Study of Crystallinity of High-density Polyethylene by Inverse Gas Chromatography

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ABSTRACT

Method of inverse gas chromatography (IGC) has been used for the physico-chemical characterization of polymers for more than two decades. In this method the polymeric stationary phase could be characterized by using probe molecules. The retention volume of probe is a measure of the polymer-probe interaction and show changes in the polymer structure at melting point or glass transition temperature. Crystallinity of high-density polyethylenes (HDPE) of Poliran and Irapol from Iranian petrochemical companies was studied. The effects of the flow rates and the sample size on peak retention volume were investigated. Modified techniques for measurement of flow rate and coating were used. Retention diagram and degree of crystallinity were determined for a sample of low-density polyethylene and the results were compared with those obtained for HDPE. Experimental data of crystallinity and melting points showed that the Iranian HDPE is a polymer with suitable engineering properties.

Key Words: high-density polyethylene (HDPE), crystallinity, inverse gas chromatography, retention diagram, soaking method

INTRODUCTION

During the last 30 years, the inverse gas chromatography (IGC) has been a useful method for the physico-chemical characterization of polymeric materials. The method is termed "inverse" because, unlike standard gas chromatography, the polymer or polymer blend is the stationary phase [1]. IGC is a useful technique for characterizing synthetic and biological polymers, copolymers, polymer blends, glass and carbon fibers, coal and solid foods.

The technique involves using a column stationary phase of the solid material of interest. The stationary phase may be a thin polymeric coating on an inert substrate, a finely divided solid or a thin polymeric coating on the column wall. A volatile probe of known characteristics is passed through the column by an inert mobile phase and the output is monitored. The retention time of probe and the shape of chromatogram indicate the characteristics of the...
IGC has been used in determining properties such as: the glass transition phenomena [2, 3], degree of crystallinity [4, 8], polymer surface characterization [9], adsorption isotherms [10], diffusion phenomena [11–15], degree of fusion [16], degree of cross-linking of polymer network [17], polymer-polymer interaction coefficients [18, 19], polymer-solvent interaction coefficients [20–29], and polymer blend interactions [30, 31].

Most experimental methods for following the changes in crystallinity of polymeric systems have involved changes in volume, absorption spectra and optical properties [32]. Well above $T_g$, surface effects are negligible and retention volumes are measures of the thermodynamic interaction of the probe with the bulk of polymer [33]. Sharp discontinuities have been detected in variation of retention volumes with temperature for hydrocarbons on columns containing polyethylene and polypropylene near the polymer melting points [1, 4–8].

Crystallinity could be used as a selection criterion for engineering properties of high-density polyethylene (HDPE) [34]. As a result of a design change by engineers at a research laboratory, the polymer group was asked to select and characterize HDPE on the basis of four design requirements: (1) high purity, (2) high-density, (3) low thermal expansion, and (4) maximized mechanical properties. As all PE’s are semicrystalline, the degree of crystallinity significantly affects the density, thermal expansion, and mechanical properties. As the fraction of crystallinity approaches 1.0, the polymer density approaches the density of a perfect HDPE crystal.

The thermal expansion coefficient of the amorphous, or liquid phase will be greater than that of the crystalline phase. Again, a higher degree of crystallinity should result in a lower thermal expansion coefficient. Similarly, the modulus of the amorphous phase will be lower than that of crystalline phase. Clearly, as the degree of crystallinity increases, the thermal expansion should decrease, the mechanical properties must improve, and the density to increase. The optimum requirements are crystallinity $\geq 75\%$ and melting point $\geq 127\, ^\circ C$ for HDPE.

**EXPERIMENTAL**

**Materials**

The following polymers and chemicals used were: HDPE (Poliran-HD0035, MFI=0.35 g, d=0.964), HDPE (Irapol-5620, d=0.952), LDPE (Poliran-LF0450, MFI=4.5, d=0.9240), n-dodecane (>98%, d=0.748, Merck), toluene (>99%, d=0.865, Riedel).

**Coating Method**

Routinely, coating is carried out by dissolving the polymer in a suitable solvent, adding the support, slowly evaporating the solvent (usually in a rotary evaporator), drying the coated support in the oven, and sometimes sieving it repeatedly. During this lengthy procedure a significant part of the polymer may be lost on the walls of the evaporating vessel. Further losses may occur during sieving. The amount of the polymer on the column is one of the key quantities in calculation of $V_g$ and the polymer loss may be very significant. For example, a 5ft column, 1/4 in. o.d., may hold 10 g of support. With typical 7% loading, a loss of 7 mg of the polymer would cause 1% error in calculated $V_g$ values. This is much more than acceptable error for a single source.

Consequently, most researchers [18, 35] have analyzed the coated support for its polymer content by either extraction or calcination. However, both methods were shown to be subjected to significant errors. To achieve a better control of the amount of polymer, we used soaking method for deposition of the whole sample of PE on glass beads [18].

In this method PE was dissolved in hot toluene as usual. The support was piled on a watch glass or a similar dish and a small amount of solution was applied on top of the support pile. Care was taken to wet the pile as much as possible without letting the solution touch the surface of the dish, either around or under the pile.

The solvent was allowed to evaporate and the pile was thoroughly mixed, then a next portion of the solution was applied and the whole procedure was repeated until all the solution was used up. It takes typically 10–20 additions and requires only a few hours. Then the support was dried in the oven at 80 °C.
Table 1. Column parameters.

<table>
<thead>
<tr>
<th>Column</th>
<th>Polymer</th>
<th>Length (m)</th>
<th>Loading (%)</th>
<th>Mass of polymer (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HDPE, Poliran-HD0035</td>
<td>1</td>
<td>0.6</td>
<td>0.1868</td>
</tr>
<tr>
<td>2</td>
<td>HDPE, Irapol-5620</td>
<td>1</td>
<td>0.6</td>
<td>0.1800</td>
</tr>
<tr>
<td>3</td>
<td>LDPE, Poliran-LF0450</td>
<td>1</td>
<td>0.6</td>
<td>0.1817</td>
</tr>
<tr>
<td>4</td>
<td>Reference column</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Support: Glass bead of 80–80 mesh was used for all the columns.

for 10 h and quantitatively it was transferred into the column with standard precautions of quantitative analytical chemistry. Vibration and tapping were employed to ensure uniform packing of column.

Washed glass wool plugs were placed in the ends of the column. The method was fast, the amount of polymer was precisely known, and the analysis of the column material was not needed. The columns were conditioned at 80 °C with fast carrier gas flow rate for 5 h prior to use. The experimental data are presented in Table 1.

Apparatus and Procedure
Measurements were carried out on a Perkin-Elmer Sigma 300 dual-column gas chromatograph, equipped with a thermal conductivity detector. Dried helium was used as carrier gas. The flow rate was controlled by a precision needle valve, and measured by a modified soap bubble flowmeter. The flow rate was measured at room temperature and it was monitored frequently by taking an average of three readings. Flow rate was typically about 15 mL/min. The inlet and outlet pressures were also frequently monitored [20].

Dodecane was injected with 10 μm Hamilton syringe. To avoid the problems related to the overloading of the column by the probe, syringe was filled with the probe, emptied it two or three times and then the air probe-vapour mixture left in the syringe was injected onto the column. The amount injected in this way was not very reproducible, but the obtained peaks were always symmetrical. Two or three successive injections were made for each probe at each temperature. Columns were prepared from 1m×6mm o.d. copper tube packed with known amount of polymer coated on 60–80 mesh glass beads. The glass beads were coated by a toluene solution of the polymer at a temperature about 10 °C below the polymer melting point and let the solvent to evaporate.

The Perkin-Elmer laboratory computing integrator, LCI-100 was used for recording and integration of the detector output signal. The column parameters are given in Table 1.

RESULTS AND DISCUSSION

Effect of Flow Rate of Carrier Gas on Retention Volume
The dependence of corrected retention volume on flow rate was studied. In case of no flow rate dependence, determination of crystallinity could proceed. On the other hand with flow rate dependence, the flow rate would be reduced to the lowest practical value, which is consistent with good peak resolution. If the corrected retention time still depended on flow rate, measurements must be made at several flow rates and extrapolated to zero flow. The dependence of retention volume on flow rate is shown in Figure 1.

![Figure 1. Dependence of retention volume on flow rate.](image-url)
The origin of the flow rate dependence of retention volumes for bulk sorption can be readily understood. A change of carrier gas flow rate affects the rate movement of a band of solute through the column and the residence time over the stationary phase. As the flow rate is decreased, the polymer-solute system is allowed to come closer to or even reach equilibrium, leading to larger specific retention volumes.

As the temperature is increased, the dependence on flow rate is diminished, due to an increase in the rate of diffusion. At higher temperatures, retention volumes can therefore be used without correction for flow rate effects.

The flow rate must be stable, and measured properly. The old-fashioned soap-bubble meter seems to be still the most reliable device for measurement of small flow rate. However, two precautions must be taken: (1) the bubble-meter must be thermostatted (we used adapted burettes with a water jacket) and (2) the diffusion of the carrier gas across the soap bubble must be either prevented or accounted for. The latter effect is not significant when nitrogen is used as the carrier gas, but is very important with helium and hydrogen. We have used a convenient design of the bubble-meter [36].

Effect of the Amount of Injection
In the previous experiments, it was demonstrated that there was a remarkable change in the retention time for dodecane with change in the amount of sample injected (Figure 2). The model for retention behaviour was derived for linear partition isotherms, which implies that the retention volumes are independent of the amount of injected sample. This condition was applied to provide infinitely dilute solutions of vapour in the stationary phase. Since a finite amount of polymer is subjected with injection, its effect on the retention volume must be studied.

The amount of the injection may alter the measured retention volume for several reasons, of which the most important are non-linearity of the partition isotherms and adsorption effects on uncoated support. Figure 2 shows that there is a negligible change in retention time for dodecane over 10 fold changes in sample size. The retention time was constant at 0.01-0.1 µm ranges.

Retention Diagrams for HDPE
As in conventional gas chromatography it is convenient to express the results of these experiments in terms of the retention volume \( V_g \), defined as the volume of carrier gas required eluting the probe molecules. The fundamental quantity from which the various interactions may be deduced is the specific retention volume \( V_g \) [1], as it is defined by eqn (1):

\[
V_g = \frac{(t_r - t_m)F_m}{W} \times \frac{273.15}{T_{room}} \times \frac{3}{2} \left( \frac{P_i/P_o}{P_{H_2O}/P_o} \right) \left( 1 - \frac{P_{H_2O}}{P_o} \right)
\]

Where \( t_r \) and \( t_m \) are retention times for probe and marker, \( F_m \) is the flow rate of carrier gas measured at room temperature \( (T_{room}) \), \( W \) is the mass of the stationary phase; \( P_{H_2O} \) is the water vapor pressure at room temperature; \( P_i \) and \( P_o \) are the inlet and outlet pressures, respectively. The value of \( V_g \) for dodecane is determined for the polymer at different temperatures. The data are plotted in a general retention diagram in the form of \( \log V_g \) as a function of the reciprocal of absolute temperature \( (1/T) \). Figure 3 shows such a curve for two HDPE's.

The GC retention volume reflects the interaction of a probe vapour with the polymer. Changes
in the polymer structure, which occur at the melting point or the glass transition temperature, should therefore exert a marked effect on the retention volumes. Sharp discontinuities have been detected in the retention volumes with temperature for hydrocarbons on columns containing polyethylene and polypropylene near their melting points [33].

In gas-liquid chromatography (GLC), a plot of the logarithm of the retention volume versus the reciprocal of absolute temperature should be a straight line with slope related to the heat of solution. Polymer stationary phases undergoing transitions deviate from such linearity, leading to a typical Z-shaped retention diagram. Such deviation from linearity and reversal from the normal behaviour have been attributed to a change in retention mechanism occurring at the phase transition [1].

In principal, the observed retention volume for polymer stationary phases may be considered as a sum of three partial retention volumes related with dissolution of sorbate in the polymer phase, its adsorption on the polymer surface and on the free support surface

\[ V_i = K_b m + K_A A_s + K_{A'} A' s \]  

where \( K_b \), \( K_A \) and \( K_{A'} \) are distribution coefficients for dissolution of probe by amorphous phase, adsorption by polymer surface and free surface, respectively. \( A_s \), and \( A' s \) are polymer and free support surface areas. Since the melting of polymer occurs in a temperature range, the beginning of increase of retention volume to reach a maximum can be due to its melting range. The melting ranges were (119–134 °C) for Poliran-HD0035 and (113–131 °C) for Irapol-5620 HDPE's. On the other hand, higher values of \( V_g \) for Irapol-5620 HDPE can be due to higher amount of amorphous phase, which cause much retention of probe in the bulk of polymer.

Error Analysis
Estimation of the standard deviation of \( V_g \), \( SV_g \), can be obtained from the standard deviations of the individual parameters by the following equation:

\[ SV_g = \sqrt{\sum \left( \frac{dV}{d^2} \right)^2 S^2} \]  

For example, the error analysis performed on the data generated in IGC measurement of Poliran-HD0035 HDPE/dodecane at 100 °C is presented in Table 2. As it is seen in this table, it is in the range of experimental errors.

Degree of Crystallinity of HDPE Samples
The retention diagram must be related to the crystallinity of a polymer sample. The retention volume decreased to a minimum and then increased to a sharp
maximum as the temperature increased (Figure 3). Based on the assumption that the probe molecules interact only with the amorphous polymer, the crystallinity regions are assumed to be impenetrable. The retention volume therefore depends on the amount of the amorphous material on the column.

By extending the linear portion of a retention curve to lower temperatures, the hypothetical retention volume for a totally amorphous sample at any temperature may be obtained. The linearity of the curve above the melting point of the polyethylene stationary phase was further confirmed by regression analysis of least squares (Tables 3).

In fact, the extrapolation of the linear portion of the curves in Figure 3 to lower temperature region should represent the theoretical retention curve for the 100% amorphous polymer. The deviation from linearity would then be due to a decrease in the amount of amorphous polymer (corresponding to an increase in the amount of impenetrable crystalline polymer).

The amount of amorphous polymer at any temperature below \( T_m \) could be estimated by comparing the experimental value of \( V_g \) with its theoretical value \( V'_g \) obtained from the extrapolated curve at the same temperature, then:

\[
\text{Crystallinity} = 100 \left( 1 - \frac{V_g}{V'_g} \right)
\]

It is possible to determine the degree of crystallinity of the polymer at various temperatures using this expression. The values obtained for two HDPE samples are shown in Figure 4. As it is seen in Figure 4, crystallinities of Poliran-HD0035 and Irapol-5620 were about 81% and 79.8%, respectively. Crystallinity decreases as the temperature increases and finally approaches to zero at temperature of melting range. After this temperature, the polymer is as an amorphous form. It should be pointed out that this method should in principal be sensitive to the presence of very small crystallites, which cannot be detected by standard X-ray diffraction methods. Unlike the density method, the presence of voids or air bubbles should not affect the results either. The disadvantage, however, is that the polymer must be in the form of a thin film in order to be studied. In spite of this, the advantages of this method are: simplicity, obtaining additional information on thermodynamic interactions and structural changes such as glass interactions.

Study of Crystallinity of Low-density PE

The retention diagram and crystallinity of the low-density PE of Poliran-LF0450 was also investigated. Figures 5 and 6 show retention diagram and

<table>
<thead>
<tr>
<th>HDPE</th>
<th>Slope</th>
<th>Std. dev.</th>
<th>Intercept</th>
<th>Std. dev.</th>
<th>R squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irapol-5620</td>
<td>-4.765</td>
<td>0.0637</td>
<td>2076.08</td>
<td>1.066</td>
<td>0.997</td>
</tr>
<tr>
<td>Poliran-HD0035</td>
<td>-3.136</td>
<td>0.079</td>
<td>1377</td>
<td>0.46</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4. Variation of HDPE crystallinity with temperature.

Figure 5. Retention diagram of Poliran-HD0035 LDPE.
The maximum of crystallinity for LDPE was about 43% with melting range 100–114 °C. HDPE and LDPE of Poliran were also compared and the results are shown in Figures 7 and 8. As it is seen, the transition for HDPE is sharp and retention volumes for LDPE had higher values than those of HDPE due to its higher amount of amorphous phase.

CONCLUSION

Since all PE's are semicrystalline, the degree of crystallinity significantly affects the density, thermal expansion, and mechanical properties. Therefore, crystallinity can be used as a selection criterion for engineering properties of HDPE. The optimum requirements are crystallinity >75% and melting point >127 °C for HDPE [34]. Our results showed that the degree of crystallinity and melting point of HDPE of Poliran and Irapol were about (81 and 79.8%) and (135 and 132 °C), respectively. Therefore, Iranian HDPE is a product with suitable engineering properties.

REFERENCES