

1-1-2014

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Ethem Kaya

*University of Southern Mississippi, Ethem.Kaya@usm.edu*

Tara Smith

*University of Southern Mississippi*

Lon J. Mathias

*University of Southern Mississippi, Lon.Mathias@usm.edu*

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## Recommended Citation

Kaya, E., Smith, T., Mathias, L. J. (2014). UV Curable Coatings for Improved Gas Barrier Properties of Poly(ethylene terephthalate). *Progress in Organic Coatings*, 77(1), 194-201.

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# UV CURABLE COATINGS FOR IMPROVED GAS BARRIER PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)

*Ethem Kaya, Tara Smith, and Lon J. Mathias\**

*Department of Polymer Science  
University of Southern Mississippi  
118 College Drive #10076, Hattiesburg, MS 39406-0076  
Lon.mathias@usm.edu*

## ABSTRACT

A new high-barrier coating based on methyl ( $\alpha$ -hydroxymethyl)acrylate (MHMA) for poly(ethylene terephthalate) (PET) was developed along with the process for preform dipping and cure prior to blow molding into bottles. The UV curable coating gives excellent barrier improvement when coated onto PET biaxially oriented thin films. Blown bottle side walls from coated PET preforms also show 2-3 times improvement over uncoated side walls. The effect of photoinitiator concentration, initiator types, and temperature on photopolymerization kinetics of MHMA was investigated. Once the photoinitiator, Irgacure 819<sup>®</sup>, concentration became larger than 1 mol-%, a decrease in rate of propagation was observed. The conversion also decreased with higher initiator concentration. Irgacure 819<sup>®</sup> reduced the auto-acceleration peak and reached maximum rates of polymerization much faster than Irgacure 651<sup>®</sup>. It also gave a slightly higher conversion. Overall conversion for combinations of these photoinitiators were high, above 80%. Real-time FTIR (RT-FTIR) studies of copolymerization of MHMA and methyl methacrylate (MMA) showed that conversion was fairly high up to 25 mol-% MMA. However, once MMA feed ratio exceeded 10 mol-%, a decrease in barrier performance was observed.

*Keywords:* Photopolymerization, PET, hydrogen bonding, gas barrier, permeability

## 1. Introduction

Gas barrier, the ability of a material to limit the permeation of certain gases through polymeric structures, is a key factor in the design of food and beverage packaging.

Poly(ethylene terephthalate) (PET) is increasingly used for packaging applications due to its transparency, ease of processing, and low cost. Its semi-crystalline nature inherently gives rise to moderate gas barrier properties. However, a three- to five-fold decrease in permeability is needed for certain applications such as packaging beer, fruit juices, and baby foods. For this reason, increasing emphasis has been put on methods to decrease the solubility and diffusivity of gasses in and through PET.

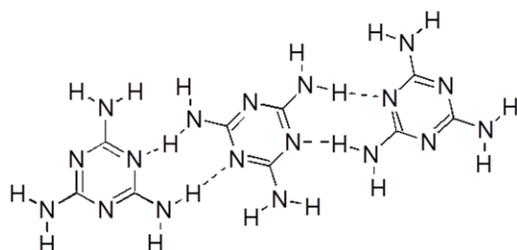
Impermeable inorganic materials have been used as fillers for PET,<sup>1,2</sup> in stand-alone coatings,<sup>3,4</sup> and in hybrid organic-inorganic coatings.<sup>5</sup> Improvements in barrier are generally related to a decrease in diffusivity by formation of a torturous pathway in the case of inorganic fillers, or by the high density of inorganic coatings. Generally, inorganic coatings are brittle, and cracking or hole formation quickly deteriorates barrier properties.

In polymers, free volume must be reduced or excluded to form high barrier materials.<sup>6</sup> Thus, polymers with high degrees of hydrogen bonding, tight chain packing, and/or high degrees of molecular order in the amorphous phase exhibit the best gas barrier properties. Ethylene/vinyl alcohol (EVOH) copolymers have excellent barrier properties under dry conditions, and have been widely investigated as barrier coatings,<sup>7-10</sup> although properties suffer nearly a hundred fold decrease when exposed to moisture. Moisture plasticizes EVOH and can irreversibly change the EVOH morphology, resulting in increased free volume.<sup>11</sup>

Tiemblo, *et. al.*,<sup>12</sup> correlated fractional free volume to gas diffusivity of methacrylic ester copolymers with varying side chain lengths. Fractional free volume was calculated based on the specific volume of the polymer and the specific van der Waals volume. Additional methylenes

in the side chain increased the fractional free volume, which in turn increased diffusion of gas molecules. Varying the size of the gas penetrant did not significantly affect the diffusivity, implying that the high flexibility of the side chains allows kinetic transport.

The influence of molecular packing was exhibited in the high oxygen barrier of self-assembled melamine coatings. Melamine was vapor deposited onto PET films to form a transparent coating with high barrier to oxygen.<sup>13</sup> Although melamine is a small molecule, it assembled into regular arrays due to the presence of symmetrical and complementary hydrogen bond donor and acceptor sites (Figure 1).



**Figure 1.** Structure of the supramolecular assembly of melamine.

Coatings of hyperbranched polyesters based on bis(hydroxymethyl)propionic acid improved oxygen barrier of PET and polypropylene,<sup>14</sup> although the coatings were moisture sensitive. The hyperbranched polyester had an average of 64 hydroxyl end-groups per molecule. Hyperbranched polymers with 15-30% methacrylate groups included for crosslinking showed the best barrier properties compared to uncrosslinked or lightly crosslinked systems. Unexpectedly, addition of semi-crystalline poly( $\epsilon$ -caprolactone) to the shell of hyperbranched polyesters decreased barrier properties. Moisture sorption in these systems was comparable to amorphous EVOH, and depended greatly on the concentration of hydroxyl groups.<sup>15</sup>

A number of epoxy-amine derivatives have demonstrated excellent barrier properties.<sup>16, 17</sup> Brennan, *et. al.*,<sup>18, 19</sup> synthesized new high-barrier thermal plastics based on bisphenol-A diglycidyl ether and bisphenols with an amide linkage. Lower oxygen permeabilities were

obtained by either reducing the number of methylene units or increasing the population density of amide groups, which increased hydrogen-bonding interactions. Interestingly, the barrier properties of poly(hydroxy amide ethers) improved in the presence of moisture. A further detailed investigation into the effect of polymer structure showed that replacing methylene units with meta-linked phenylene units decreased permeability.<sup>20</sup> Also, barrier properties improved as the aromatic backbone unit became planar (improving chain packing) or had a strongly polar pendent functional group that strengthened hydrogen bonding.<sup>21</sup>

In the present work, an alcohol-functionalized methacrylate, methyl ( $\alpha$ -hydroxymethyl)acrylate (MHMA), was applied to PET films, then photopolymerized to produce a coated structure possessing three times the oxygen barrier of the biaxially-oriented PET substrate alone. MHMA with various feed ratios of MMA was coated on biaxially-oriented PET samples. The materials containing less than 10 mol-% MMA gave very good barrier improvement. Coatings based on two additional monomers synthesized in our research group with MHMA/MMA (50/50) gave excellent barrier improvement. Furthermore, PET preforms were dipped in MHMA solution and the obtained thin coating photopolymerized to produce a coated preform that could be blown into a bottle possessing at least two times the oxygen and carbon dioxide barriers of uncoated bottles.

## **2. Experimental**

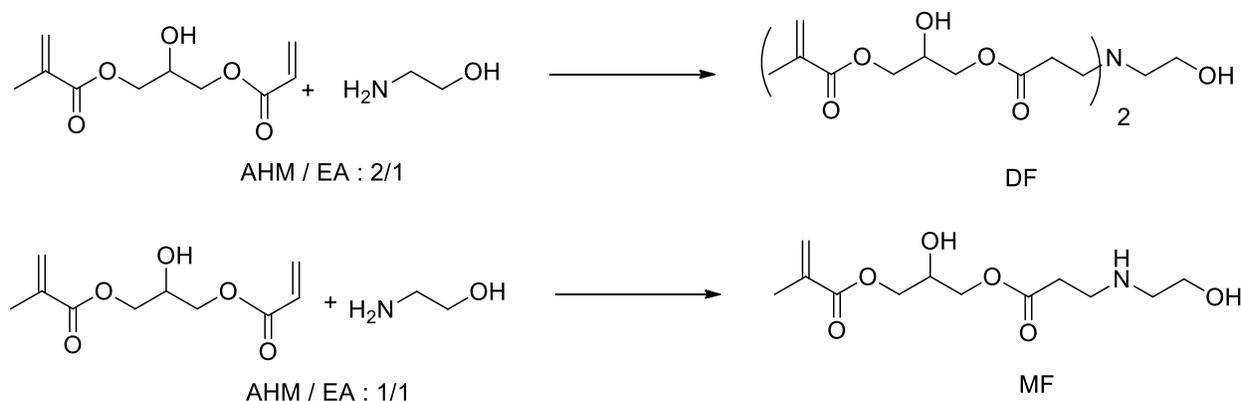
### *2.1. Materials*

MHMA was purchased from Nippon Shokubai, Co., Toyko, Japan, and passed through a short column of dry silica gel to remove inhibitor. Photoinitiators, 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651<sup>®</sup>) and phenyl bis(trimethylbenzoyl)phosphine oxide (Irgacure 819<sup>®</sup>) were donated by Ciba Specialty Chemicals, Basel, Switzerland. Biaxially oriented PET

thin films were purchased from 3M, Minneapolis, MN, and used as received. Amorphous PET preforms were provided by KoSa, Spartanburg, SC. All other chemicals were purchased from Aldrich Chemical Company, Milwaukee, WI, and used as received

## 2.2. Synthesis of MF and DF

3-(*N*-Propionate ethylene glycol amino)-2-hydroxypropyl methacrylate (MF), and 3-(*z,N*-bis(propionate) ethylene glycol amino)-2-hydroxypropyl methacrylate (DF) monomers were synthesized by Michael addition reaction of ethanol amine (EA) with one and two equivalents of 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM), respectively. The synthesis routes are given in Figure 2. Equimolar amounts of AHM and EA were charged into a round bottom flask at ambient temperature and stirred overnight to give MF. The synthesis of DF was carried out with EA and two equivalents of AHM stirred overnight at ambient temperature and then for two hours with the temperature increased to 45 °C. The yields were quantitative based on NMR analysis.



**Figure 2.** Overall synthesis routes for DF and MF monomers.

### 2.3. Instrumentation

Fourier transform infrared spectra were obtained with a Mattson 5000 spectrometer. Thermal analyses were performed using a TA instrument 2960 controlled by a thermal analyst 2100, using pierced lid crimped aluminum pans under nitrogen with a heating rate of 10 °C/min. Routine solution <sup>1</sup>H nuclear magnetic resonance (NMR) was performed on a Varian *Mercury<sup>PLUS</sup>* 300 MHz spectrometer.

### 2.4. Photopolymerization

For a typical photopolymerization, 1 mol-% Irgacure 819<sup>®</sup> was dissolved in MHMA. Approximately 2.0 mg of the mixture was placed in a bottom-impressed aluminum DSC pan (approximately 200 μm thickness). A TA Instruments 930 differential photocalorimeter (DPC) was used to measure heats of reaction. The chamber of the DPC was allowed to purge with nitrogen for 5 min before irradiation, and a nitrogen blanket was maintained throughout the reaction. The sample was equilibrated for 30 sec at the desired reaction temperature and irradiated for 5 min, with the light shutter opening set for 30 sec after the beginning of data acquisition. The enthalpy value  $\Delta H_{\text{theor}} = 13.1$  kcal/mol was used as the theoretical heat evolved for methacrylate double bonds.<sup>22</sup>

Instantaneous rates of polymerization were calculated according to Equation 1,<sup>23, 24</sup> where  $\Delta H_{\text{pol}}$  is the heat released per mole of double bonds reacted,  $Q/s$  is the heat flow per second,  $M$  the molar mass of the monomer,  $n$  the number of double bonds per monomer molecule, and  $mass$  being the mass of monomer in the sample.

$$\text{Equation 1 Rate} = (Q/s)M/n\Delta H_{\text{pol}}mass$$

### 2.5. Real-time FTIR

The polymerization kinetics of MHMA and MMA mixtures were studied by real-time FTIR and the detailed description of the instrument was given by T.Y. Lee, et al.<sup>25</sup> A modified Bruker 88 spectrometer which allows light to impinge on a horizontal sample using a fiber-optic cable was used to obtain infrared spectra of samples. The samples were placed between two sodium chloride discs whose edges were sealed by using vacuum grease to prevent both oxygen diffusion into the samples and evaporation of MMA. A 200 W high pressure mercury Xenon lamp (ScienceTech Co.) served as the light source to induce free radical polymerization. Disappearance of methacrylate double bond at  $1636\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  was monitored under continuous UV irradiation with a scanning rate of 2 scans/sec. Conversion was calculated according to Equation (2), where  $A_o$  is the absorbance at  $t=0$  and  $A_t$  is the absorbance at  $\text{time}=t$ .

$$\text{Equation 2 } \% \text{ Conversion} = [(A_o - A_t)/A_o] \times 100$$

### 2.6. Pencil and Persoz Hardness Test

Hardness of coatings was measured according to ASTM designation D3363<sup>26</sup> using a range of pencils from B to 9H. The pencil lead was flattened before using. The pencil was held at a  $45^\circ$  angle from the coating surface and pushed forward on the substrate. The first pencil which could scratch the coating gave the measured pencil hardness. A BYK Gardner pendulum hardness tester was used to determine Persoz pendulum hardness of the coatings. The measurements were conducted at room temperature on polymer coated PET substrates, and repeated at least five times.

### 2.7. PET film coatings

PET films were coated using the following procedure. MHMA was passed through a short column of dry silica gel to remove inhibitor. Photoinitiator was dissolved in the monomer

and the resulting solution was spread using a small paintbrush on discs of 3M transparency film (biaxially-oriented PET) and placed in a polypropylene chamber. The chamber was purged with nitrogen for 10 minutes and remained under nitrogen throughout the cure process. The samples were then irradiated with an external UV light source (long wave UV/hand held model). Finished samples were tested by colleagues at Case Western Reserve University for oxygen and carbon dioxide barrier using Mocon oxygen and carbon dioxide analyzers.

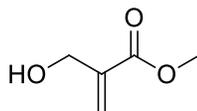
### *2.8. Preform dipping experiments*

A general procedure for preform dipping follows. MHMA was passed through a short column of dry silica gel to remove inhibitor. 2,2'-Azobisisobutyronitrile (AIBN) was recently recrystallized from methanol. A 50 mL Erlenmeyer flask equipped with a magnetic stir-bar was charged with MHMA (42.2 g, 0.37 mol), 0.5 mol-% AIBN (0.299 g, 0.0018 mol) and sealed with a rubber septa. Nitrogen was bubbled through the monomer-initiator solution for 10 min in order to remove dissolved oxygen. The flask was then placed in a preheated oil bath at 35 °C for 94 min. A substantial increase in viscosity was observed. The viscous solution was immediately exposed to oxygen and 34.4 grams was poured into a flask cooled to 0 °C in order to quench the thermal polymerization. Then, 1 mol-% Irgacure 651<sup>®</sup> (0.76 g, 0.00296 mol) was dissolved in the viscous solution. The solution was allowed to stand for 24 h at 0 °C. Nitrogen was bubbled through the viscous solution for 10 min. Preforms were weighed and placed in a nitrogen-purged dry-box equipped with the UV lamp source. Each preform was dipped into the solution and irradiated for 9 minutes, rotating a quarter turn every minute.

## **3. Results and Discussion**

MHMA is a unique monomer in that it is an  $\alpha$ -substituted methacrylate (Figure 3). It shows very fast photopolymerization rates and gives high conversions under typical radical

polymerization conditions. Poly(MHMA) is completely amorphous, and offers many advantages (estimated 1.5-3.5 times lower) over current commercially available barrier coatings. When polymerized, MHMA is completely transparent with optical clarity rivaling polycarbonate.



MHMA

**Figure 3.** Structure of methyl( $\alpha$ -hydroxymethyl)acrylate (MHMA).

Another unique property of poly(MHMA) is its very high density (Table 1).<sup>27</sup> This high density leads to excellent solvent resistance and extremely low moisture absorption.

Poly(MHMA) is completely insoluble in acetone, methanol, ether and water, and only partially soluble in *N-N*-dimethylformamide, dimethyl sulfoxide, and hexafluoroisopropanol. These properties combine to give poly(MHMA) excellent physical and barrier properties.

**Table 1**

Density comparison for methacrylate monomers.<sup>27</sup>

Polymer	Density (g/cm <sup>3</sup> )
MHMA	1.388
HEMA	1.07
MMA	1.19

### 3.1. Coating experiments on PET biaxially oriented thin films

Initial coating experiments involved application of thin monomer films to biaxially oriented PET films. The substrates were not washed prior to coating. An MHMA solution was prepared containing 1 mol-% Irgacure 651<sup>®</sup> photoinitiator. Approximately 0.5 mL of the MHMA solution was placed in the middle of a 90 mm diameter film. The solution was brushed outward using a small paintbrush, and samples were placed in a chamber with a nitrogen atmosphere. After purging the chamber, the samples were irradiated with UV light from an

external hand-held UV source through a UV transparent cover of polypropylene. Some samples were coated twice in order to cover coating defects such as small pin holes.

Surprisingly, these crude MHMA photocured coatings resulted in excellent oxygen (Table 2) and carbon dioxide barrier properties (Table 3). Cured film thicknesses ranged from 0.8-1.8 mils, which showed oxygen permeability reduced 2.5-3.7 times to that of the uncoated substrate. Carbon dioxide permeability also showed marked decreases compared to the uncoated substrate (3-4 times lower).

**Table 2**

Oxygen permeation results for PET thin films coated with MHMA and photocured.

Sample #	Cure Time (h)	Total Thickness (mils)	Coating Thickness (mils)	P <sup>a</sup>	D <sup>b</sup> x10 <sup>13</sup>	S <sup>c</sup>	P <sub>o</sub> /P
Control	0	4.3	0	0.133	2.0	0.075	--
1	1	5.2	0.9	0.049	1.1	0.052	2.7
2 <sup>d</sup>	1	5.6	1.3	0.042	0.9	0.054	3.2
3 <sup>d</sup>	1	6.1	1.8	0.036	0.82	0.051	3.7
4	1	5.1	0.8	0.053	1.2	0.045	2.5

<sup>a</sup>P – cc(STP) cm / m<sup>2</sup> / day / atm; <sup>b</sup>D – m<sup>2</sup> / sec; <sup>c</sup>S – cc(STP) / cm<sup>3</sup> / day; <sup>d</sup> Two coats photocured

**Table 3**

Carbon dioxide permeation results for PET thin films coated with MHMA and photocured.

Sample #	Cure Time (h)	Total Thickness (mils)	Coat (mils)	P <sup>a</sup>	D <sup>b</sup> x10 <sup>13</sup>	S <sup>c</sup>	P <sub>o</sub> /P
Control	0	4.3	0	0	0.6	1.66	--
1	1	5.2	0.9	0.9	0.26	1.07	3.5
2 <sup>d</sup>	1	5.6	1.3	1.3	0.25	1.09	3.7
3 <sup>d</sup>	1	6.1	1.8	1.8	0.24	1.06	4
4	1	5.1	0.8	0.8	0.3	1.09	3

<sup>a</sup>P – cc(STP) cm / m<sup>2</sup> / day / atm; <sup>b</sup>D – m<sup>2</sup> / sec; <sup>c</sup>S – cc(STP) / cm<sup>3</sup> / day; <sup>d</sup> Two coats photocured

An important factor in altering the nature of PET is the effect a coating has on recycling. During the recycling process, PET bottles are subject to washing in hot caustic solutions. The poly(MHMA) coating was completely removed from PET thin films by a 2 wt-% solution of

sodium hydroxide at 80 °C in the absence of agitation. Therefore, PET recycling will not be hindered by MHMA barrier coatings.

Scotch<sup>®</sup> tape adhesion testing of MHMA-treated PET films was conducted on samples that had been UV cured for 60 minutes. The coated surface was not affected by the adhesion test. Furthermore, bending the coated film did not cause cracking or breaking of the coating layer. However, when the coated PET was folded over and creased, cracking of the coating was observed.

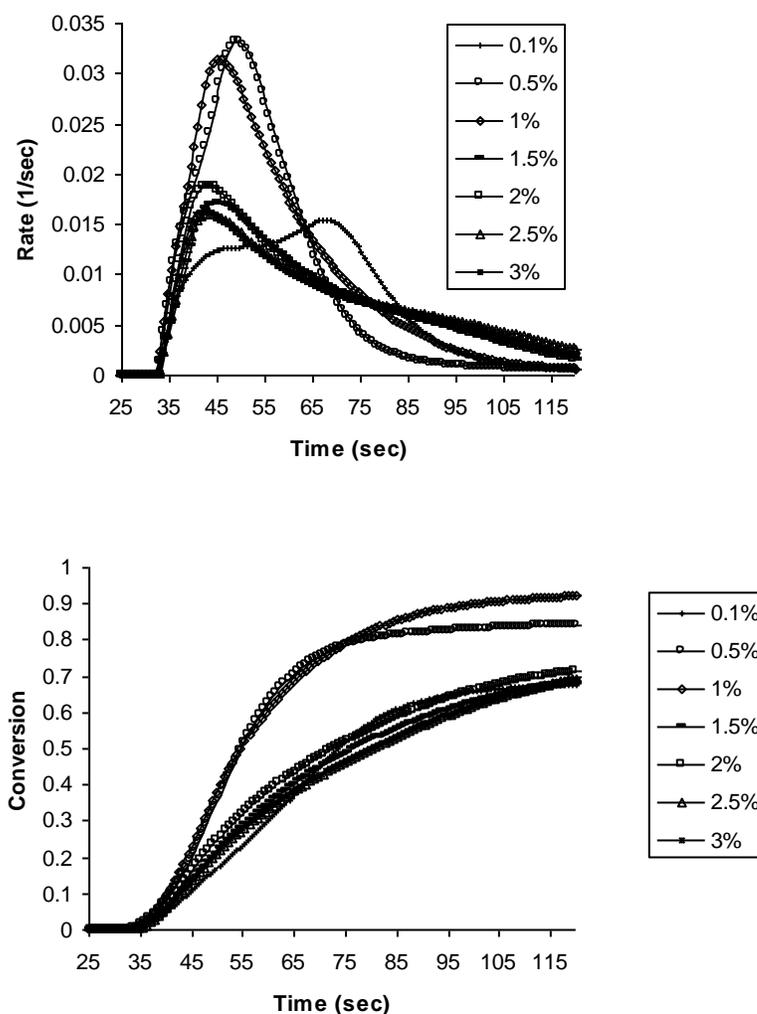
In order to probe the importance of the MHMA hydroxyl group to adhesion, methyl methacrylate (MMA) monomer was coated onto PET thin films using the same method as was employed with MHMA. The obtained coatings of MMA were not homogeneous. Cracks formed during the photochemical cure, and the Scotch<sup>®</sup> Tape adhesion test caused significant loss of the coating. Adhesion of poly(MHMA) on aluminum surface was stronger, although poly(MMA) could be removed easily. Adhesion of both polymers to a cleaned glass substrate was excellent.

### *3.2. UV photopolymerization and photoDSC*

One of the main objectives in the UV curing of coatings is to obtain a high degree of conversion at the surface and throughout the coating layer. The concentration and type of initiator significantly effects overall conversion and rate of polymerization. In order to obtain good through-cure of a coating, the light has to penetrate throughout. The use of a high concentration of photoinitiator may lead to light absorption resulting in a gradient of conversion and lower overall conversion.<sup>28</sup> This is especially crucial for barrier properties of the coating since the residual monomer can act as a plasticizer of the matrix and increase the free volume

leading to lower barrier. Therefore, it is important to find the optimal photoinitiator and concentration range to obtain fast polymerization with high conversion.

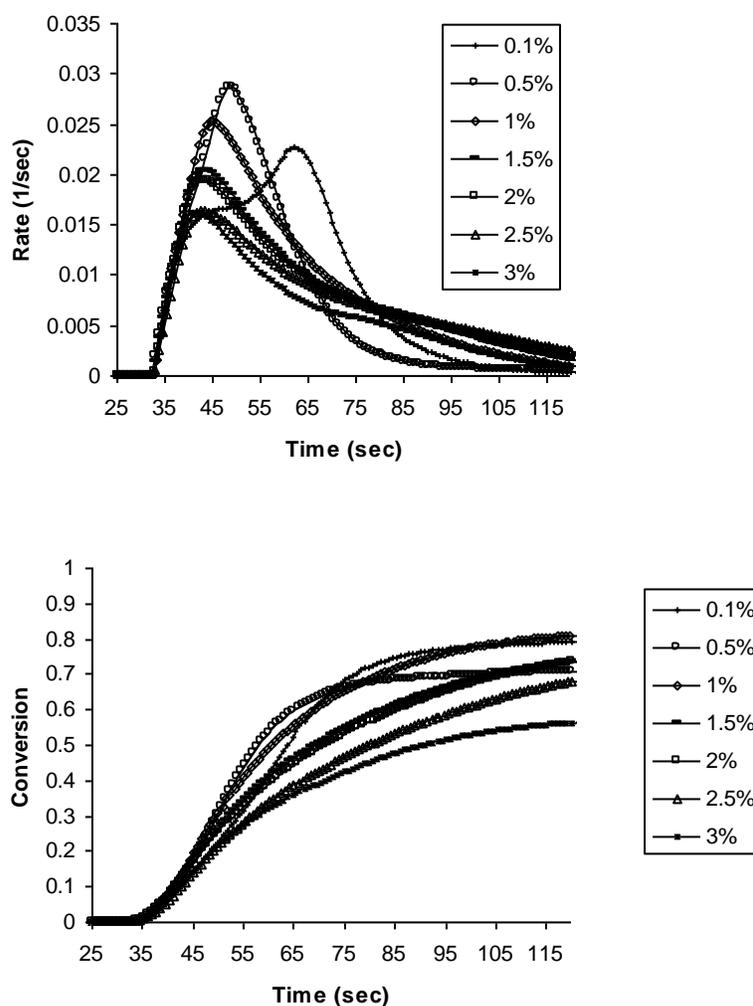
Figure 4 shows the effect of cure time and initiator concentration on the rate and conversion of polymerization of MHMA. The data given are for Irgacure 819<sup>®</sup> at up to 3 mol-% in the monomer. Above this concentration, the solubility of photoinitiator became an issue, whereas up to 5 mol-% Irgacure 651<sup>®</sup> easily dissolved in MHMA. Once the photoinitiator, Irgacure 819<sup>®</sup>, concentration became larger than 1 mol-%, a decrease in rate of propagation was observed. This must be due to screening of UV light which reduced intensity in lower layers of monomer. The higher levels of photoinitiator absorb more UV light, preventing it from penetrating through the entire sample. This also effects overall conversion, which decreased at initiator concentrations above 1 mol-%. The overall conversions for 0.5 and 1 mol-% initiator concentration were above 80 %, whereas once the initiator concentration was higher than 1 mol-% the conversion decreased to around 60 %. Another interesting observation is that the decrease in rate of photopolymerization with cure was very sharp for 0.5 and 1 mol-% initiator concentration once the polymerization rate reached its maximum. These sharp decreases were not observed for higher photoinitiator concentrations. The autoacceleration peak was not observable for systems other than that with 0.1 mol-% photoinitiator concentration, which gives a plateau region before autoacceleration.



**Figure 4.** A) Rate versus time B) Conversion versus time plots for MHMA with various Irgacure 819<sup>®</sup> initiator concentrations at 30 °C.

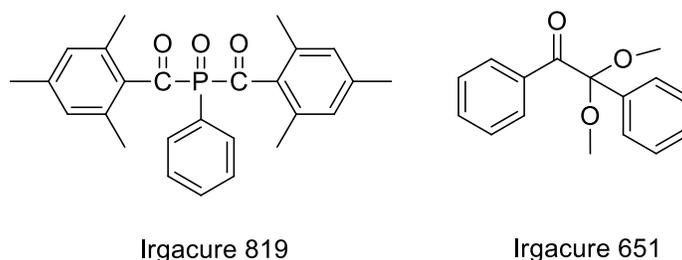
It is known that elevated rates of photopolymerization are usually observed when the reactions are performed at higher temperature. Figure 5 shows changes in the rate and conversion of MHMA with Irgacure 819<sup>®</sup> initiator concentration at 50 °C. Contrary to our expectation, the overall rate and conversion did not change dramatically at 50°C. A slight decrease was observed for the systems with 0.5 and 1 mol-% Irgacure 819<sup>®</sup>, although no change was observed for the other photoinitiator concentrations. The slight decrease may be as a result

of a reduction of the extent of the monomer hydrogen bonding at higher temperatures (pseudo-dimer effect) which the rate increase due to increasing temperature didn't compensate for. Jansen, et al., reported similar result for photopolymerization of undecyl amide N-ethyl acrylate. Even though the rate of polymerization of that system at 50 °C was higher than the rate at 30 °C, the rate showed a decreasing trend when the temperature was over 40°C degrees.<sup>29</sup> The autoacceleration was more pronounced for 0.1 mol-% photoinitiator concentration at 50 °C.

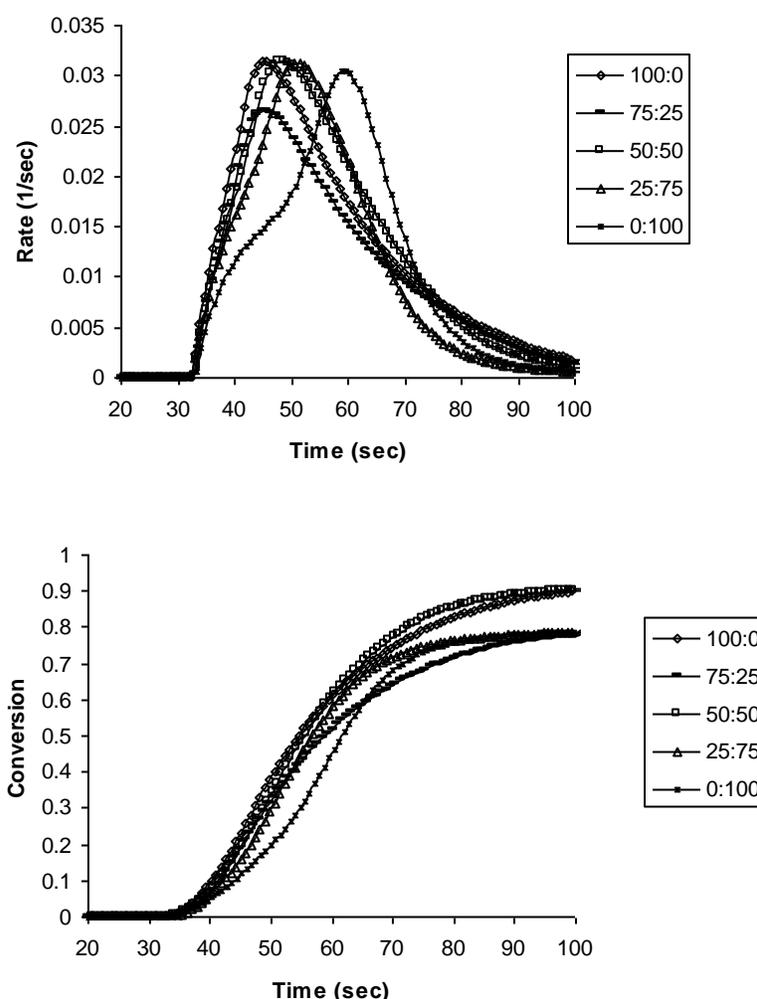


**Figure 5.** A) Rate versus time and B) Conversion versus time plots for MHMA with various Irgacure 819<sup>®</sup> initiator concentrations at 50 °C.

The effect of initiator type (Irgacure 651<sup>®</sup> or Irgacure 819<sup>®</sup> with chemical structures given in Figure 6) on photopolymerization rates and conversions was investigated with respect to various ratios of these two photoinitiators, as shown in Figure 7. The total concentration of photoinitiators was kept constant at 1 mol-%, while Irgacure 651<sup>®</sup> ratio was changed from 0 to 100%. Irgacure 819<sup>®</sup> is able to generate four initiating radicals per photoinitiator molecule, whereas Irgacure 651<sup>®</sup> is only able to create two radicals for photoinitiation.<sup>30, 31</sup> It is expected that the number of formed radicals plus absorbance differences of these two photoinitiators will have a dramatic effect on photopolymerization of MHMA. The initial monomer-initiator solutions for Irgacure 819<sup>®</sup> are yellow, whereas they were clear for Irgacure 651<sup>®</sup>. However, the initial yellowness of the solution disappeared with curing. Figure 7 shows rate and conversion versus time plots of various ratios of the two different initiators. Irgacure 819<sup>®</sup> reduced the autoacceleration peak and caused maximum rates of polymerization much faster than Irgacure 651<sup>®</sup>. It also gave a slightly higher conversion, although overall conversion for combinations of these photoinitiators were all high and above 80%. The peak maximum shifted to the right on the time scale with increasing Irgacure 651<sup>®</sup> concentration.



**Figure 6.** Structure of Irgacure 651<sup>®</sup> and Irgacure 819<sup>®</sup> photoinitiators.

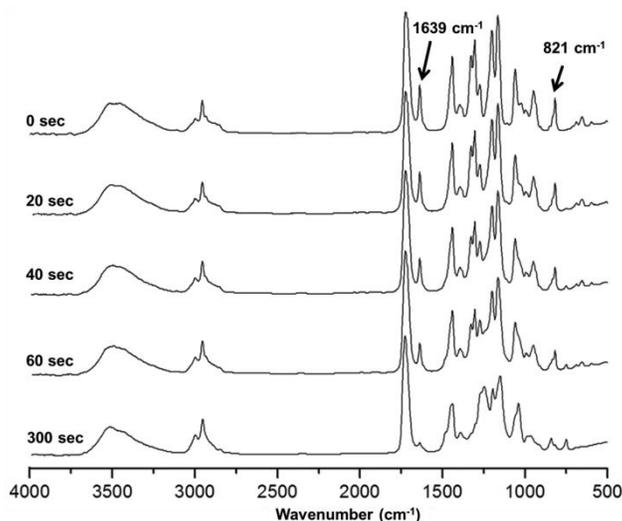


**Figure 7.** Rate versus time plots for MHMA with Irgacure 819<sup>®</sup> vs. 651<sup>®</sup> initiator at 30°C (75:25 shows 0.75 mol-% Irgacure 819<sup>®</sup>: 0.25 mol-% Irgacure 651<sup>®</sup>)

### 3.3. Copolymerization of MHMA

To investigate copolymerization kinetics along with thermal and barrier properties of the materials obtained, a series of copolymers of MHMA with various mol fractions of MMA was prepared. The polymerization of MHMA/MMA (50/50) mixture was followed by real-time FTIR with various time intervals. The mixture was applied between two salt plates and exposed to hand-held UV source for given times. Unfortunately, the absorbance spectra of MMA and MHMA almost completely overlap which makes it impossible to evaluate the effect of hydrogen bonding on copolymerization of MHMA and MMA. The broad O-H stretching band around

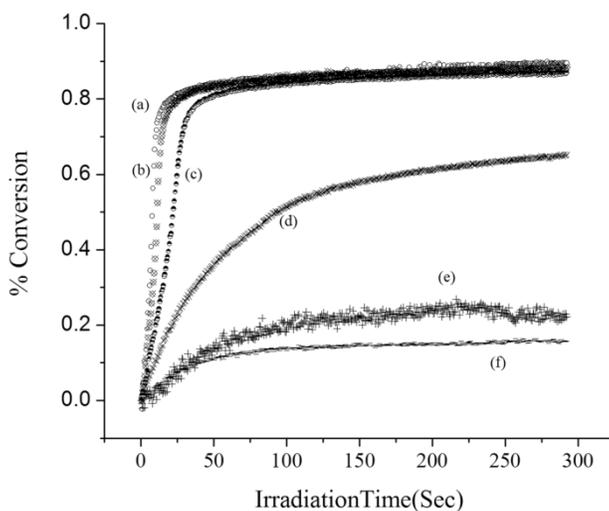
3475  $\text{cm}^{-1}$  as shown in Figure 8 was due to combinations of hydrogen bonding structures in this systems. Absorptions at 821  $\text{cm}^{-1}$  and 1639  $\text{cm}^{-1}$  are due to vinyl groups. The intensity of these two peaks decreased with time, and there were no spectral changes after 300 sec. At this point residual double bonds were still observed. The copolymers showed expected characteristic peaks. The band at 2956 and 3000  $\text{cm}^{-1}$  are ascribed to  $-\text{CH}_3$  vibration, and the sharp peak around 1727  $\text{cm}^{-1}$  to the  $\text{C}=\text{O}$  vibration band.



**Figure 8.** FTIR spectra of MHMA/MMA (50/50) mixture exposed to UV for various time intervals.

Figure 9 is a plot of %-conversion versus irradiation time and shows the effect of methyl methacrylate concentration on MHMA polymerization rate and conversion. Jansen, et al., suggest that acrylate monomers capable of hydrogen bonding have much higher rates compared with non-hydrogen bonding analogues with the same secondary functionality.<sup>29</sup> The enhanced rate of photopolymerization was attributed to hydrogen bonding causing preorganization of the monomers. Viscosity differences may also play a significant role. Because MHMA has a hydroxyl group at the alpha position to the vinyl, which is capable of hydrogen bonding with carbonyl groups or other hydroxyl groups of other MHMA monomers, it is expected that

MHMA will have a much higher rate of polymerization than MMA. In Figure 9, the RT-FTIR plot supports the importance of hydrogen bonding in enhancing the rate of polymerization of MHMA. The rate is given by the slope of the plots. As expected, MHMA has a significantly higher rate of polymerization and a greatly increased final conversion (around 75 % in 10 sec) than does MMA.



**Figure 9.** RT-FTIR plot of % conversion as a function of irradiation time (a) MHMA, (b) MHMA:MMA with a ratio of 90:10, (c) MHMA:MMA (75:25), (d) MHMA:MMA (50:50), (e) MHMA:MMA (10:90), (f) MMA.

Water absorption experiments have been conducted in order to calculate water uptake of films based on MHMA alone, MMA alone, and MHMA/MMA (50/50). For comparison, two other samples including copolymers of MHMA with butyl acrylate (BA) and methacrylic acid (MA) were prepared. The samples were soaked into water, and the weight change and optical transmittance were observed. The results are given in Table 4. Water uptake of homopolymer of MMA is ca. 0.4 wt-%, whereas poly(MHMA-co-MA) (50/50) showed the greatest uptake at 27 wt-% gain in 24 hours. Interestingly, water absorbance of poly(MHMA-co-MMA) (50/50) was low 3.6 wt-% in 24 hours, and the copolymer film did not change its transmittance. These two parameters are very important for application of a coating on PET.

**Table 4**

Water absorption and transmittance changes.

Film Composition	Wt-% gain	Transmittance
P(MHMA)	19.8	Changed in 24 h
P(MHMA/MA) (50/50)	27	Changed in 24 h
P(MHMA/BA) (50/50)	4.7	Changed in 48 h
P(MHMA/MMA) (50/50)	3.6	Same
P(MMA)	0.4	Same

To understand the effect of MMA concentrations on barrier properties of MHMA coatings, several film samples with various mol fractions of MMA ranging from 1 mol-% to 25 mol-% were prepared. Increasing MMA mol fraction gave rise to increasing oxygen permeability of coated samples (Table 5). The results are very surprising because MHMA-co-MMA coating with low MMA concentration had very good oxygen barrier. Once MMA concentration exceeded 10 mol-%, a decrease in barrier performance was observed.

Two more samples based on reaction between MF and DF with MHMA/MMA (50/50) mixture were also prepared and the results are given in Table 5. These combinations gave excellent barrier improvement and showed oxygen permeability reduced 1.8 and 2.5 times that of uncoated substrate. This marked improvement of oxygen barrier is presumably due to increasing hydroxy group concentration capable of forming a tight hydrogen bonding network.

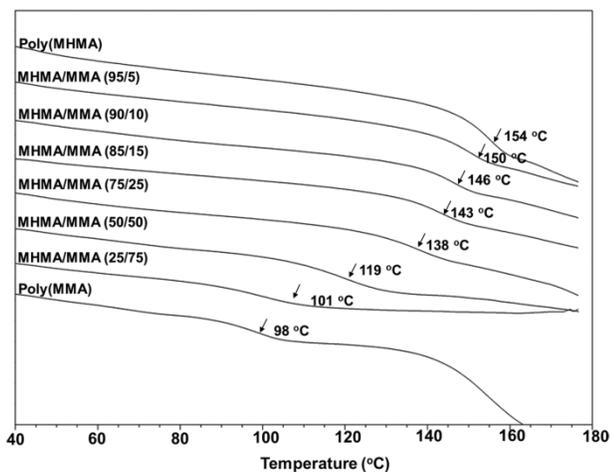
**Table 5**

Oxygen barrier of MHMA copolymers on PET thin films.

Sample	Composition	Total Thickness (mils)	Coating thickness (mils)	P <sup>a</sup>	D <sup>b</sup> x10 <sup>13</sup>	S <sup>c</sup>	P <sub>o</sub> /P
Control	-	4.2 ± 0.1	-	0.160	2.1	0.089	1.0X
5	MHMA	4.7 ± 0.1	0.5 ± 0.2	0.091	1.9	0.054	1.8X
6	MHMA/MMA (95/5)	4.8 ± 0.1	0.6 ± 0.2	0.085	1.6	0.063	1.9X
7	MHMA/MMA (90/10)	5.0 ± 0.2	0.8 ± 0.3	0.079	1.6	0.057	2.0X
8	MHMA/MMA (75/25)	5.1 ± 0.1	0.9 ± 0.2	0.094	1.8	0.059	1.7X
9	MHMA/MMA/DF (45/45/10)	4.9 ± 0.1	0.7±0.2	0.087	7.8	0.056	1.8X
10	MHMA/MMA/MF (45/45/10)	4.9 ± 0.2	0.7±0.3	0.064	1.3	0.056	2.5X

<sup>a</sup>P – cc(STP) cm / m<sup>2</sup> / day / atm; <sup>b</sup>D – m<sup>2</sup> / sec; <sup>c</sup>S – cc(STP) / cm<sup>3</sup> / day

Figure 10 shows the DSC thermograms of pure poly(MHMA), pure poly(MMA), and several copolymers with various ratios of MHMA/MMA under nitrogen with a heating rate of 10 °C/min. The samples were dried at 110 °C before DSC runs to remove water and residual monomers. The feed ratios and glass transitions are given in Table 9. All copolymers showed a single  $T_g$  which shifted to lower temperature with increasing MMA concentration. The pure poly(MHMA) and pure poly(MMA) have  $T_g$ 's of 154 and 98, respectively. It has been shown before that intermolecular interaction leads to tighter packing of amorphous regions resulting in reduced free volume.<sup>10</sup> Therefore, high  $T_g$  plus hydrogen bonding are two important factors that affect barrier properties of poly(MHMA). It must be noted that even the copolymer with 75/25 monomer ratios gave a  $T_g$  of 138 °C which may explain the high barrier properties of this copolymer.



**Figure 10.** DSC thermograms for homo and copolymers.

### 3.4. Hardness of the coatings

The hardness of MHMA and MMA coatings were measured using the pencil hardness test. The hardness of coatings was determined to be 6H for all coatings. The coatings were homogenous and transparent. To confirm results, the Persoz hardness test was also used. The basic idea of this test is that the amplitude of the pendulum's oscillation will decrease more

quickly when engaging a softer surface. The results of pendulum hardness evaluation are in accordance with pencil hardness test, and there was no significant change of hardness for copolymer films up to 25 mol-% MMA. All films gave almost the same result ranging from 71 to 77 sec.

### *3.5. Preform dipping experiments*

Currently, barrier coatings for drink bottles are applied after the bottle has been blown, or as a sandwiched laminate layer included in the preforms. This processing approach has the disadvantage of requiring coating processes at the blow molding sites, or producing the entire bottle (preform and bottle) at the same site. Because preforms are injection molded in only a few locations worldwide, barrier coated bottles would be ideally processed by coating preforms prior to shipping to the blow molding facilities. This would lower the number of manufacturing sites that require the additional processing step.

It was important to tailor coating mixture viscosity because MHMA monomer was not viscous enough for dip coating PET preforms. Attempts to dip and quickly photocure gave little barrier coating on the preform. Therefore, viscosity needed to be increased without using additives that could diminish final barrier properties. In order to circumvent this problem, MHMA was thermally polymerized for a short time, and quenched at low conversion (~ 8%). This resulted in a viscous solution of poly(MHMA) dissolved in MHMA monomer. Photoinitiator was then dissolved in the viscous solution, and preforms dipped and photocured to give transparent coatings on the preforms.

Table 6 gives the oxygen barrier results of the blown bottle sidewalls. Samples 11-13 show some improvement, especially sample 14 and 15, which exhibited marked improvement over PET control. Dipping solutions for sample 14 and 15 were deoxygenated with nitrogen

bubbling prior to dip coating which most likely increased the degree of cure. The results in Table 6 demonstrate that a number of variables can influence gas barrier for even a one-component coating. Increasing thickness increased the barrier slightly, although decreasing the amount of residual monomer made a significant improvement in barrier properties.

**Table 6**  
Oxygen barrier results of blown bottle sidewalls.

Sample #	Total Thickness (mils)	P <sup>a</sup>	D <sup>b</sup> x10 <sup>13</sup>	S <sup>c</sup>	P <sub>o</sub> /P
Control	8.2	0.183	2.84	0.075	--
11	12.0	0.122	2.08	0.068	1.5
12	13.7	0.102	1.86	0.063	1.8
13	13.4	0.100	1.69	0.069	1.8
14	14.9	0.064	1.5	0.048	2.9
15	14.5	0.088	1.4	0.071	2.1

<sup>a</sup>P – cc(STP) cm / m<sup>2</sup> / day / atm; <sup>b</sup>D – m<sup>2</sup> / sec; <sup>c</sup>S – cc(STP) / cm<sup>3</sup> / day

### 3.6. Inherent barrier properties of UV cured MHMA

In order to determine the inherent barrier properties of photocured MHMA films, monomer thin films were cured on aluminum foil substrates. The thin aluminum substrate could be peeled away to give free-standing UV cured films. This gave poly(MHMA) films synthesized following an analogous procedure to PET thin film coatings using preform dip coating. MHMA stand-alone films showed outstanding barrier to oxygen (P = 0.0071 for 20 mil thick sample). This demonstrates that optimizing curing conditions, coating thickness, and conversion can lead to packaging materials with even lower gas permeabilities.

## 4. Conclusions

MHMA is a viable material for use in solvent-free barrier coatings on PET. The hydroxyl group serves as an anchor, or compatibilizing agent, to enhance adhesion to the surface of the polyester. The strong hydrogen bonding interactions in the polymer lead to its high

density, high solvent resistance, and high barrier properties. Barrier improvements of nearly four times that of uncoated PET thin films were obtained for both oxygen and carbon dioxide. Film obtained by reaction of MHMA/MMA(50/50) with 10 mol-% MF gave a barrier improvement 2.5 times that of neat PET substrate. Coated preforms that were blown into bottles showed nearly a three-fold decrease in oxygen permeability. Recycle process testing suggests that hot caustic solution, such as can be found in commercial recycling ventures, will remove the barrier coating. A unique pre-polymerization approach to increased viscosity without additives proved effective for controlling coating amounts deposited by dip coating.

### **Acknowledgements**

This work was accomplished with bottle blowing assistance from KoSa, Spartanburg, SC, and gas permeability measurements performed by the groups of Professors Eric Baer and Anne Hiltner of Case Western Reserve University, Cleveland, OH. The authors gratefully acknowledge continued consultation with Dr. David A. Schiraldi, Case Western Reserve University (formerly of KoSa), and Dr. Sanjay Mehta of KoSa for valuable discussions; Tai Yeon Lee and Dr. Charles Hoyle, University of Southern Mississippi, for real-time FT-IR studies; and Richard Liu, Yushan Hu, and Vamsi Prattipati, along with Dr. Anne Hiltner, and Dr. Eric Baer, for carrying out gas barrier measurements at Case Western Reserve University.

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