Reaction product	CH
6.87	Triplet	1	Reaction product	CH
7.27	Singlet	-	Chloroform-d	
7.31	Triplet	1	Reaction product	CH
7.89	Doublet	1	Reaction product	CH
9.80	Quartet	4	AA	O=CH

The ^{1}H-NMR spectrum of anthranilamide (dissolved in $CDCl_3$) is shown in Figure 1(b) with results summarized in Table II. A prominent feature of this spectrum is the broad singlet that appears at 5.67 ppm. The peak is broad because it represents exchangeable protons that are rapidly traded in the $CDCl_3$ solution. They are the four protons comprising both the amide (O=CNH_2) and the amine (NH_2) groups of anthranilamide. Also shown in Figure 1(b) are peaks representing anthranilamide's four aromatic protons that are respectively centered at 6.63, 6.67, 7.20, and 7.34 ppm.

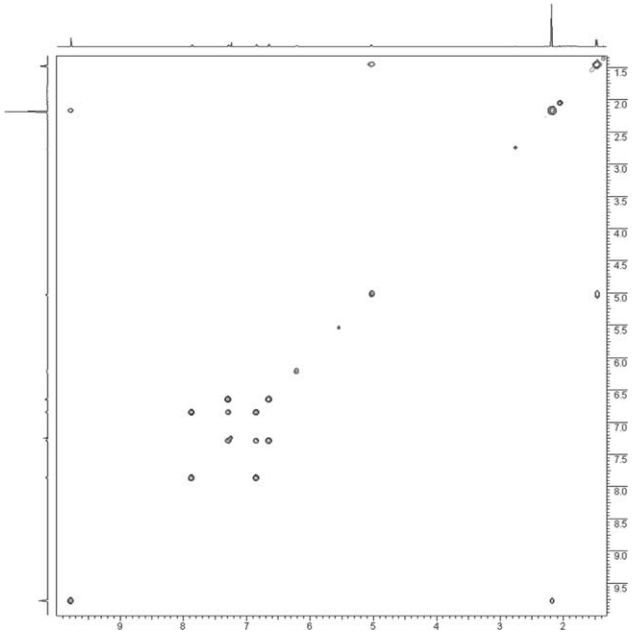

Figure 2. ^{1}H–^{1}H COSY NMR spectrum of the reaction between anthranilamide and AA, in $CDCl_3$, after 2 days at 60°C.

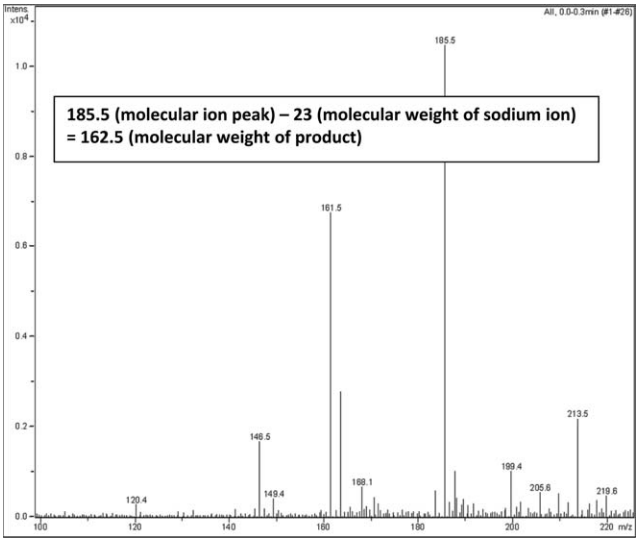

Figure 3. ESI mass spectrum of the product from the reaction between anthranilamide and AA in $CDCl_3$ and methanol.

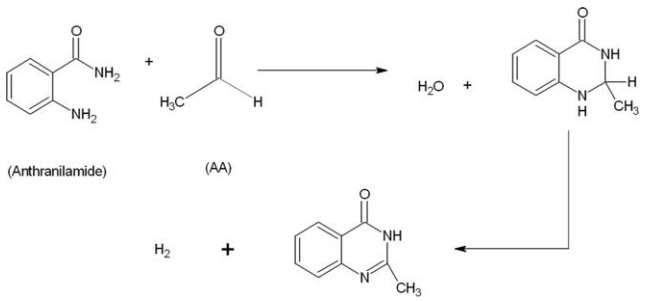

Figure 4. Proposed reaction mechanisms for anthranilamide and AA.

To investigate the interactions of anthranilamide with AA, each was dissolved in $CDCl_3$ and then combined into one tube, at room temperature. The resulting spectrum showed a simple combination of the ^{1}H-NMR spectra of AA [Figure 1(a)] and anthranilamide [Figure 1(b)]. It was evident that no reaction had occurred and that energy must be added to this system to initiate a reaction. A second attempt to obtain a reaction was made; however, this time after the solutions were combined into one tube, it was sealed. For this process, the lower portion of the NMR tube and its contents were frozen in liquid nitrogen and vacuum was applied to continually remove air from the system. The neck of the NMR tube was then melted in a flame to seal the tube.

The sealed NMR tube was held at 60°C for 48 h to achieve a reaction. The spectrum shown in Figure 1(c) indicates that after heating, AA and an additional compound were present in the solution. The identification of AA is confirmed by the doublet at 2.21 ppm and the quartet at 9.80 ppm. These peaks have locations and integration factors similar to those seen in Figure 1(a), with the doublet at 2.21 ppm slightly larger than expected. Examination of Figure 1(c) reveals several indications that the second component was produced through a reaction of anthranilamide with AA.

The first evidence indicating formation of a reaction product is the presence of a new peak (doublet) at 1.50 ppm with an integration factor of three. The location and integration factor indicate that this peak represents a methyl group (CH_3). The peak is a doublet indicating that it is coupled to another functional group comprised of only one proton. An additional indication that a reaction occurred is the quartet peak at 5.06 ppm, with an integration factor of one. The fact that this peak is a quartet means that it is coupled to three other protons. This combination implies the formation of a HC–CH_3 linkage. In addition, the broad singlet (representing exchangeable protons) that previously appeared in anthranilamide's spectrum at 5.67 ppm now appears to have shifted to 6.24 ppm. This upfield shift implies a change in the chemical environment or reaction. These results are summarized in Table III.

To provide further clarification, a ^{1}H–^{1}H COSY NMR experiment was conducted on the heated sample to obtain the spectrum shown in Figure 2. As can be seen, the quartet peak at 5.06 ppm is coupled with the doublet at 1.50 ppm. There is no evidence, however, of the peak at 5.06 ppm being coupled to any other protons. This means that either this group is not bonded to any group other than the methyl group, or it is bonded to a heteroatom(s).

Analysis of the previous two NMR spectra could lead to the prediction of at least two different reaction mechanisms by which anthranilamide scavenges AA. One possible mechanism would have produced a larger organic compound that comprised a terminal CH_3 group and a CH group attached to two heteroatoms (oxygen and nitrogen). The molecular weight of this compound would have been 180.2 g/mol. NMR software programs were used to predict and draw the ^{1}H-NMR spectrum

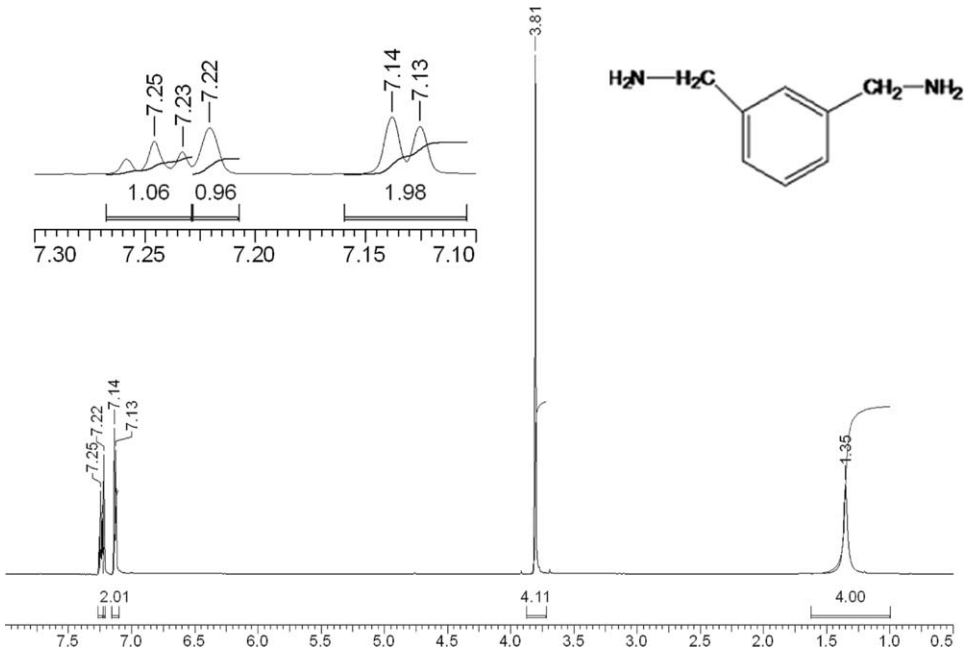

Figure 5. ^{1}H-NMR spectrum of MXDA in $CDCl_3$.

Table IV. Peak Assignments for the ^{1}H-NMR Spectrum of MXDA in $CDCl_3$

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
1.35	Singlet	4	MXDA	Two NH_2
3.81	Singlet	4	MXDA	Two CH_2
7.14	Doublet	2	MXDA	Two CH
7.22	Singlet	1	MXDA	CH
7.25	Triplet	1	MXDA	CH

of this compound. The predicted spectrum exhibited a peak pattern similar to that of the experimentally determined spectrum, with one exception. In Figure 1(c) the experimental quartet peak appears at 5.06 ppm. In the case of the predicted spectrum, however, this peak was seen at about 5.53 ppm.

A second possible reaction mechanism would result in the formation of a bicyclical organic compound with water as a byproduct. This bicyclical reaction product has a terminal methyl group (CH_3) and a CH group attached to two heteroatoms. For this compound, with a molecular weight of 162.2 g/mol, the CH group bonds to two nitrogen atoms, instead of a nitrogen atom and an oxygen atom. The predicted spectrum of this reaction product closely matched the experimental spectrum shown in Figure 1(c). The location of the predicted quartet peak representing the CH group was 4.98 ppm, whereas its measured spectral location was 5.06 ppm. In addition, the ^{1}H-NMR spectrum shown in Figure 1(c) contains a larger than expected doublet at 2.21 ppm. A peak near this location is a typical indicator for the presence of water, which may have contributed to its area.

As a means to support the ^{1}H-NMR experimental and predicted results, ESI mass spectrometry was used to analyze samples of unreacted anthranilamide and the heated anthranilamide and AA. Each of these samples was dissolved in $CDCl_3$ with a small aliquot of methanol added to aid with the ionization process. The resulting mass spectrum for anthranilamide yielded a base peak located at 159.1 mass to charge ratio (m/z). The molecular weight of anthranilamide, however, is known to be 136.1 g/mol. The difference between these two masses is 23 g/mol, the molecular weight of sodium (Na). Before analysis the sample was stored in a glass container. Sodium is a known component of glass that can leech into a container's contents as a contaminant.

The mass spectrum of the reaction product obtained from heated anthranilamide and AA is given in Figure 3. For this

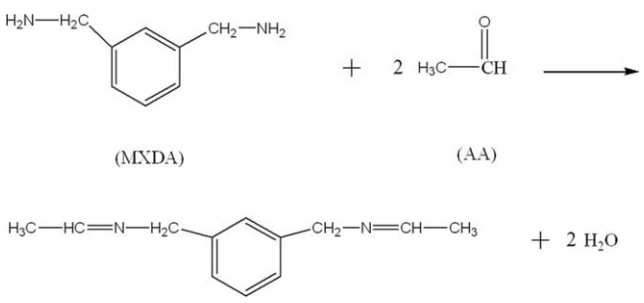

Figure 6. Proposed reaction scheme for MXDA and AA.

spectrum, the base peak is at 185.5 m/z. Subtracting the mass of sodium from the molecular ion peak yields a mass of 162.5 g/mol. This molecular weight corresponds to that of the product (162.2 g/mol) formed in the second proposed reaction mechanism, as shown in the upper portion of Figure 4.

Examination of the patent by Rule et al.[12] also indicates that the second proposed mechanism is correct. U.S. Patent 6,274,212 describes the interaction of anthranilamide and AA (in the presence of PET) as, "combining with polyester an organic additive compound comprising at least two hydrogen-substituted heteroatoms bonded to carbons of the organic additive compounds, the organic additive compound being reactive with AA in the polyester to form water and a resulting organic compound comprising an unbridged 5- or 6-member ring including at least two heteroatoms". The patent also states that "the two heteroatoms are both nitrogen".

The mass spectrum shown in Figure 3 exhibits an additional peak of interest at 161.5 m/z. ESI mass spectrometry generally ionizes a compound by adding an ion such as hydrogen (H) or sodium (Na). This method does not typically remove a hydrogen atom; however, if this had occurred the peak at 161.5 m/z would correlate very well with the mass of the product (162.2 g/mol) from the upper portion of the reaction mechanism shown in Figure 4. Since such ion removal is not typical, a compound with a molecular weight of about 160 g/mol (ionized by a hydrogen atom to 161 g/mol) would be more likely to correspond with the secondary molecular ion peak at 161.5 m/z.

Figure 4 shows a proposed reaction mechanism for anthranilamide and AA in which the final product possesses a molecular weight of 160.2 g/mol. This proposed reaction mechanism starts with the already identified reaction scheme, but adds one more step to the reaction. The second step is a desaturation reaction in which the bicyclical organic product formed in the first reaction gives off a dihydrogen molecule that yields a similar two-ring structured organic compound, with a double bond in its second ring. The formation of this final product has been observed by several authors.[13–16] Abdel-Jalil et al.[13] showed that this product can be generated with the aid of time, energy, and a catalyst. Beyond what was previously stated, Rule et al.[12] gave no further indication of the exact composition for their resulting organic compound.

Additional experiments were conducted to determine if the final reaction product could be produced and ^{1}H-NMR experiments were used to observe if double bond formation had occurred in

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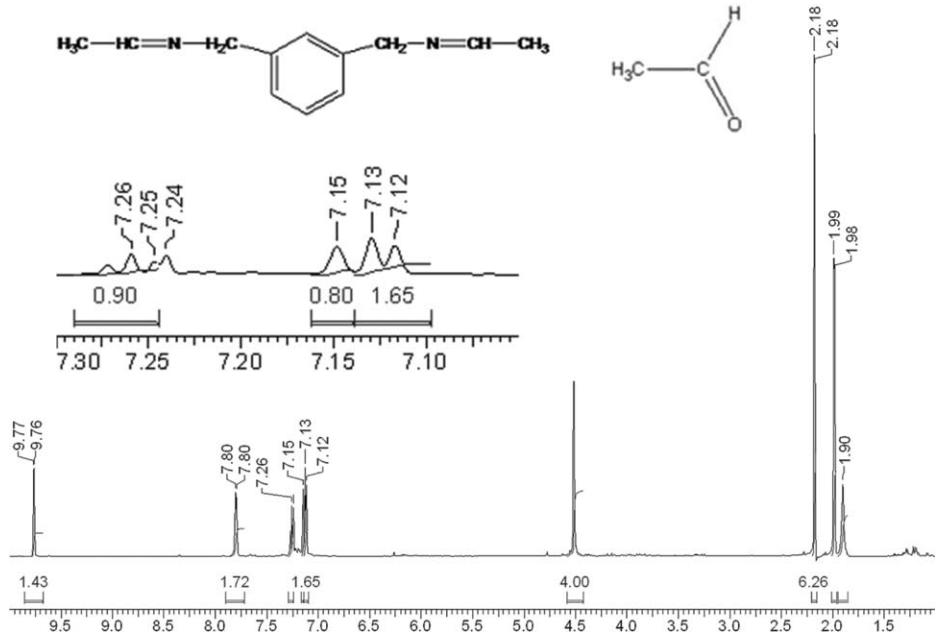

Figure 7. ^{1}H-spectrum of the reaction between MXDA and AA in $CDCl_3$.

the second ring. The sealed NMR tube containing the dissolved mixture of anthranilamide and AA was heated over a 4-week period, at 60°C. Periodic ^{1}H-NMR spectra were obtained and analyzed; however, no evidence of double bond formation in the second ring was observed. It is important to note that the current experiment was conducted in the absence of a catalyst, which was a component in the experiments of Abdel-Jalil et al.[13] It is possible that the proposed final reaction step, shown in Figure 4, could be obtained when anthranilamide is added to PET. All PET resins contain small amounts of residual polymerization catalysts. When anthranilamide is added, to act as an AA scavenger, these residual catalysts could aid in the formation of the final product shown in the reaction scheme.

MXDA AA Scavenging Mechanism

Investigations into the AA scavenging reaction between MXDA and AA were conducted in the same manner as for anthranilamide and AA. Figure 5 shows the structure and ^{1}H-NMR spectrum of MXDA dissolved in $CDCl_3$ and results are summarized in Table IV. Peaks appearing between 7.0 and 7.3 ppm represent the aromatic protons and are expanded for detailed viewing. The singlet at 3.81 ppm corresponds to the two CH_2 groups adjacent to the aromatic center of the compound. The ^{1}H-NMR spectrum of MXDA contains a very broad peak located at 1.35 ppm. The broadness of this peak indicates the presence of exchangeable protons, representing MXDA's two primary amine groups (NH_2).

The MXDA and AA were dissolved separately in $CDCl_3$ and then combined into one tube. Mixing the two solutions at room temperature caused the instantaneous formation of a solid, orange product. Dilution of this product altered its color from orange to a dark yellow with a slight greenish appearance. The color of this sample was similar to that observed for a previously prepared 10,000 ppm (wt/wt) MXDA/PET blend sample, after twin-screw extrusion.[11]

Table V. Peak Assignments for the ^{1}H-NMR Spectrum of the Reaction Between MXDA and AA in $CDCl_3$

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
1.90	Singlet	-	H_2O	
1.99	Doublet	4.5	AA	CH_3
2.18	Doublet	6	Reaction product	Two CH_3
4.51	Singlet	4	Reaction product	Two CH_2
7.14	Doublet	2	Reaction product	Two CH
7.15	Singlet	1	Reaction product	CH
7.24	Singlet	-	Chloroform-d	
7.26	Triplet	1	Reaction product	CH
7.80	Quartet	2	Reaction product	Two HC=N
9.77	Quartet	1.5	AA	O=CH

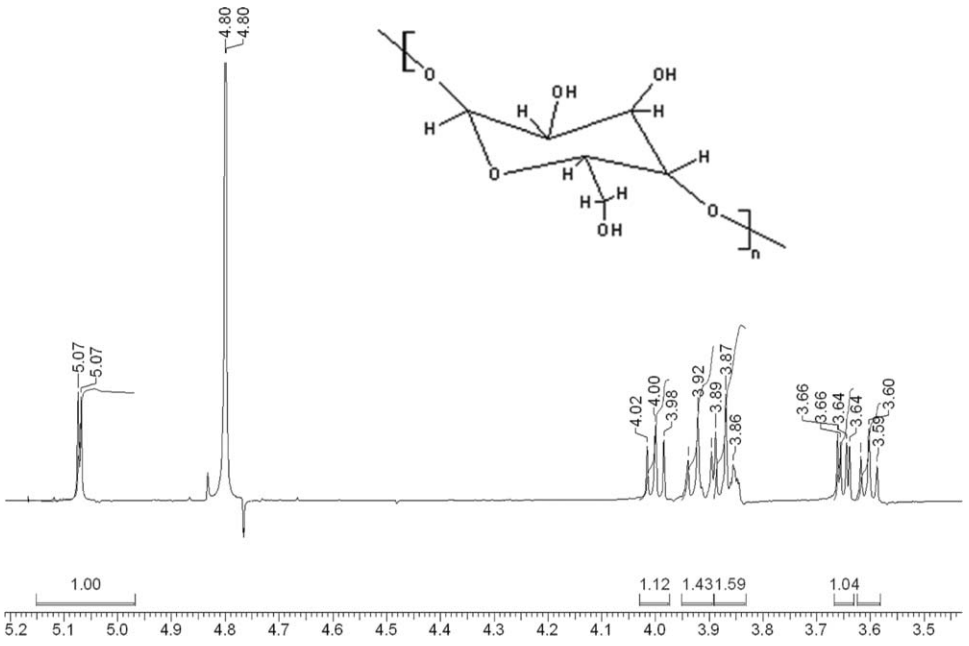

Figure 8. ^{1}H-NMR spectrum of alpha-cyclodextrin in D_2O.

Similar color formation in polyamide/PET blends was documented by Bandi et al.[10] They showed that their color was generated as a result of reactions between the MXD6 amine groups and generated AA from PET. These reactions resulted in the formation of imine (N═CH) groups, which they identified as the chromophore. MXDA is a monomer from which MXD6 is manufactured. MXDA has two primary amines, whereas MXD6 has only one.

The AA scavenging mechanism for MXDA is shown in Figure 6. Similar to the reaction for MXD6 and AA, the aldehyde group (O═CH) of AA reacts with a primary amine group from MXDA. Since MXDA has two primary amine groups, one molecule of MXDA can react with up to two molecules of AA. The result of this reaction can therefore generate up to two imine groups and up to two molecules of water, as a byproduct.

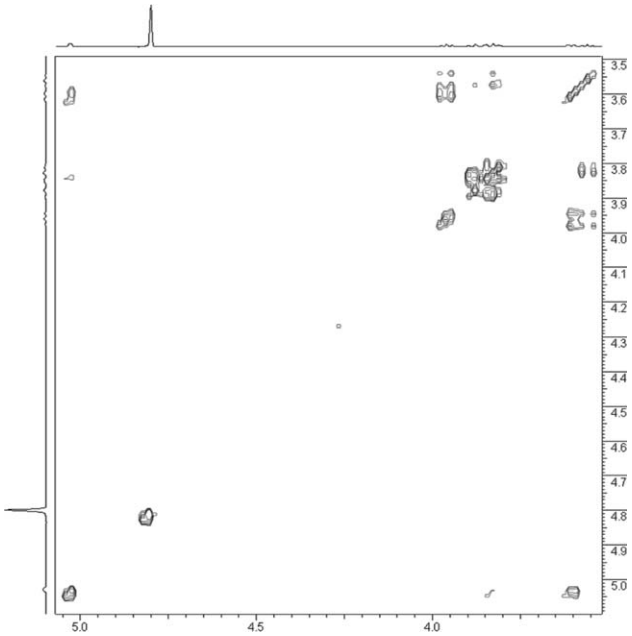

Figure 9. ^{1}H–^{1}H COSY NMR spectrum of alpha-cyclodextrin in D_2O.

The ^{1}H-NMR spectrum representing the reaction between MXDA and AA is shown in Figure 7. These results that are summarized in Table V confirm the reaction scheme shown in Figure 6. The singlet at 1.90 ppm indicates that water has been formed and new peak is found at 7.80 ppm. This peak is a quartet and represents the two imine (HC═N) groups resulting from reactions between the two amine groups from MXDA and the aldehyde group from AA. The absence of the singlet at 1.35 ppm (shown in Figure 5) indicates that all the primary amines have been consumed in this reaction and have been converted to imine groups. Only reaction products and AA remain in this solution.

Alpha-Cyclodextrin AA Scavenging Mechanism

Alpha-cyclodextrin has a polar, molecular structure; therefore, all experiments in which its AA scavenging ability was examined with ^{1}H-NMR were performed with D_2O as the solvent. Individual ^{1}H-NMR spectra of alpha-cyclodextrin and AA were initially obtained in D_2O. Figure 8 shows alpha-cyclodextrin's repeat unit, inserted above its ^{1}H-NMR spectrum. Peaks shown in this spectrum correspond only to the hydrogen atoms bonded to carbon atoms (CH groups). Hydroxyl group protons are not seen, as a result of the D_2O solvent. The hydrogen atoms of the hydroxyl groups are rapidly exchanged with the deuterium atoms in D_2O causing them to be grouped into the water peak at 4.80 ppm. An ^{1}H–^{1}H-NMR COSY experiment was also conducted to aid in identification of the various CH groups of alpha-cyclodextrin. This spectrum is shown in Figure 9 with results given in Table VI.

The previous ^{1}H-NMR spectrum of AA [Figure 1(a)] was obtained in $CDCl_3$. The change in solvents required a spectrum

Table VI. Peak Assignments for the ^{1}H-NMR Spectrum of Alpha-Cyclodextrin in D_2O

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
3.60	Triplet	1	α-Cyclodextrin	CH
3.61	Doublet of doublets	1	α-Cyclodextrin	CH
3.83	Triplet	1	α-Cyclodextrin	CH
3.88	Triplet	2	α-Cyclodextrin	CH_2
3.96	Triplet	1	α-Cyclodextrin	CH
4.80	Singlet	-	D_2O	
5.03	Doublet	1	α-Cyclodextrin	CH

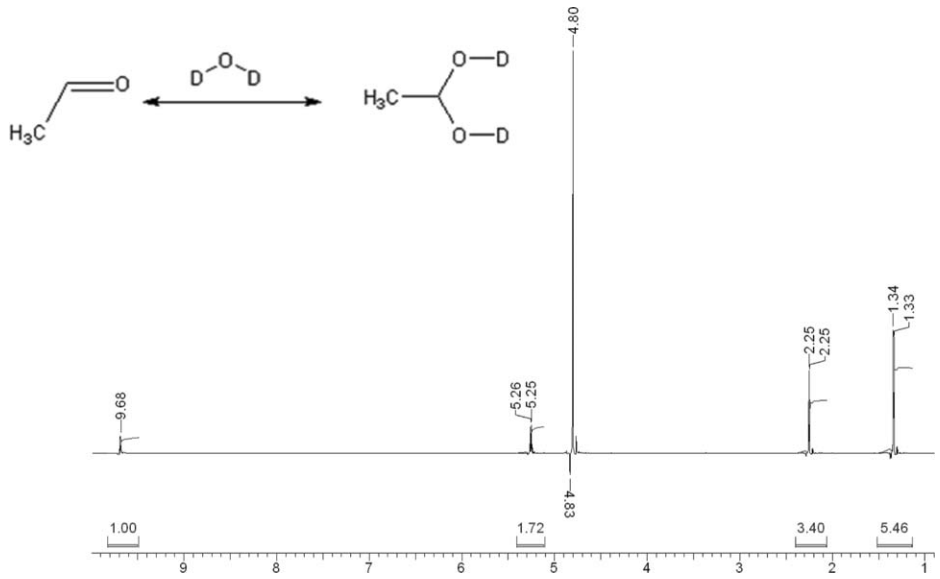

Figure 10. ^{1}H-NMR spectrum of AA in D_2O and the equilibrium reaction between AA and D_2O.

of AA in D_2O, as shown in Figure 10. The spectral patterns showed significant differences in the two solvents. This occurred because in the presence of D_2O (which is slightly acidic) AA forms an equilibrium product, according to the reaction scheme illustrated in the upper portion of Figure 10. NMR software was used to predict the ^{1}H-NMR spectrum of a solution containing AA and its acetal-based equilibrium product. The predicted and the experimental spectra were equivalent, in support of the proposed equilibrium reaction scheme.

In Figure 10, the doublet at 2.25 ppm and the quartet at 9.68 ppm correspond respectively to the methyl and aldehyde protons of AA. The doublet at 1.34 ppm (CH_3 group) and the quartet at 5.25 ppm (CH group) represent the equilibrium product. Any hydroxyl protons are hidden in the water peak at 4.80 ppm. It appears that the equilibrium product is twice as prevalent as AA since its respective integration factors are double those of AA. These results are given in Table VII.

Table VII. Peak Assignments for the ^{1}H-NMR Spectrum of AA in D_2O

			Peak assignment	
Peak location (ppm)	Peak type	Integration factor	Chemical compound	Functional group
1.34	Doublet	6	Equilibrium product	CH_3
2.25	Doublet	3	AA	CH_3
4.80	Singlet	-	D_2O	
5.25	Quartet	2	Equilibrium product	CH
9.68	Quartet	1	AA	O=CH

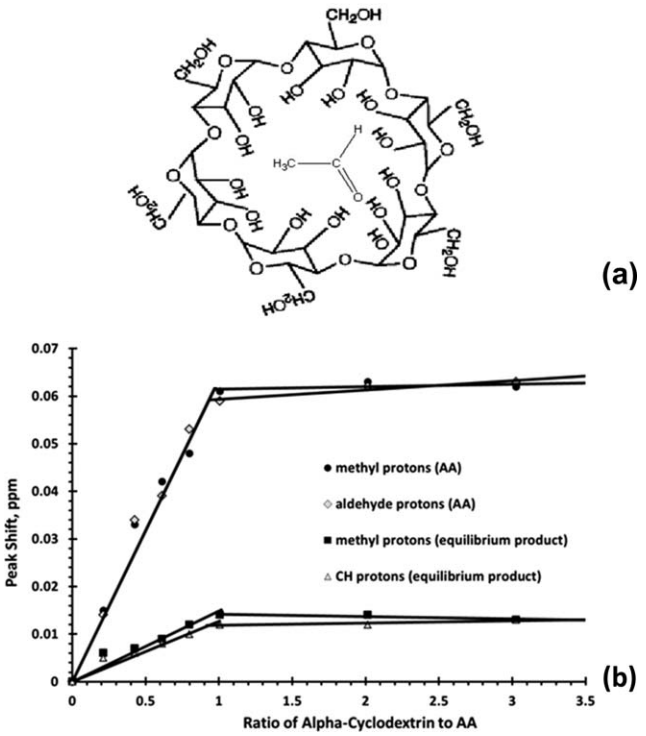

Figure 11. (a) Interaction mechanism for AA and alpha-cyclodextrin. (b) Peak shifting of the protons of AA and its equilibrium product as a function of molar ratio of alpha-cyclodextrin to AA in D_2O.

Cyclodextrins are reported to act as AA scavengers through a size-enclosing mechanism.[6, 17–23] They have lipophilic internal structures and hydrophilic exteriors, making them easily soluble in water or D_2O. The lipophilic interiors of cyclodextrins are favorable for entrance of aldehydes and other organics.[4] As illustrated in Figure 11(a); alpha-cyclodextrin encapsulates AA into its cyclical structure, without the need for a chemical reaction. The force by which AA is held inside alpha-cyclodextrin is hydrogen bonding.

Several authors have shown that ^{1}H-NMR can be used to validate cyclodextrin's size-enclosing mechanism through concentration dependent NMR "titration" studies.[24–27] In the current experiment, a procedure, similar to that detailed by Hao et al., [24] was followed. For this work, alpha-cyclodextrin was the host molecule and AA the guest molecule. Samples were prepared by separately weighing and then dissolving each component in D_2O. These two solutions, in separate vessels, were then combined into one NMR tube to achieve the desired molar ratios. Nine samples were prepared. They included pure alpha-cyclodextrin, pure AA, and molar ratios of alpha-cyclodextrin to AA of 0.2 : 1, 0.4 : 1, 0.6 : 1, 0.8 : 1, 1 : 1, 2 : 1, and 3 : 1.

The four sets of protons monitored during ^{1}H-NMR evaluations are identified in Figure 10. For AA the protons are from the aldehyde and the methyl groups. For the acetal-based equilibrium product, the methyl and the CH protons were monitored. As the relative concentrations of alpha-cyclodextrin to AA increased, the peak locations changed or shifted. Figure 11(b) shows results obtained from the NMR "titration" experiment, conducted to study the AA scavenging mechanism of alpha-cyclodextrin. This plot shows that as the concentration of alpha-cyclodextrin increased relative to that of AA, the chemical shift of protons for AA and its equilibrium product also increased until a saturation point was reached. The saturation point for the alpha-cyclodextrin and AA complex occurred at a ratio of one to one, indicating that each molecule of alpha-cyclodextrin can accommodate one molecule of AA.

CONCLUSIONS

Investigations of the AA scavenging mechanisms of anthranilamide, MXDA, and alpha-cyclodextrin indicated that anthranilamide and MXDA each sequester AA through specific reaction schemes. Mechanisms through which anthranilamide scavenges AA include reactions between the amide or amine groups of anthranilamide and the aldehyde group of AA to produce a two-ring, organic structure with water as a byproduct. Each of the two primary amines of MXDA reacts with an aldehyde group of AA to create an imine group and water, as a byproduct. The imine groups act as chromophores, producing colors from yellow to orange brown that appear darker with increasing concentration. Alpha-cyclodextrin scavenges AA through a hydrogen bonding/size-enclosure mechanism, with each molecule of alpha-cyclodextrin able to accommodate one molecule of AA.

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