

# Modeling the Solubility of Ternary Mixtures of Ethylene, *iso*-Pentane, *n*-Hexane in Semicrystalline Polyethylene

Wenjuan Yao, Xiaoping Hu, Yongrong Yang

UNILAB Research Centre for Chemical Reaction Engineering, College of Material Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, Zhejiang, China

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**ABSTRACT:** The coabsorptions of ethylene and *iso*-pentane, and ethylene and *n*-hexane were measured by the use of a pressure decay method. The solubility data of ethylene-*iso*-pentane and ethylene-*n*-hexane in semicrystalline polyethylene (PE) of crystallinity of 48.6% were obtained at temperatures 70, 80, and 90 °C, and the total pressure 2 MPa, *iso*-pentane partial pressure 80–190 KPa, *n*-hexane partial pressure 20–90 KPa. The presence of *iso*-pentane or *n*-hexane in the corresponding ternary system leads to increase the solubility of ethylene, while the solubility of *iso*-pentane or *n*-hexane remains unchanged with an increase of the ethyl-

ene partial pressure, even slightly decreases. Assumed that the presence of *iso*-pentane or *n*-hexane decreases the crystallinity of the polymer sample, a coabsorption model was built to model the solubility of each gas in the ternary systems. The relative root mean square errors of the coabsorption model for ethylene-*iso*-pentane-PE system and ethylene-*n*-hexane-PE system are 5.13% and 4.64%, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3654–3662, 2007

**Key words:** coabsorption; solubility; polyethylene (PE); modeling; ternary

## INTRODUCTION

During the gas-phase production of polyethylene (PE), the atmosphere surrounding the growing PE particles contains ethylene and  $\alpha$ -olefins typically 1-butene, 1-hexene, or 1-octene, used as comonomer. Furthermore an inert solvent such as *iso*-pentane or *n*-hexane is used as condensing agent in the condensed-mode gas-phase PE process. So many different components are present in a gas-phase reactor and simultaneously absorb in the polymer. The reaction rate and the final structure of the polymer chains are directly related to the solubilities of the monomer and comonomer in the PE grains.<sup>1–7</sup> Knowledge of the solubility of gas mixtures in polymer is important in both the polymer and the petrochemical industries.

At present most of the experimental and theoretical studies of the solubility of gases in polymers are limited to the absorption of a single gas.<sup>2–5,7–11</sup> However, the solubility of the gases mixture at given partial pressures is usually nonadditive. It has been observed experimentally that the solubility of a gas in a polymer sample may or may not be enhanced by the presence of another gas depending on the nature of the latter gas. Li and Long determined exper-

imentally a 50–50 mixture of the ethylene and methane components and showed that absorption of the more soluble ethylene enhances the solubility of the mixture well above that predicted from independent absorption.<sup>12</sup> However, they did not determine the relative composition of the absorbed vapor mixture in the polymer. Robeson and Smith examined absorption of an ethane-butane mixture in LDPE at atmospheric pressure.<sup>13</sup> They found that the absorption of ethane is not affected by the presence of butane, unless at 30°C. McKenna studied the presence of 1-butene or nitrogen does not affect the solubility of ethylene, but the absorption of 1-butene will change the crystallinity of PE.<sup>5</sup> Moore and Wanke obtained the preliminary results of the coabsorption of ethylene and 1-hexene, and showed that the amount of 1-hexene absorbed in the LLDPE in the presence of ethylene is much less than the solubility of pure 1-hexene in the same sample.<sup>14</sup> We also got the primary result that showed the presence of *iso*-pentane or *n*-hexane affect the solubility of ethylene in semicrystalline PE but it is not conversely.<sup>15</sup> Compared with the importance of the solubility data of gas mixtures in polymer, the earlier coabsorption solubility data are not adequate, especially for the conditions encountered during gas-phase polymerization.

Furthermore, to develop a sound understanding of the kinetics of the polymerization process, and hence the quality of the product resin, a model capable of predicting the solubility data is required, other than the solubility data of gas mixtures in polymer. Nath

Correspondence to: Y. Yang (yangyr@zju.edu.cn).

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et al. proposed the united atom force field using in Monte Carlo simulation to simulate the solubility of ethylene and 1-hexene mixtures in linear amorphous PE (modeled as  $C_{70}$ ).<sup>16,17</sup> They reported that the presence of 1-hexene increases the solubility of ethylene in PE and the two gas molecules exhibit a tendency to cluster near the polymer chain ends. McCabe et al. examined the coabsorption of pentane and methane mixture and pentane and butane mixture in LDPE with the SAFT-VR approach.<sup>18</sup> Paricaud et al. considered strong synergies consisting in the ternary system 1-butene-1-hexene-PE and used SAFT-VR to predict the solubilities.<sup>19</sup> They provided an explanation of the coabsorption effects in terms of the interactions between gas and PE molecules. Banaszak et al. employed the osmotic ensemble hyperparallel tempering method to simulate the coabsorption of ethylene-1-hexene in LLDPE, and then used the simulations to parameterize the SAFT-PC equation of state.<sup>20</sup>

All these models only account for the concentration of gas in amorphous region of the semicrystalline polymer and do not capture the semicrystalline structure of polymer. The presence of the crystallites impacts the solubilities of gases in amorphous polymer, as suggested by Michaels and Hausslein (M-H theory).<sup>21</sup> And under typical gas phase reactor conditions, the crystallinity of polymer is dependent on the temperature, and may be decreasing as a function of increasing gas content.<sup>5,19,22</sup> Therefore, to account for the coabsorption behavior of gas mixtures in semicrystalline polymers, an elaborate model is needed.

Considering the chemical simplicity and immediacy that characterize such ternary systems, activity coefficient theory could provide a useful tool to understand and determine the coabsorption behavior. Furthermore, activity coefficient theory can expediently account for the effects of crystallites on the solubility of gases in the amorphous region of the semicrystalline polymer, while molecular simulations and equation of states cannot do. In previous work, we studied the solubility of ethylene, *iso*-pentane, and *n*-hexane in PE near the operating temperatures and pressures of the polymerization processes, and develop a model to fit the experimental data. In this work, the purpose is to study the solubility of gas mixtures of ethylene-*iso*-pentane and ethylene-*n*-hexane in LLDPE. We compared the ternary experimental results with the corresponding binary solubilities and used the coabsorption model based on the activity coefficient theory to describe and explain the coabsorption behavior of ternary systems.

The article is organized as follows. A brief description of the model was depicted. And then the solubility of each gas in ternary systems of ethylene-*iso*-pentane-LLDPE or ethylene-*n*-hexane-LLDPE was measured. Finally, the experimental solubility data

were modeled and discussed for the validity of our hypotheses and the coabsorption effects.

## MODEL DETAILS

In this work the coabsorption of ternary mixture is based on the activity coefficient theory for the polymer solution. The amorphous regions of the polymer sample correspond to liquidlike states and can be described with UNIFAC-FV. With the introduction of crystallites, the swelling in the amorphous phase of the semicrystalline polymer is constrained, thereby reducing the solubility of molecules in the amorphous phase of the polymer as compared to that in a hypothetical, purely amorphous polymer under the same conditions. To account for this elastic constraint, following Michaels and Hausslein, we employed the UNIFAC-FV-M-H model.<sup>21</sup>

### Activity of gas component

For the amorphous liquid phase, the activity of the gas  $a_i$  can be calculated from the following expressions:<sup>10</sup>

$$\ln a_i = \ln a_i^c + \ln a_i^{fv} + \ln a_i^{int} + \ln a_i^{el} \quad (1)$$

These are the free energy contributions in the gas-polymer system from combinatorial, free-volume, interactional, and elastic factors. In three-component systems including polymer, the contributions are discussed as follows.

The combinatorial factor can be gotten from the Flory-Huggins lattice theory:<sup>23</sup>

$$\ln a_i^c = \ln \phi_i + 1 - \sum_{i=1}^2 \phi_i \quad (2)$$

The third term on the right-hand side of eq. (2) is the sum of volume fraction of two gas component in polymer.

Because the polymer molecules are much tightly packed than the gas molecules, the free volume contribution takes into account the different liquid structures between gases and polymer. Assuming the volumes are additive, Flory equation of state can be used to express the free-volume factor:<sup>24</sup>

$$\ln a_i^{fv} = 3c \ln \left( \frac{\bar{v}_i^{1/3} - 1}{\bar{v}_m^{1/3} - 1} \right) - c \left( \frac{\bar{v}_i}{\bar{v}_m} - 1 \right) \left( 1 - \frac{1}{\bar{v}_i^{1/3}} \right)^{-1} \quad (3)$$

where  $\bar{v}_i$  is the reduced volume of the small molecule, and the reduced volume of the ternary mixture  $\bar{v}_m$  can be calculated from the specific volume  $v_m$

and the specific hard-core volumes  $v_m^*$  for the mixture,  $\bar{v}_m = v_m/v_m^*$ . The  $v_m$  and  $v_m^*$  can be, respectively, obtained from:

$$v_m = \sum_{i=1}^3 w_i v_i \quad (4)$$

$$\frac{1}{v_m^*} = \sum_{i=1}^3 \frac{w_i}{v_i^*} \quad (5)$$

According to the UNIFAC group contribution method, the gas-polymer mixture system is considered as a solution of functional groups rather than a solution of molecules. So the interactional factor is:<sup>10</sup>

$$\ln a_i^{\text{int}} = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \quad (6)$$

Michaels and Hausslein proposed a theory suggesting that the segment tension crystallization driving force competition is an equilibrium phenomenon.<sup>21</sup> They assumed that the amorphous regions of the semicrystalline polymer are composed of two types of segments: elastically effective and elastically ineffective. The former consist exclusively of intercrystalline tie segments and are responsible for chain deformation by absorption. The latter consist of loops, isolated chains, and chain ends terminating in the amorphous regions and these segments are not elastically deformed. The activity due to elastic as:

$$\ln a_i^{\text{el}} = \frac{\left[ \frac{V_i \Delta H_i^f \rho_a}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right) - \phi_i + \left( \frac{\ln a_i^{\text{int}} + \ln a_i^{\text{fv}}}{\phi_3^2} \right) \phi_i^2 \right]}{\left( \frac{3}{2f\phi_3} - 1 \right)} \quad (7)$$

where  $f$  is designated as the elastically effective mass fraction of the amorphous polymer.

On the basis of the assumption, the amount of elastically ineffective amorphous polymer is constant with temperature. So making  $\delta$  to be the elastically ineffective portion of the total polymer, the relationship between  $f$  and  $\delta$  is given by:

$$f = 1 - \frac{\delta}{1 - w_{\text{crys}}} \quad (8)$$

where  $w_{\text{crys}}$  is the crystallinity of polymer. Since the crystallinity is temperature-dependent, the parameter  $f$  should be variable from eq. (8).<sup>5,22</sup> The elastically effective segments contain two parts: the inherent and the premelted polymer. Parameter  $f$  is the function of temperature and parameter  $\delta$  is characteristic of each semicrystalline polymer and independent of temperature and gas concentration and type.

In this article, we employ a predictive approach for the melting point and crystallinity of an arbitrary

PE sample as a function of temperature developed by Paricaud et al.<sup>19</sup> The approach is based on Flory's theory of copolymer crystallinity and requires only the experimental crystallinity  $w_{\text{crys},25}$  or polymer density  $\rho_{25}$  at 25°C as an input parameter. Paricaud et al. assumed PE can be treated as a "copolymer," which contains both crystallizable ethylene groups and noncrystallizable units such as those on the alkyl branches along the chain. The crystallinity  $w_{\text{crys}}$  represents the weight fraction of crystallizable units and the probability that a given polymer unit crystallizes on cooling. They made correlations of the melting point  $T_m$  and the probability  $P$  as a function of  $w_{\text{crys},25}$  using the experimental data for the two main types of catalyst (Ziegler-Natta and metallocenes, in brief ZN and Me) used in polymerization reactors.<sup>5,22</sup>

The melting point of PE can be described in terms of the following functions of:

$$T_m(\text{ZN})/^{\circ}\text{C} = 13.689w_{\text{crys},25}^2 + 5.015w_{\text{crys},25} + 124.33 \quad (9)$$

$$T_m(\text{Me})/^{\circ}\text{C} = -81.498w_{\text{crys},25}^2 + 163.3w_{\text{crys},25} + 63.415 \quad (10)$$

According the assumption, the probability  $P$  is able to characterize the cooling rate indirectly. A parameterization of the probability  $P$  in terms of  $w_{\text{crys},25}$  can also be given:

$$P(\text{ZN}) = -0.0581w_{\text{crys},25}^2 + 0.1279w_{\text{crys},25} + 0.9303 \quad (11)$$

$$P(\text{Me}) = -0.0538w_{\text{crys},25}^2 + 0.1397w_{\text{crys},25} + 0.9142 \quad (12)$$

The correlations of the two types of catalyst go through the point for an ideal infinitely long and linear PE molecule:  $w_{\text{crys},25} = 1.0$ ,  $T_m = 145^{\circ}\text{C}$ . The crystallinity  $w_{\text{crys}}$  satisfies:

$$w_{\text{crys}}(T) = \frac{w_{\text{crys},25} P_{\text{crit}}^{\xi} \left[ \frac{P}{(1-P)^2} - \frac{e^{-\beta}}{(1-e^{-\beta})^2} + \xi_{\text{crit}} \left( \frac{1}{1-P} - \frac{1}{1-e^{-\beta}} \right) \right]}{P_{\text{crit},25}^{\xi} \left[ \frac{P}{(1-P)^2} - \frac{e^{-\beta_{25}}}{(1-e^{-\beta_{25}})^2} + \xi_{\text{crit},25} \left( \frac{1}{1-P} - \frac{1}{1-e^{-\beta_{25}}} \right) \right]} \quad (13)$$

### Correlating the crystallinity of polyethylene with the gas content

On the crystallization thermodynamics, impurities or chain ends impact the melting point of polymer. When there was small molecular diluting agent such as plasticizer and monomer unreacted, the melting point of crystalline polymer decreased.

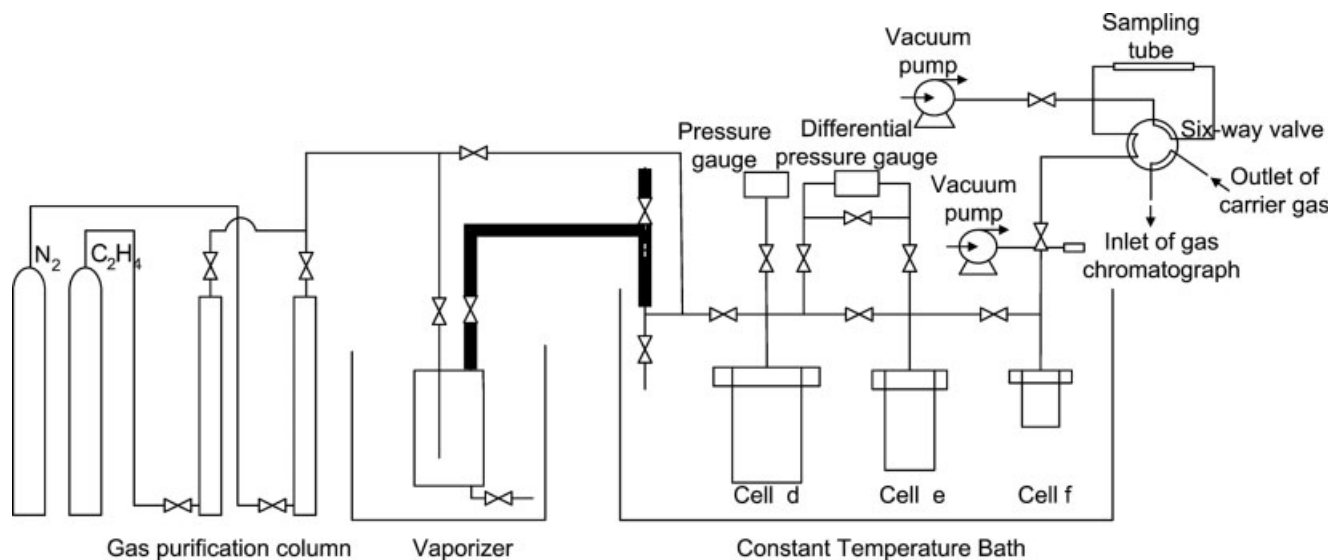


Figure 1 Schematic diagram of absorption apparatus.

McKenna observed that the crystallinity and the melting point of polymer decrease as a function of increasing butene content, and proposed an empirical relationship between the butene fraction of a PE sample and the crystallinity or the melting point.<sup>5</sup> It has been shown experimentally that the presence of a gas may or may not enhance the solubility of another gas. For instance, Paricaud et al. found the absorption of 1-hexene in PE enhances the solubility of 1-butene, while the absorption of nitrogen does not change the solubility of 1-butene, even slightly decreases.<sup>19</sup> Nath et al. studied the solute-solute and solute-polymer intermolecular pair correlation functions of the ethylene-1-hexene-PE ternary mixture. It was found that although the relative strength differs from, the absorption of a small molecule cannot change the intermolecular interactions.<sup>17</sup>

Therefore, we define that the coabsorption is a behavior that the absorption of one gas in polymer gives rise to an increase in the solubility of the other gas. The reason is the presence of large amounts of the former in the polymer decreases the crystallinity and further leads to an increase in the amount of amorphous region and an increase in the latter gas. Whether the coabsorption behavior takes place depends on the nature of the first gas. The change of the crystallinity of polymer sample because of the presence of a gas is temporary.

To combine with the relationship between the crystallinity and the temperature, we assume the change of the crystallinity at 25°C  $\Delta w_{m,25}$  is given by the solubility of the gas  $S_A$ , which causes the coabsorption behavior:

$$\Delta w_{m,25} = m + n \ln(1 - S_A) \quad (14)$$

where  $m$  and  $n$  are two adjustable parameters dependent on the property of the gas. It should be noted that  $S_A$  is the sum of the solubility of two small molecules when these all can cause the change of the crystallinity of polymer sample.

To sum up, our coabsorption model contains three adjustable parameters, and the crystallinity of the polymer is dependent on temperature and the solubility of gas.

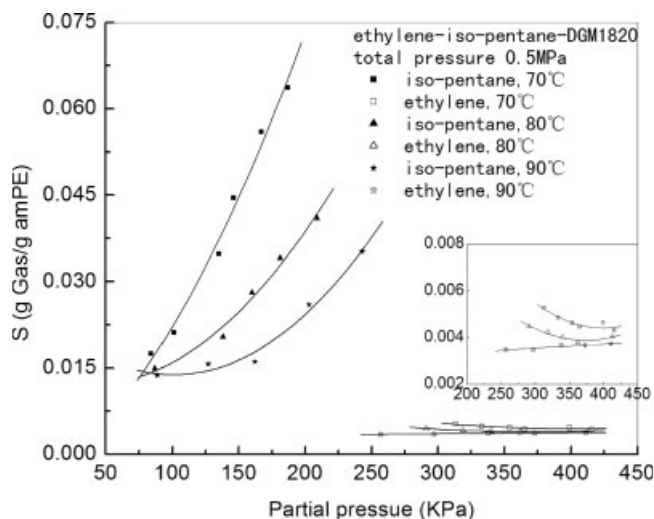
## EXPERIMENTAL

### Apparatus

Figure 1 shows the schematic diagram of the pressure-decay apparatus. There are three main parts: one part for gas inlet, the second for vapor generation, and the third for solubilities measurement. A pressure gauge accuracy 0.25 was equipped to measure the pressure in cell d. A differential pressure gauge (range 1 MPa, accuracy 0.04 MPa, and 14 MPa F.S.) was used to monitor the pressure change. The temperature of the cells was controlled using two water bathes ( $\pm 0.1$  K). All the incoming lines were wrapped with heating tapes to prevent any condensation of vapor. The composition of the gaseous mixture was measured with a gas chromatograph.

The PE powder was placed in cell f and the apparatus was evacuated. *Isopentane* or *n-hexane* was formed vapor in a vaporizer by a constant-temperature bath. When the systems got equilibrium, the valve between cell d and cell e and the valve between cell e and cell f were closed. Then the valves between the vaporizer and cell d were opened, the vapor was introduced into cell d. After

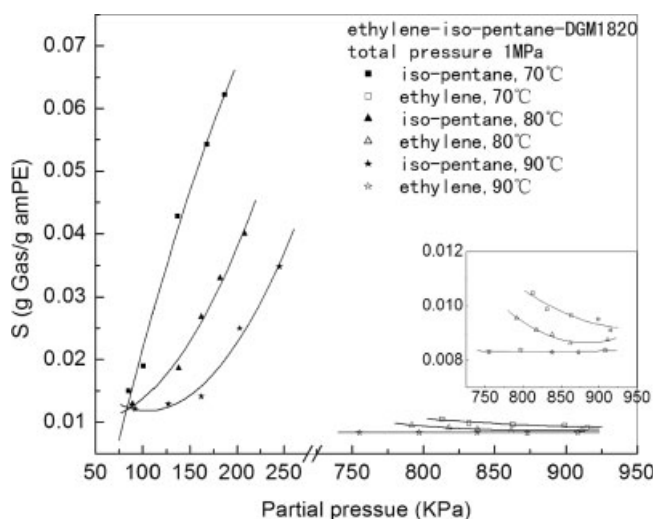




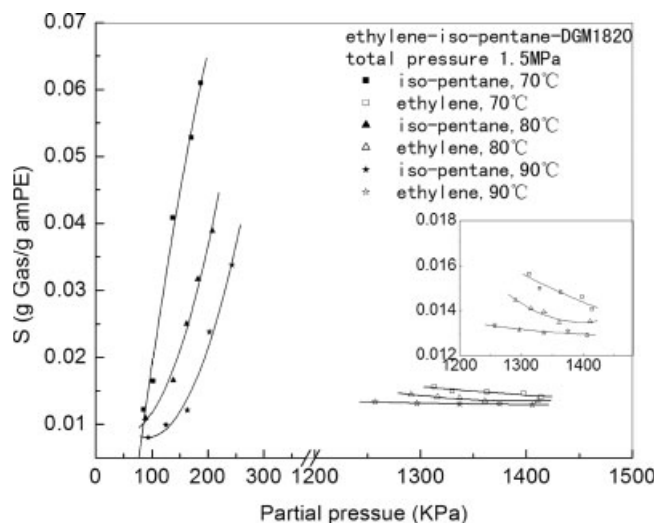
**Figure 2** Solubility data of ethylene and *iso*-pentane in the ethylene-*iso*-pentane-DGM1820 ternary system at the total pressure 0.5 MPa.

measured the pressure with a differential pressure gauge, the vapor was introduced into cell e at the same pressure. Ethylene stream was introduced in the cell e and mixed with the vapor.

The valve between cell d and cell e was closed and the valve between cell e and cell f was opened to get the gaseous mixture meet PE powder. The pressure decay  $\Delta P$  resulting from gas dissolution and volume expansion was measured with the differential pressure gauge. And then the valve between cell e and cell f was closed, and the gaseous mixture was introduced into the sampling tube through the six-way valve. After absorption, the apparatus was degassed with nitrogen.



**Figure 3** Solubility data of ethylene and *iso*-pentane in the ethylene-*iso*-pentane-DGM1820 ternary system at the total pressure 1 MPa.



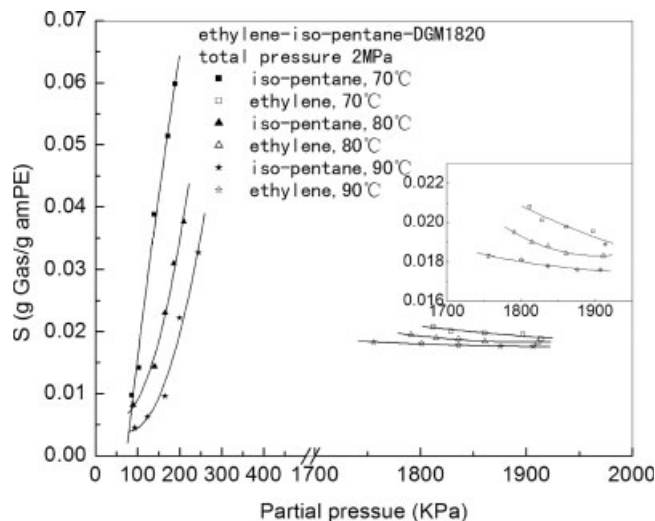
**Figure 4** Solubility data of ethylene and *iso*-pentane in the ethylene-*iso*-pentane-DGM1820 ternary system at the total pressure 1.5 MPa.

According to the ideal gas equation of state, the amount of gas and vapor dissolved into the PE was determined using the following equations, respectively:

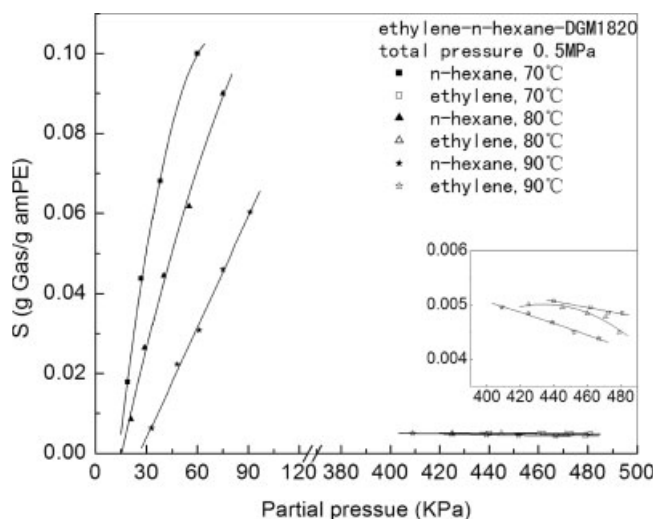
$$n_{\text{vapor}} = \frac{P_{\text{vapor}1}V_1}{RT} - \frac{P_{\text{vapor}2}V_2}{RT}$$

$$n_{\text{gas}} = \frac{(P_1 - P_{\text{gas}1})V_1}{RT} - \frac{(P_1 - \Delta P - P_{\text{gas}1})V_2}{RT}. \quad (15)$$

where  $V_1$  is the inner volume of the cell e;  $V_2$  is the volume of vapor or gas at the absorption equilib-



**Figure 5** Solubility data of ethylene and *iso*-pentane in the ethylene-*iso*-pentane-DGM1820 ternary system at the total pressure 2 MPa.

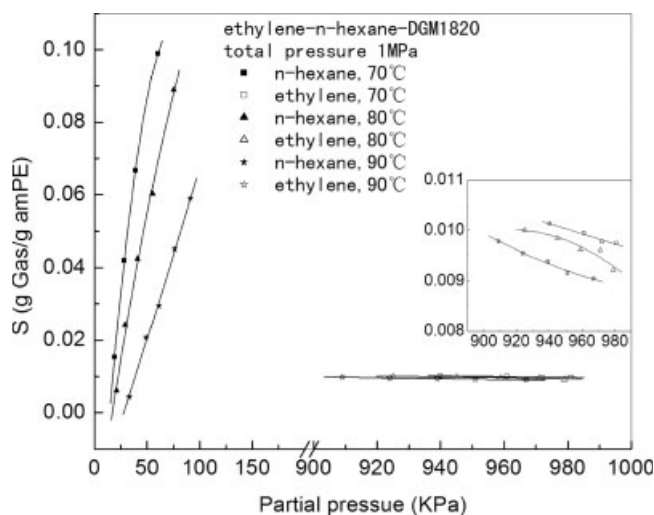


**Figure 6** Solubility data of ethylene and *iso*-pentane in the ethylene-*n*-hexane-DGM1820 ternary system at the total pressure 0.5 MPa.

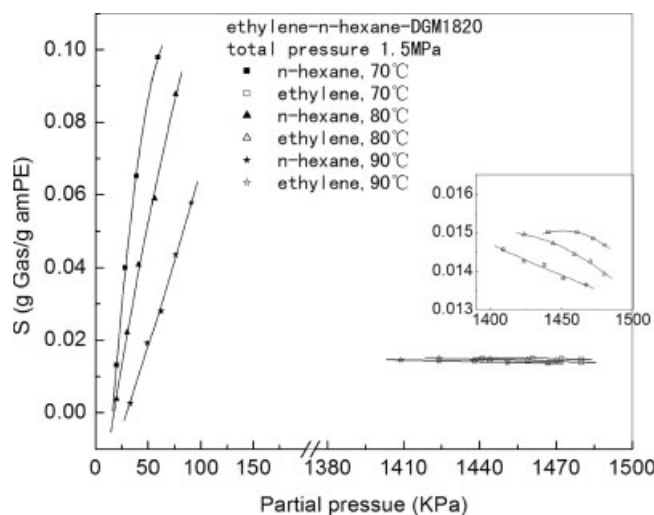
rium, so it is the summation inner volume of the cell  $e$  and  $f$  subtract from the volume of the polymer.

### Materials

A PE powder, DGM1820 obtained from Qilu Petrochemical (Zibo, China) was used in this study. It had particle diameter 0.5–0.6 mm, a density 0.920 g/mL, and a crystallinity of 48.6%, as determined by differential scanning calorimetry and X-ray diffraction. Prior to experiments, the sample was outgassed at 60°C and protected within nitrogen. Two gaseous mixtures were ethylene-*iso*-pentane and ethylene-*n*-hexane. The purity of ethylene was at least 99% and received from Zhejiang University Gas Station. *Is*o-



**Figure 7** Solubility data of ethylene and *iso*-pentane in the ethylene-*n*-hexane-DGM1820 ternary system at the total pressure 1 MPa.



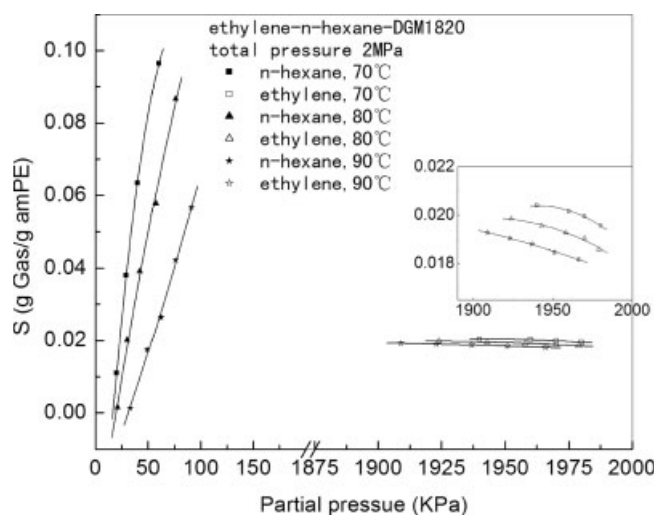
**Figure 8** Solubility data of ethylene and *iso*-pentane in the ethylene-*n*-hexane-DGM1820 ternary system at the total pressure 1.5 MPa.

pentane and *n*-hexane were analytically pure. The experiments were performed at temperatures of 70, 80, and 90°C for each ternary system and at total pressures up to 2 MPa, *iso*-pentane partial pressures 80–190 KPa, and *n*-hexane partial pressures 20–90 KPa, respectively.

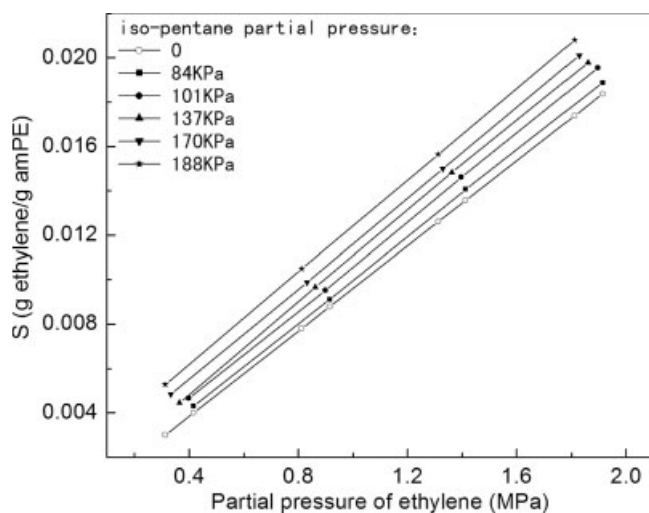
## RESULTS AND DISCUSSION

### Solubility of gases in ternary system

In the ethylene-*iso*-pentane-PE ternary system, the solubilities of ethylene and *iso*-pentane in DGM1820 at different temperatures and total pressures are shown in Figures 2–5. Figures 6–9 show the experi-



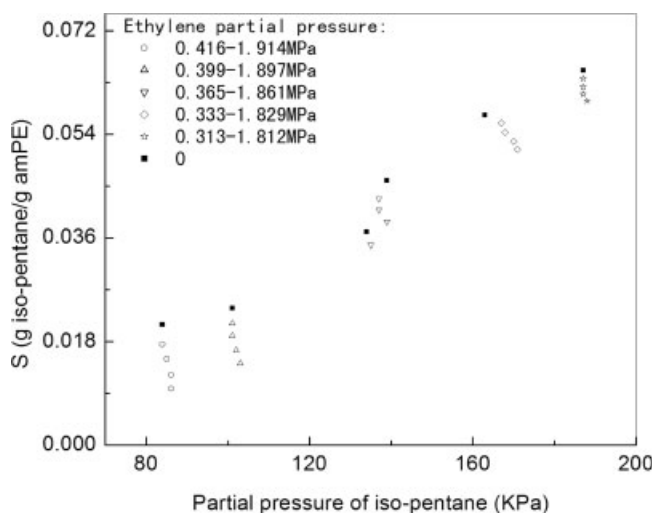
**Figure 9** Solubility data of ethylene and *iso*-pentane in the ethylene-*n*-hexane-DGM1820 ternary system at the total pressure 2 MPa.



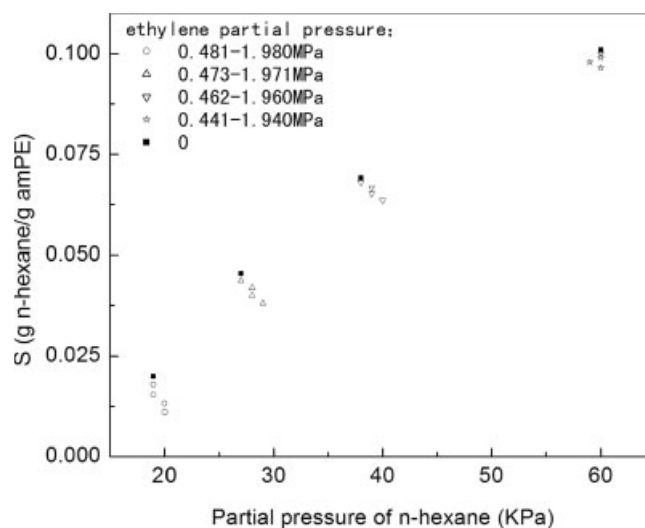
**Figure 10** Solubility of ethylene with various *iso*-pentane partial pressures at 70°C.

mental solubility data of ethylene and *n*-hexane in DGM1820 in the ethylene-*n*-hexane-PE ternary system. The solubility data are expressed in terms of grams of gases per gram of amorphous polyethylene.

In the literature, the solubility of ethylene in PE was shown to be proportional to the pressure at each of the different temperatures and can be expressed in terms of Henry's law. Figures 2–9 show the solubility of ethylene in a ternary system is also linear with pressure. However, due to the presence of *iso*-pentane or *n*-hexane, the solubility of ethylene in the ternary system is higher than that in the binary system at given temperature and pressure. Figure 10 shows that for a fixed ethylene partial pressure the solubility of ethylene increase with the *iso*-pentane partial pressure increasing. And the fig-



**Figure 11** Solubility of *iso*-pentane with various ethylene partial pressures at 70°C.



**Figure 12** Solubility of *n*-hexane with various ethylene partial pressures at 70°C.

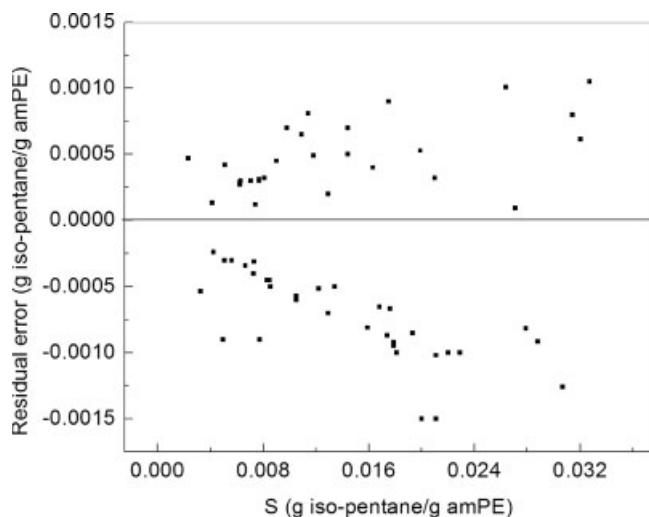
ure also shows that when the *iso*-pentane partial pressure is fixed the increasing extent of the solubility of ethylene is a little different.

Furthermore, the solubility of ethylene in the ethylene-*n*-hexane-DGM1820 ternary system increases with increasing partial pressure of *n*-hexane, consistent with what is found in the case of ethylene-*iso*-pentane-DGM1820. This experimental observation can be explained as follows: the presence of *iso*-pentane or *n*-hexane decreases the crystallinity of the polymer sample and as a consequence favors the solubility of ethylene.

On the other hand, a different behavior is observed: the presence of ethylene hardly increases the solubility of *iso*-pentane or *n*-hexane, even slightly decreases. Figures 11 and 12 show respectively, the solubilities of *iso*-pentane and *n*-hexane when ethylene is added as the coabsorbent at 70°C. For *iso*-pentane or *n*-hexane, solubility decreases slightly with an increase in ethylene partial pressure. Obviously, the solubility of ethylene is far lower than that of *iso*-pentane or *n*-hexane. Thus, the presence of ethylene cannot affect the crystallinity of polymer. When *iso*-pentane or *n*-hexane is absorbed into the amorphous region, ethylene is an inert existence and occupies a small proportion of space where should be the former.

**TABLE I**  
Parameters  $m$  and  $n$  for Ternary Systems by the Coabsorption Model

Ternary system	$m$	$n$
Ethylene- <i>iso</i> -pentane-DGM1820	-0.117	-0.0185
Ethylene- <i>n</i> -hexane-DGM1820	-0.120	-0.0158

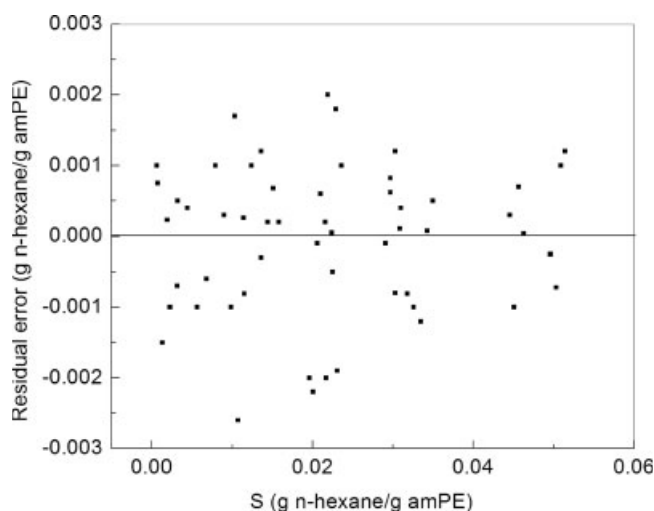


**Figure 13** Residual error for *iso*-pentane in ethylene-*iso*-pentane-DGM1820 ternary system.

### Modeling the solubility data with the coabsorption model

The coabsorption model was used to fit the solubility data in ternary systems in Figures 2–9. The model contains the unknown parameters  $\delta$ ,  $m$ , and  $n$ . The parameter  $\delta$ , the fraction of elastically ineffective chains in the polymer, is obtained from the previous study where ethylene, *iso*-pentane, and *n*-hexane were absorbed in polymer respectively.<sup>25</sup> And the parameters  $m$  and  $n$  were fitted by the use of a total of 107 data points from two ternary systems. The results are shown in Table I.

The obtained values of parameters were used to compute the residual error for *iso*-pentane and *n*-hexane, as shown in Figures 13 and 14.



**Figure 14** Residual error for *n*-hexane in ethylene-*n*-hexane-DGM1820 ternary system.

**TABLE II**  
Comparison of Solubility Modeling Methods

Ternary system	Relative root mean square error (%)		
	Coabsorption model	No coabsorption	UNIFAC-M-H
Ethylene- <i>iso</i> -pentane-DGM1820	5.13	6.58	11.36
Ethylene- <i>n</i> -hexane-DGM1820	4.64	7.25	14.19
Total	4.89	6.92	12.78

The UNIFAC correlation of Michaels–Haussein method was used to fit the solubility data, and the results were compared with the earlier. And we compared the results from the coabsorption model with those from the model not to consider the coabsorption behavior. So we show the relative root mean square error of the three solubility modeling methods: coabsorption model, UNIFAC-M-H method, and non-*co*-absorption model for each ternary system in Table II.

### CONCLUSIONS

The coabsorptions of ethylene and *iso*-pentane, and ethylene and *n*-hexane were measured by the use of a pressure decay method. The solubility of ethylene, *iso*-pentane, and *n*-hexane in semicrystalline PE were obtained at the total pressure 2 MPa and temperatures 70, 80, and 90°C. The presence of *iso*-pentane or *n*-hexane in the corresponding ternary system leads to increase the solubility of ethylene, while the solubility of *iso*-pentane or *n*-hexane remains unchanged with an increase of the ethylene partial pressure, even slightly decreases. A coabsorption model was built to model the solubility of each gas in the ternary systems. It was assumed that the presence of *iso*-pentane or *n*-hexane decreases the crystallinity of the polymer sample and advance ethylene to absorb in PE.

We express our appreciation to Qilu Petrochemical Co. for the material donations.

### NOMENCLATURE

$a_i$	the gas activity
$\bar{v}$	the reduced volume (mL)
$v$	the specific volume (mL)
$v^*$	the specific hard-core volume (mL)
$f$	fraction of elastically effective chains in the amorphous region
$w_{\text{cry}}$	the crystallinity of semicrystalline polymer
$T_m$	the melting point of polymer (°C)



$w_{\text{crys},25}$	crystallinity of semicrystalline polymer at 25°C
$P$	probability that a crystallizable unit crystallizes on cooling
$S_A$	solubility of gas in polymer, g/g amPolymer
$m, n$	adjustable parameters
$V_1$	the inner volume of the cell e (mL)
$V_2$	the volume of vapor or gas (mL)

### Greek Symbols

$\phi$	volume fraction of gas in mixture (%)
$\Gamma$	the group activity
$\delta$	fraction of elastically ineffective chains in the whole polymer

### Superscripts

$c$	combinatorial contribution
$fv$	free-volume contribution
$int$	interactional contribution
$el$	elastic contribution

### Subscript

$m$	the mixture
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