



Amoco Chemicals

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## The Effect of Purified Isophthalic Acid Modification on the Thermal Crystallization of PET

### Summary

Purified Isophthalic acid (PIA) is the preferred modifier for PET resins used in container applications. Incorporation of PIA in PET allows the fabricator more control over thermal crystallization during preform injection molding and stretch-blow molding. The use of PIA widens the PET process window resulting in clearer, brighter bottles. The usefulness of PIA modification of PET led to the desire to have more fundamental understanding of modification. This report presents the results of a controlled study to determine the effect of PIA modification on PET's isothermal crystallization rate, as a function of modification level and temperature. It also compares PIA with two other modifiers, cyclohexanedimethanol (CHDM) and diethylene glycol (DEG). The value of the information presented here is twofold: (a) to provide a quantitative assessment of PIA's effectiveness relative to other modifiers in terms of cost/performance; (b) to serve as a fundamental tool for optimizing PIA-modified PET compositions for specific applications.

Two nominal modification levels, 2.0 and 4.0 mole %, were selected for this study. These levels cover the typical range used in packaging applications, such as beverage containers and APET thermoformed sheet. These levels were used for the PIA and the CHDM-modified resins. In the case of DEG, the nominal level selected for study was 4.0 mole %. This level represents added DEG (since some DEG occurs naturally during polymerization as a result of side reactions).

The resins studied were prepared by melt polymerization and solid-stating to an IV of  $0.80 \pm 0.01$ . Extruded amorphous films, 5-mil thick, was used for the isothermal crystallization study. Isothermal crystallization data were obtained by depolarized light intensity (DLI). Supplemental crystallization data were obtained by dynamic and isothermal differential scanning calorimetry. The DLI study covered the temperature range between 110° C and 230° C.

The results of this study showed that PIA modification decreased crystallization rates on heating amorphous films and on cooling from the melt. However, DEG modification increased the rate of crystallization upon heating amorphous films and had a lesser effect compared to PIA in retarding crystallization upon cooling from the melt. In

addition, DEG presented the added disadvantage of reducing glass transition temperature ( $T_g$ ). On a mole basis, PIA was essentially equivalent with CHDM in preventing onset of crystallization upon cooling from the melt. This result suggests that the two modifiers are equally effective for stretch-blow-molding applications where crystallization from the melt is a critical concern. On crystallization by heating, CHDM resulted in larger decrease in crystallization rate per mole modifier compared to PIA. Crystallization from the amorphous state is a critical concern in some thermoforming applications, where higher levels of PIA may be necessary in order to achieve performance equivalent to CHDM. This difference however may be more than offset by the higher price of CHDM.

### Introduction

The widespread incorporation of modifier comonomers in PET packaging resins has grown from the need to produce containers with a high degree of clarity, in a wide variety of custom shapes, and free from residual acetaldehyde. The presence of the modifier disrupts PET polymer chain regularity and results in slower thermal crystallization and in a drop in melting point. The benefit resulting from these changes is to prevent development of haziness in the molded preform, which is prone to occur in PET homopolymer either during cooling inside the mold or during the preheat prior to blow molding. In homopolymer this is more likely in thicker cross-sections such as the bottom of a one-piece beverage bottle. The demand for slower crystallization rates increased with the switch from HDPE base-cup to one-piece beverage bottles. Returnable-refillable bottles with a thicker cross-section overall generate additional demand for resins with slower crystallization rates. Lower melting points result in lower acetaldehyde because lower processing temperatures can be used to reduce degradation.

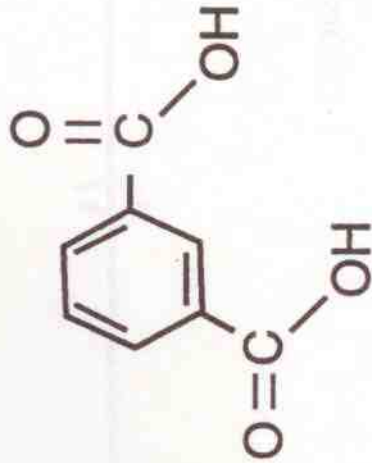
PIA is the most cost effective high-performance PET modifier used today. Typical PIA substitution levels used in solid-stated (0.78-0.83 IV) packaging resins are in the order 1-3 %. Another high performance PET modifier is cyclohexanedimethanol (CHDM). The quoted selling price for CHDM is higher than that for PIA. Diethylene glycol (DEG), which always occurs naturally to some extent in melt-polymerized PET as a byproduct is believed to be also used as modifier by a few resin producers.

Illustration 1 shows the chemical formulas for these three modifiers. The computer modeling simulations shown in Illustrations 2-4 help visualize the disruption in chain regularity caused by the presence of a modifier in the polyester backbone. The minimum energy conformations were laid on top of a PET homopolymer segment with four repeat units to show how the modifier changes the molecular geometry in the modified polymer. Two minimum energy conformations of PIA-modified PET were

ILLUSTRATION 1

# Commercial PET Modifiers

- Isophthalic acid
- Cyclohexane dimethanol



- Diethylene glycol

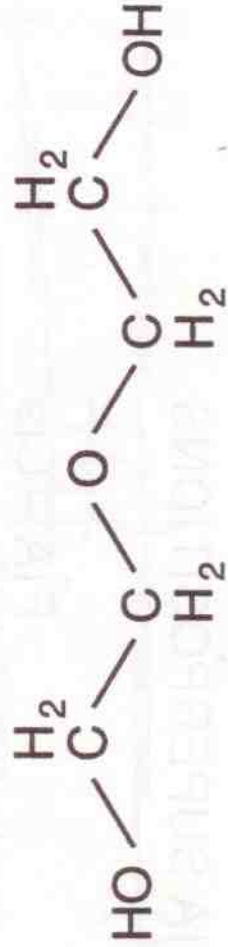
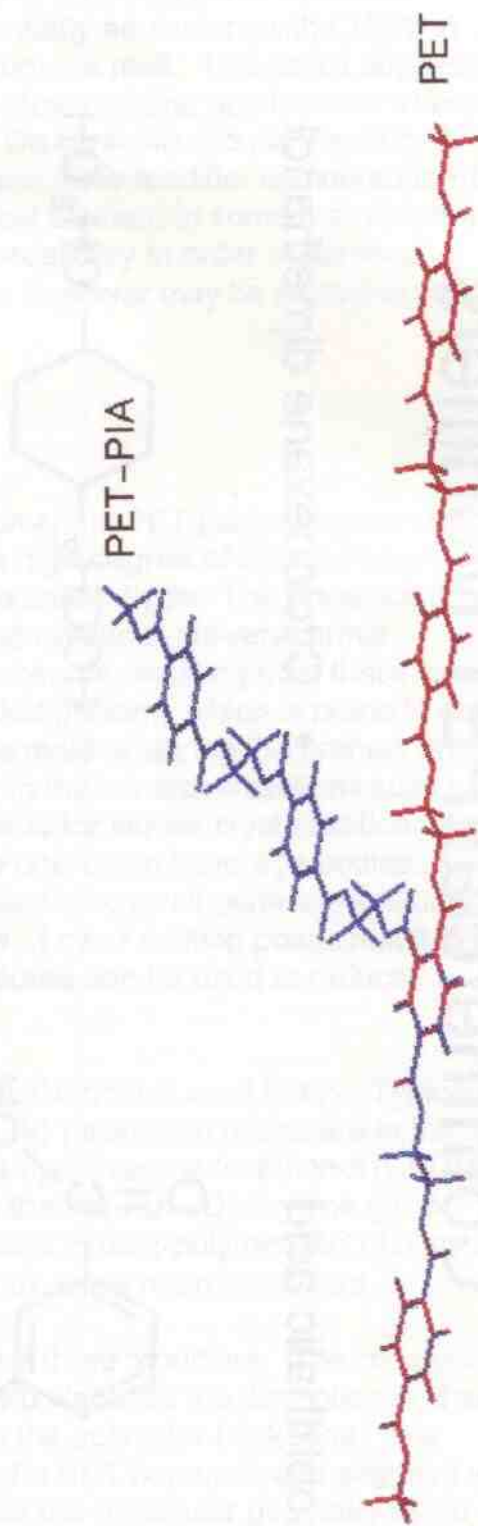
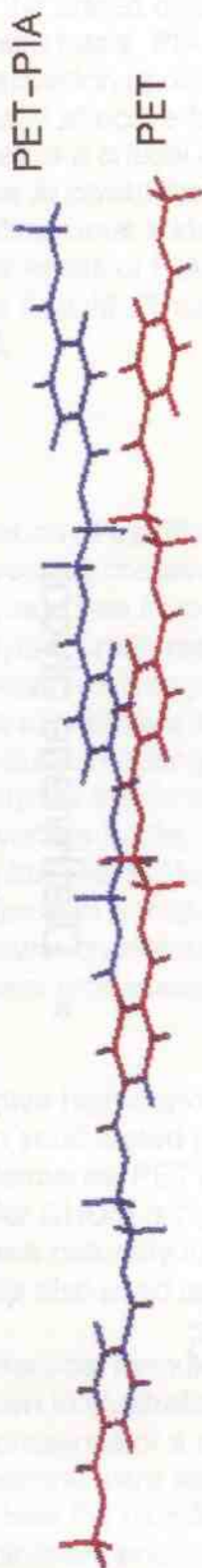


Illustration 2.

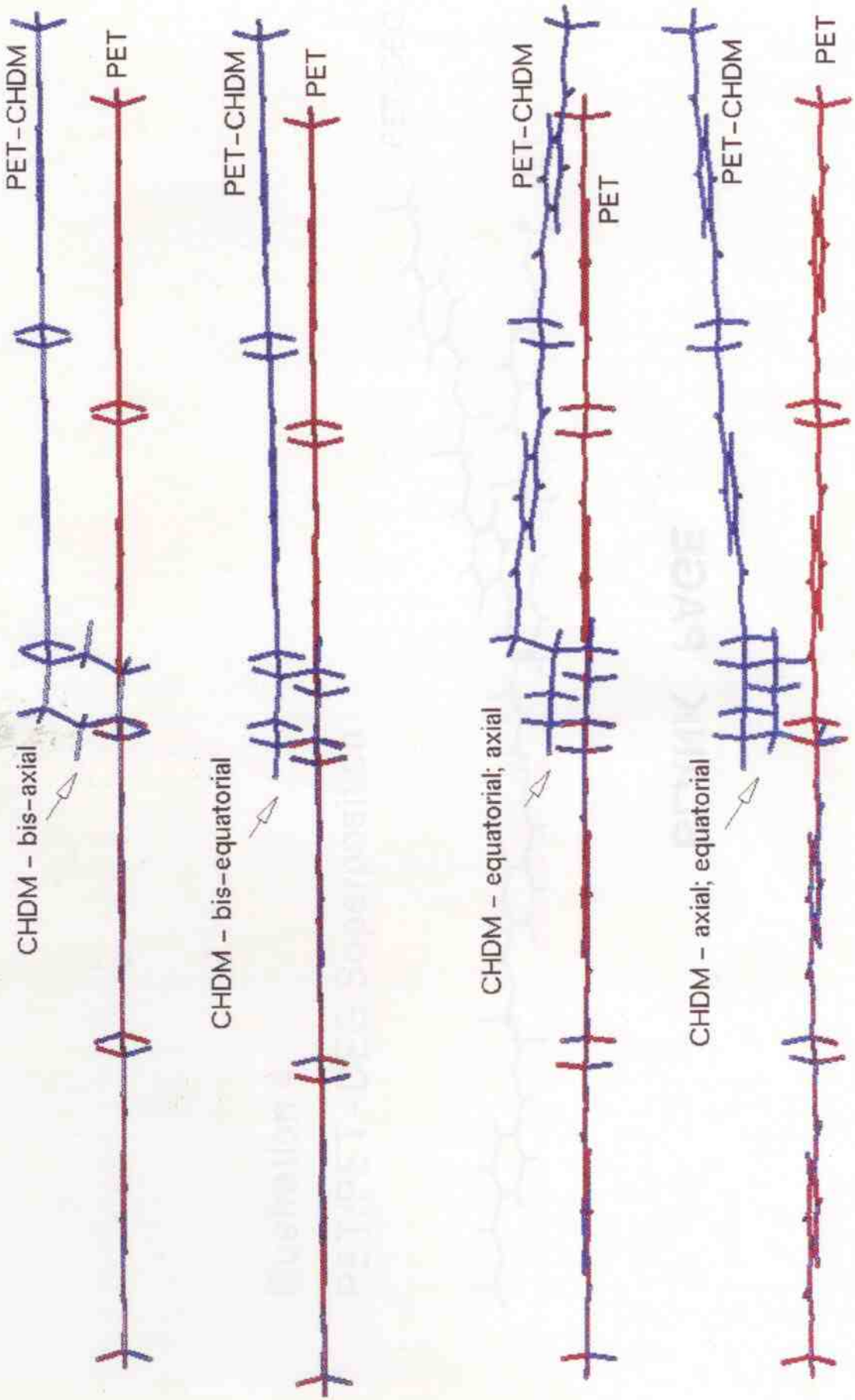
PET/PET-PIA SUPERPOSITIONS

PIA - Cis



PIA - Trans

Illustration 3.  
PET / PET-CHDM SUPERPOSITIONS

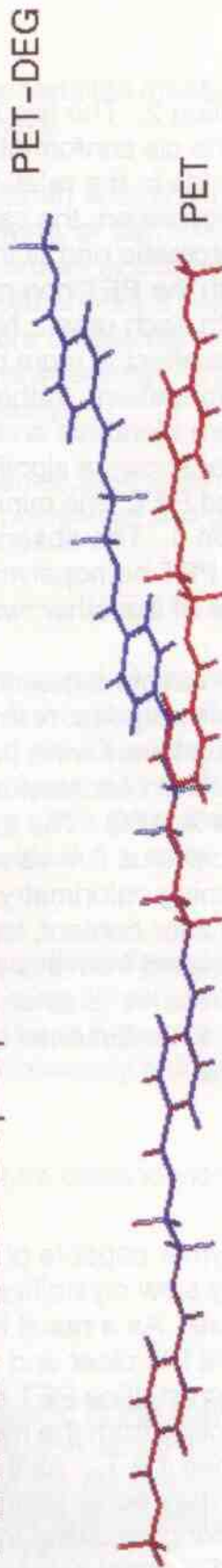


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Illustration 4.

PET/PET - DEG Superposition



identified and are shown in Illustration 2. The two minimum energy conformations are designated as cis and trans. For the cis conformation, the carbonyl groups of the isophthalate unit are on the same side in the relationship to the aromatic ring of the isophthalate unit. In the trans conformation, the carbonyl groups are pointing away from each other in relation to the aromatic ring of the isophthalate unit. Overlapping the modified polymer segments with the PET homopolymer segments shows that the polymer segments will not align with each other. Non-alignment between chains inhibits thermal crystallization. The effect is more pronounced with the trans conformation than with the cis conformation. In the case of CHDM-modified PET, four minimum energy conformations were identified and are shown in Illustration 3. Overlapping with PET homopolymer shows a significant degree of non-alignment in all cases. In the case of DEG-modified PET, one minimum energy conformation was identified and is shown in Illustration 4. The observed non-alignment between the DEG-modified and the overlapped PET homopolymer segments is not as pronounced overall as that observed in the case of the other two modifiers.

The work described in this report presents a quantitative comparison between PIA and other commercial modifiers. For this purpose, resins containing PIA or CHDM at 2.0 and 4.0 mole % nominal modification levels were prepared under similar polymerization conditions to minimize factors other than composition. In the case of DEG, the one nominal level studied was 4.0 mole % DEG. The thermal crystallization behavior of these resins was evaluated on amorphous film samples by isothermal depolarized light intensity (DLI) and differential scanning calorimetry (DSC) techniques (both dynamic and isothermal). The effects of modifier content, temperature, and resin IV were investigated. The information generated from this study provides a quantitative assessment of PIA's effectiveness relative to other modifiers in terms of cost/performance and will serve as a fundamental tool for optimizing PIA-modified PET formulations for specific applications.

### Background

Polyethylene terephthalate is a polymer capable of attaining high degrees of crystallinity but possesses relatively slow crystallization rates. It has a glass transition temperature above room temperature. As a result it can exist both in amorphous and in semicrystalline form. Amorphous PET is clear and results upon rapid quenching of molten resin to below the  $T_g$ . Semicrystalline PET results upon heating amorphous resin above the  $T_g$  or upon slow cooling from the melt or even upon rapid cooling from the melt down to a temperature above the  $T_g$ . All these phenomena represent various types of thermal crystallization and may occur during various stages of container manufacturing, such as preform cooling following injection molding, preform heating prior to stretch blow molding, or APET sheet extrusion and thermoforming. Thermal crystallization results in the development of haze and eventually to opaqueness when left to proceed to high degrees of crystallinity. In the case of thermal crystallization, the

crystalline structure is in the form of spherulites measuring 2-3  $\mu\text{m}$  in diameter, which scatter visible light thus causing haziness.

Another type of crystallization occurs when amorphous PET is subjected to strain during stretch-blow molding, fiber drawing, or film stretching. Strain-induced crystallization can proceed 2 or more orders of magnitude (depending on strain rate) faster than thermal crystallization.<sup>1</sup> Furthermore it results in the development of extended chain crystals, which are more or less cubic and smaller ( $< 0.5\mu\text{m}$ ) and do not scatter light and thus do not reduce transparency. The strain-induced crystallization of PIA-modified PET is currently under study.

PET isothermal crystallization has been studied extensively<sup>1</sup> and has been found to follow the general theory for polymer nucleation and growth which is described by the Avrami equation:

$$1 - x = e^{-kt^n}, \quad (1)$$

where  $x$  is the fraction of crystallized material at time  $t$  at a given temperature, relative to the maximum possible crystallinity at that temperature. The Avrami rate constant  $k$  determines the rates of nucleation and growth processes which control crystallization. It is strongly dependent on temperature and also on factors such as molecular weight and the presence of nucleating agents. The Avrami exponent " $n$ " describes the mechanism of crystallization and has, ideally, a small integer value depending on the nucleation and growth pattern.

The Avrami rate constant follows a complicated dependence with temperature. Since nucleation is favored by high supercooling at low temperature whereas growth is favored by chain diffusion which is faster at higher temperatures, there is an intermediate temperature range, approximately half-way between  $T_g$  and  $T_m$ , where crystallization is the fastest.

One proposed model for the temperature dependence of the rate constant is given by the expression<sup>2</sup>:

$$k(T) = k_0 \exp \left[ \frac{-U}{R(T - T_\infty)} - \frac{A}{T(T_m^0 - T)f} \right], \quad (2)$$

where  $k_0$ ,  $U$ , and  $A$  are parameters specific to the polymer. The first term represents an Arrhenius-type contribution due to diffusion, while the second term represents the thermodynamic driving force.  $U$  and  $A$  are the corresponding activation energies.  $R$  is the ideal gas constant. The factor  $f$  is a temperature correction, which according to Ross<sup>3</sup> can be approximated by  $f = \frac{2T}{(2T_m^0 + T)}$ . The constant  $T_\infty$  is the temperature

