

Modeling Solubility of Gases in Semicrystalline Polyethylene

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Received 2 December 2005; accepted 9 June 2006

DOI 10.1002/app.24969

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An absorption model of gases in semicrystalline polymer was built that was based on the activity coefficient theory in polymer solution and associated with crystallinity dependent on temperature. The solubility of ethylene, isopentane, and *n*-hexane in three types of polyethylene (PE) were obtained by the use of a pressure-decay method at temperatures of 333–363 K and pressures of up to 2 MPa, 80–300 KPa, and 19–100 KPa, respectively. Experimental data from three gases in each PE sample were used for the single-parameter fitting, and fitting error was within about 12%. It was found that a single parameter was merely dependent on the properties of PE used. It was shown that, unlike with the Flory–Huggins model and the UNIFAC–M–H method, correlation between the crys-

tallinity of the semicrystalline polymer and temperature had to be taken into account in order for the solubility data of alkane, olefin, and aromatic hydrocarbons in polyethylene to fit well, especially in the temperature range near the melting point of the polymer. The four free-energy contributions to the total gas activity were experimentally determined to be about 47%–60% combined, the free-volume contribution about 12%–25%, and the elastic effect about 22%–35%, but the interactional contribution was zero. The contributions changed with the size of the gas molecules. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1737–1744, 2007

Key words: adsorption; polyethylene (PE); modeling; amorphous; melting point

INTRODUCTION

During the initial stage of gas-phase polymerization, semicrystalline polymer is produced surrounding the catalytic sites.^{1–3} After that, the monomers must be sorbed into the polymer and diffuse through the polymer to reach the catalytic sites. For reasons of quality, safety, and economics, as much as possible of the gases absorbed in the freshly produced polymer particles must be removed. Thus it can be seen that the rate of the polymerization reaction and the design of devolatilization equipment both directly depend on the solubility of gases such as olefins and alkanes in semicrystalline polymer.^{4–6} The present investigation was undertaken to fill the important need for an elaborate model of the solubility of gases in polyolefins in conditions similar to its polymerization and devolatilization.

At temperatures below the melting point of the semicrystalline polymer, there were amorphous and crystalline regions of the sample. It is usually assumed that the crystalline region is not accessible to gas molecules and that absorption occurs only within the amorphous region.^{1–7} Despite the being the solid phase, the amor-

phous parts have a liquidlike structure. When the gases are absorbed in the amorphous regions, a gas–liquid equilibrium theory for polymer solutions can be applied.⁸ At present, three types of approaches are used to model the gas–liquid equilibrium of polymer systems: activity coefficient approaches, equations of state, and molecular simulations.^{9,10} Yoon et al. and McKenna modeled the solubility of alkenes in polyethylene using the Flory–Huggins theory.^{5,11} Kiparissides et al. employed the Sanchez–Lacombe equation of state to correct their experimental solubility of ethylene in polyethylene, whereas Paricaud et al. employed the SAFT–VR approach for the same system.^{6,12} Nath et al. presented Monte Carlo simulations to study the solubility of ethylene, 1-hexene, and methane in polyethylene (modeled as C₇₀).^{10,13,14} Banaszak et al. used the osmotic ensemble hyperparallel tempering method to simulate ethylene and 1-hexene solubility in the amorphous LLDPE phase in order to parameterize the PC-SAFT equation of state.¹⁵

All these models are based on the assumption that crystalline regions cannot affect the solubility of gases in an amorphous polymer. In fact, the absorption characteristics of the amorphous domain of semicrystalline polymers are not the same as those of a totally amorphous polymer.^{8,15} Crystallites present impose a point of junction on the polymer chains in the amorphous domain and behave as a barrier to swelling, as suggested by Flory and Rehner (the F–R theory)¹⁶ and Michaels

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Contract grant sponsor: Chinese National Natural Science Foundation; contract grant number: 20490205.

and Hausslein (the M-H theory).⁷ Therefore, the effect of the crystalline region on absorption in semicrystalline polymers must be taken into account. Doon and Ho fitted the solubility of aromatic hydrocarbons in PE by the UNIFAC-FV group contribution method in conjunction with the M-H theory or the F-R theory.⁸ Banaszak et al. adopted a simple modification of the PC-SAFT equation of state for description of alkene solubility in polyethylene using the M-H theory.¹⁵

Although these studies of the effect of the crystalline region on solubility are important, few models deal with the effect on solubility of changes in the crystallinity of semicrystalline polymers. Under typical gas-phase reactor conditions, the crystallinity of a polymer is not a constant but depends on temperature. Starck et al. and McKenna gained temperature-dependent crystallinity using differential scanning calorimetry and reported that crystallinity is temperature dependent.^{5,17} Paricaud et al. used a semiempirical approach in describing the temperature dependence of crystallinity.¹² However, the effects of constraints imposed by the crystalline region and the change in crystallinity with temperature are not included in one comprehensive model.

The purpose of the present work was to develop a model for interpreting the effects of the crystalline region on absorption in semicrystalline polymers. This model is based on the activity coefficient theory and is associated with the crystallinity dependent on temperature. The model contains only one adjustable parameter, which is characteristic of each individual polymer and independent of temperature and gases. As long as this single parameter is determined, this model can be used to predict the solubility of other gases over a wide range of concentrations and temperatures, especially the range near the melting point. The solubility of three gases in three types of semicrystalline polyethylene were obtained by a pressure decay method.

Model Details

Because gases only absorb in amorphous regions, the solubility of absorbed per unit mass of amorphous polymer differs from that of per unit mass of total polymer, and the relationship between them is:

$$S_{\text{am}} = S/(1 - w_{\text{crys}}) \quad (1)$$

where w_{crys} is the degree of crystallinity of polymer. Solubility hereinafter is expressed as the weight ratio, S_{am} (g of gas/g of amorphous polymer).

For the amorphous liquid phase, the activity of the gas, a_1 , can be calculated from the following expressions⁸:

$$\ln a_1 = \underbrace{\ln a_1^c}_{\text{combinatorial}} + \underbrace{\ln a_1^{fv}}_{\text{free-volume}} + \underbrace{\ln a_1^{\text{int}}}_{\text{interactional}} + \underbrace{\ln a_1^{\text{el}}}_{\text{elastic}} \quad (2)$$

The contributions of free energy in a gas-polymer system come from combinatorial, free-volume, interactional, and elastic factors, which are discussed below.

The combinatorial factor can be obtained from the Flory-Huggins lattice theory¹⁸:

$$\ln a_1^c = \ln \phi_1 + (1 - \phi_1) \quad (3)$$

When gases are absorbed in an amorphous polymer, the free volume of the solute increases and that of the macromolecules decreases at the same time. Assuming volumes are additive, the Flory equation of state can be used to express the free-volume factor¹⁹:

$$\ln a_1^{fv} = 3c \ln \left(\frac{\bar{v}_1^{-1/3} - 1}{\bar{v}_{\text{mix}}^{-1/3} - 1} \right) - c \left(\frac{\bar{v}_1}{\bar{v}_{\text{mix}}} - 1 \right) \left(1 - \frac{1}{\bar{v}_1^{-1/3}} \right)^{-1} \quad (4)$$

where \bar{v} is the reduced volume, which is the ratio of the specific volumes, v , to the specific hard-core volumes, v^* ; subscript 1 and subscript mix denote the gas and the gas-polymer mixture, respectively; and $3c$ is the number of external degrees of freedom per gas molecule.

According to the UNIFAC group contribution method, a gas-polymer mixture system is considered a solution of functional groups rather than a solution of molecules. So the interactional factor is¹⁹:

$$\ln a_1^{\text{int}} = \sum_k v_k^1 (\ln \Gamma_k - \ln \Gamma_k^1) \quad (5)$$

where v_k^1 is the number of groups k in gas molecule 1, Γ_k is the interaction activity of group k in the gas-polymer mixture, and Γ_k^1 is the interaction activity of group k in the pure gas component. The interaction activity of group k can be calculated from the UNIFAC equation.

Michaels and Hausslein proposed a theory that segment tension crystallization driving force competition is an equilibrium phenomenon.⁷ Designating the elastically effective mass fraction of the amorphous polymer as f and the elastically ineffective portion of the total polymer as δ , the relationship between f and δ is given by:

$$f = 1 - \frac{\delta}{1 - w_{\text{crys}}} \quad (6)$$

On the basis of this assumption, the amount of elastically ineffective amorphous polymer is constant with temperature, that is, δ is a constant. However

many researchers have reported that the crystallinity of polymers is temperature dependent.^{5,17} Parameter f should be variable according to eq. (6) because of this crystallinity. Thus, elastically effective segments have two parts: inherent polymers and premelted polymers. Parameter f is the temperature function, and parameter δ is characteristic of each semicrystalline polymer and independent of temperature and of gas concentration and type.

Paricaud et al. developed a predictive approach for the melting point and crystallinity of an arbitrary polyethylene sample that simply requires experimental data, namely, the crystallinity, $w_{\text{crys},25}$, or density, ρ_{25} , of a PE sample (measured at 298 K and 1 atm).¹²

Because of the assumption that the PE sample is a copolymer, the type of polymer formed from Ziegler–Natta (ZN) catalysts differs from that formed from metallocenes (Me). So experimental data shows correlation of the melting point of the two main types of catalyst (ZN and Me) used in polymerization reactors. The melting point, T_m , of PE can be described in terms of the following functions of $w_{\text{crys},25}$ ¹²:

$$T_m(\text{ZN})/^\circ\text{C} = 13.689w_{\text{crys},25}^2 + 5.015w_{\text{crys},25} + 124.33 \quad (7)$$

$$T_m(\text{Me})/^\circ\text{C} = -81.498w_{\text{crys},25}^2 + 163.3w_{\text{crys},25} + 63.415 \quad (8)$$

Following Flory's theory for the prediction of the temperature dependence of the crystallinity of a polymer, Paricaud et al. proposed a model polymer that is a copolymer containing both crystallizable and non-crystallizable units. The crystallinity, w_{crys} , of a polymer is dependent on the fraction of crystallized polymer units and the probability, p , that a given crystallizable unit is followed by another one along within adjacent chains in three dimensions. This means p is able to characterize the cooling rate indirectly. A

parameterization of p in terms of $w_{\text{crys},25}$ can also be given by¹²:

$$p(\text{ZN}) = -0.0581w_{\text{crys},25}^2 + 0.1279w_{\text{crys},25} + 0.9303 \quad (9)$$

$$p(\text{Me}) = -0.0538w_{\text{crys},25}^2 + 0.1397w_{\text{crys},25} + 0.9142 \quad (10)$$

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_{crys} , satisfies¹²:

$$w_{\text{crys}}(T) = \frac{w_{\text{crys},25} p^{\xi_{\text{crit}}} \left[\frac{p}{(1-p)^2} - \frac{e^{-\beta}}{(1-e^{-\beta})^2} + \xi_{\text{crit}} \left(\frac{1}{1-p} - \frac{1}{1-e^{-\beta}} \right) \right]}{p^{\xi_{\text{crit},25}} \left[\frac{p}{(1-p)^2} - \frac{e^{-\beta_{25}}}{(1-e^{-\beta_{25}})^2} + \xi_{\text{crit},25} \left(\frac{1}{1-p} - \frac{1}{1-e^{-\beta_{25}}} \right) \right]} \quad (11)$$

where

$$\beta = \frac{\Delta H_u}{R} \left(\frac{1}{T} - \frac{1}{T_m^0} \right) \quad (12)$$

ξ , is the number of consecutive crystallizable A units and ξ_{crit} is the critical length under which the blocks do not crystallize and¹²

$$\xi_{\text{crit}} = \frac{\ln D + 2 \ln((1-p)/(1-e^{-\beta}))}{\frac{\Delta H_u}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right)} \quad (13)$$

where β_{25} and $\xi_{\text{crit},25}$ are obtained from eqs. (12) and (13), respectively, at $T = 298$ K.

To sum up, our model contains only one adjustable parameter, δ , based on the activity coefficient theory and associated with the crystallinity dependent on temperature.

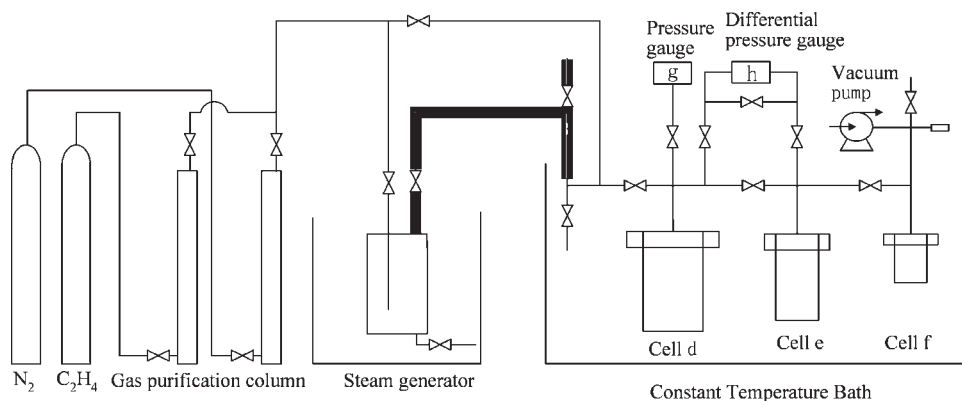


Figure 1 Schematic diagram of absorption apparatus.

TABLE I
Properties of PE Sample

Sample trademark	Melt index (g/10 min)	Density (g/mL)	Crystallinity (%)	Melting temperature (K)
MLLDPE		0.880	20.4	383.85
DGM1820	1.9	0.920	48.6	397.05
DMD1155	0.04	0.953	72.0	409.35

EXPERIMENTAL

Apparatus

Figure 1 shows the schematic diagram of the pressure-decay apparatus. There are three main parts: for the gas inlet, for vapor generation, and for solubility measurement.

Polyethylene powder was placed in cell f, and the apparatus was evacuated. A valve between cell e and cell f was closed, and then gas or vapor was introduced into cells d and e. Pressure was P_1 at the equilibrium system. A valve between cells d and e was closed, and the valve between cells e and f was opened to get the gas to meet the PE powder. The pressure decay, ΔP , resulting from gas dissolution and volume expansion was measured with a differential pressure gauge. The temperature of the cell was controlled to within 1 K of the water bath. Following the ideal gas equation of state, the amount of gas dissolved in the polyethylene was determined using the following equation:

$$n_p = \frac{P_1 V_1}{RT} - \frac{(P_1 - \Delta P) V_2}{RT} \quad (14)$$

where V_1 is the inner volume of cell e and V_2 is the sum of the inner volumes of cells e and f subtracted from the volume of the polymer.

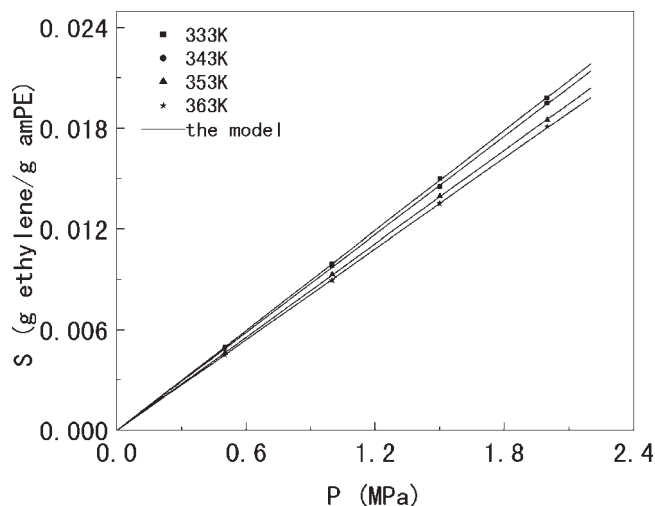


Figure 2 Solubility of ethylene in DGM1820.

Materials

Polyethylene powder with a particle diameter of 0.5–0.6 mm, obtained from Qilu Petrochemical Co. (Zibo, China), was used in this study. The powder was dried and then protected by pure N_2 gas. The properties of the three polyethylene samples are listed in Table I.

The average degree of crystallinity was determined by differential scanning calorimetry (DSC) and X-ray diffraction. The experiments were performed at temperatures of 333, 343, 353, and 363 K for ethylene and isopentane and at temperatures of 343, 353, 358, and 363 K for *n*-hexane. These temperatures were chosen because they are in the range typically used in gas-phase polymerization processes and in devolatilization equipment.

The experiments were conducted at pressures of up to 2 MPa, 19–100 KPa, and 80–300 KPa for ethylene, *n*-hexane, and isopentane, respectively.

RESULTS AND DISCUSSION

Solubility of gases in polyethylene

The solubility results for the three gases in the three types of polyethylene at different temperatures and with a wide range of pressures are shown in Figures 2–5. Solubility decreased with increasing tem-

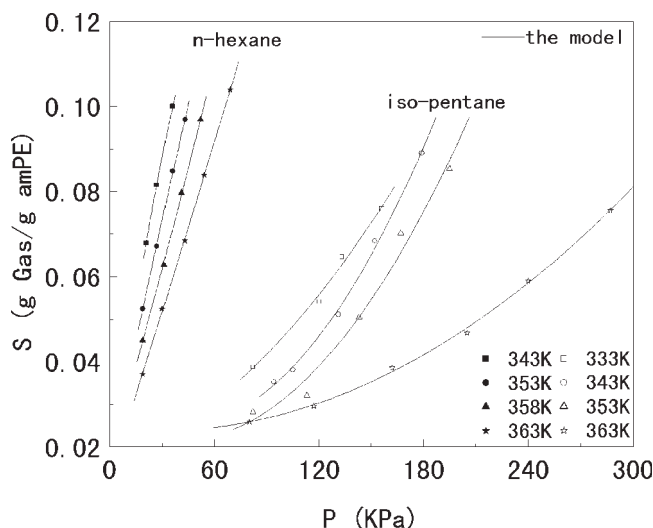


Figure 3 Solubility of isopentane and *n*-hexane in MLLDPE.

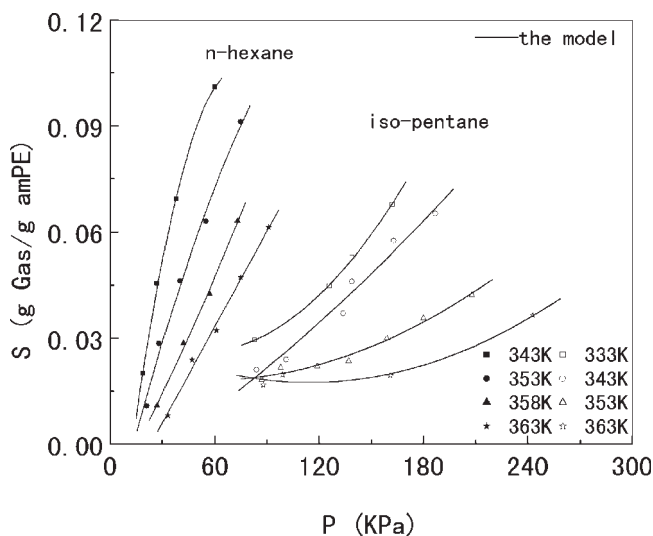


Figure 4 Solubility of isopentane and *n*-hexane in DGM1820.

perature with pressure held constant and increased with increasing pressure.

The above solubility data are expressed in terms of grams of gas per gram of amorphous polyethylene (amPE). The solubility of ethylene in DGM1820 was shown to be proportional to the pressure at each temperature shown in Figure 2. The solubility of ethylene in the other two PE samples was also linear with pressure. Hence, Henry's law could be applicable for ethylene absorption in the three PE samples, and the coefficient values (k) for Henry's law are shown in Table II.

Henry's law is simple and fits the solubility of ethylene in polyethylene well. And the Henry's law coefficient is dependent on both the temperature and property of a polymer sample. Furthermore, Henry's

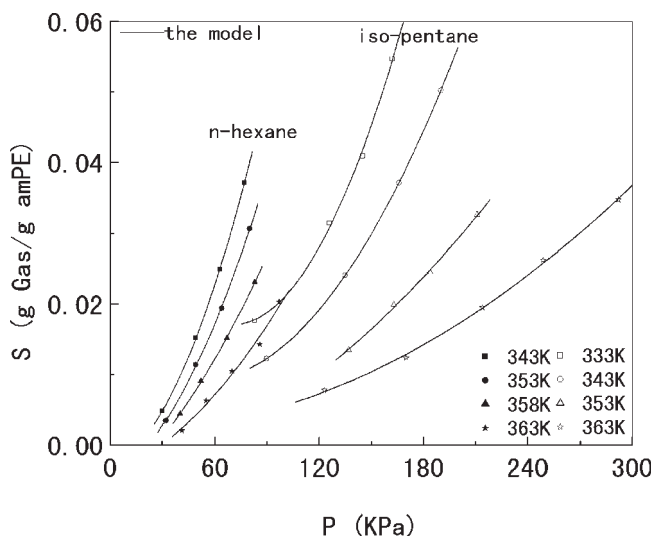


Figure 5 Solubility of isopentane and *n*-hexane in DMD1155.

TABLE II
Henry's Law Coefficients for Ethylene in PE

Temperature (K)	Henry's law coefficient, k (g C ₂ H ₄ g ⁻¹ amPE MPa ⁻¹)		
	MLLDPE	DGM1820	DMD1155
333	0.0113	0.00995	0.00483
343	0.0109	0.00960	0.00420
353	0.0105	0.00925	0.00406
363	0.0104	0.00897	0.00385

law cannot be applied to heavier hydrocarbon vapors, so the model is limited.¹¹

Our model was used to fit the solubility data shown in Figures 2–5. The model contains only one parameter, δ , the fraction of elastically ineffective chains in the semicrystalline polyethylene. All the experimental data from three gases at four temperatures in every polyethylene sample were used in the single parameter fitting. Then the value of δ was used to calculate the relative root mean square error for each gas, as shown in Table III.

As shown in Table III, our model fitted the experimental data within a 12% error. This demonstrated that parameter δ is a property of the semicrystalline polyethylene sample and independent of temperature and gas. The results are also shown in Figures 2–5 for ethylene, isopentane, and *n*-hexane in three polyethylene samples.

Comparison of Flory–Huggins model and UNIFAC–M–H method

The solubility data were first correlated with the classical Flory–Huggins equation¹⁷:

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + \chi(1 - \phi_1)^2 \quad (15)$$

The values obtained for the Flory–Huggins parameter, χ , are listed in Table IV.

It was shown that for all but one or two gas–polyethylene systems at a specific temperature, the Flory–Huggins equation with parameter χ could fit the data within a 7% error. The parameters were independent of concentration but dependent on temperature and varied with gas. In fact, the Flory–Huggins equation

TABLE III
Modeling of Solubility Data for Parameter δ

Solubility data	Error (%)		
	MLLDPE ($\delta = 0.543$)	DGM1820 ($\delta = 0.230$)	DMD1155 ($\delta = 0.0879$)
All	9.6	8.0	7.5
Ethylene	5.9	6.5	3.0
Isopentane	12.1	9.3	10.6
<i>n</i> -Hexane	8.7	11.2	5.7

TABLE IV
Modeling of Solubility Data for Parameter χ
by Flory–Huggins Model

PE	Gas	χ		
		343 K	353 K	363 K
MLLDPE	Ethylene	-0.209	-0.327	-0.418
	Isopentane	0.793	0.611	0.818
	<i>n</i> -Hexane	-0.208	-0.434	-0.218
DGM1820	Ethylene	-0.112	-0.198	-0.287
	Isopentane	1.07	1.22	1.18
	<i>n</i> -Hexane	0.415	0.476	0.815
DMD1155	Ethylene	0.732	0.621	0.574
	Isopentane	1.38	1.55	1.69
	<i>n</i> -Hexane	1.87	1.63	1.95

attributed the various effects to the single parameter χ . So it could not specifically account for the influence of the gases and temperatures on the absorption of gases in the polymer. A more elaborate theory was needed.

Unlike the Flory–Huggins equation, the UNIFAC-FV modeling method and the Michaels–Haussein (UNIFAC–M–H) method of Doong and Ho takes into account the free energy contributions of the gas and semicrystalline polymer system from combinatorial, free-volume, interactional, and elastic factors. These four contributions are calculated in the Model Details section.⁸ The UNIFAC–M–H method contains an unknown parameter, f , which is the fraction of elastically effective chains in the amorphous phase. As shown in Figure 6, the UNIFAC–M–H method was used to fit the solubility of isopentane in DGM1820 at different temperatures and did not fit the data too well.

Because of the assumption of a constant value for parameter f , the UNIFAC–M–H method is only applicable in a temperature range far below the melting point of the polymer. In this temperature range, the crystallinity of the polymer is a weak function of temperature

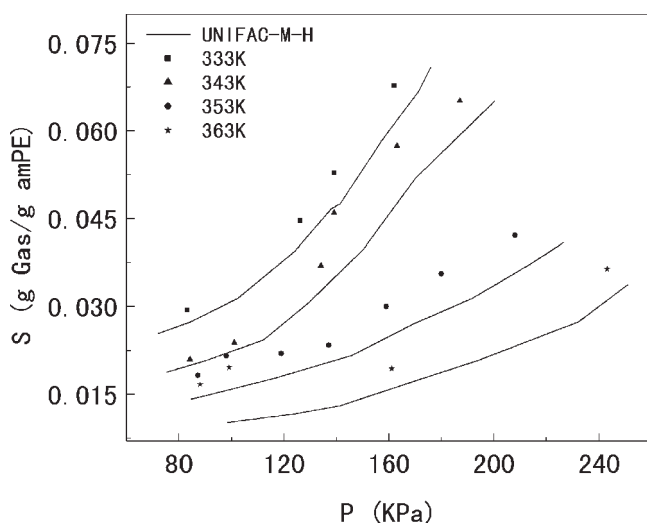


Figure 6 Solubility of isopentane in DGM1820 as fitted by UNIFAC–M–H method.

TABLE V
Modeling of Solubility Data for Parameter f by
UNIFAC–M–H Method

Solubility data	MLLDPE		DGM1820		DMD1155	
	f	Error (%)	f	Error (%)	f	Error (%)
Ethylene	0.533	15.56	0.553	5.94	0.739	12.6
Isopentane	0.229	22.7	0.230	12.9	0.424	30.0
<i>n</i> -Hexane	0.174	17.0	0.136	20.0	0.684	28.3
All	0.0913	29.8	0.237	19.8	0.611	17.4

and the change in crystallinity with increasing temperature can be neglected. However, the temperature range in the present work was near the melting point of the polymer sample, and crystallinity was obviously changed. The inability to apply the UNIFAC–M–H method was not a result of the dependence of crystallinity on temperatures. Table V shows the results using the UNIFAC–M–H method to correlate the experimental data for each gas. The f parameter was not a constant, only dependent of the polyethylene sample. To further test our model, the solubility data reported by Doong et al. for benzene and toluene in polyethylene with 45% crystallinity at temperatures from 303 to 333 K were modeled by our model and the UNIFAC–M–H method.⁸ The results are presented in Table VI.

It is obvious that a single value of parameter δ in our model or parameter f in the UNIFAC–M–H method fitted all the data quite well. This is because in the temperature range of 303–333 K, the crystallinity of the polyethylene sample did not change more than 10% and constant values of both f and δ were justified. And the magnitude of the relation between parameter δ and parameter f also established the credibility of parameter δ fitting.

Table VII lists the parameter δ data for 1-butene and 1-hexene in the series of polyethylene samples measured by Moore et al.⁴ It can be seen that our model fit well the solubility of alkanes, olefins, and aromatic series in polyethylene in a temperature range near the melting point of the polymer.

Effects of gas size on solubility

From the analysis of our theoretical model, attention should be paid to the effect of gas size on solubility.

TABLE VI
Comparison of Solubility Modeling Methods

Solubility data	Error (%)	
	Our model ($\delta = 0.433$)	UNIFAC–M–H ($f = 0.373$)
Benzene	7.51	6.74
Toluene	6.43	5.54
All	7.02	7.96

TABLE VII
Modeling of Solubility Data of Olefins in PE by Our Model

Solubility data	Error (%)			
	HDPE ($\delta = 0.210$)	LDPE ($\delta = 0.497$)	LLDPE-ZN ($\delta = 0.438$)	LDPE-Me ($\delta = 0.712$)
1-Butene	7.63	5.05	7.2	8.89
1-Hexene	4.86	9.30	10.5	6.78
All	6.24	7.25	8.69	7.07

Figures 2–5 show that the solubility of ethylene was linear in PE and nonlinear in isopentane and *n*-hexane, with the latter much greater than the former. The maximum ethylene solubility was only two-fifths of the *n*-hexane solubility when the ratio of ethylene pressure to *n*-hexane pressure was 55. It should be noted that the solubility of all gases decreased with increasing temperature.

Figure 7 depicts the four free-energy contributions to absorption of ethylene in DGM1820 at 333 K in terms of $\ln a$ with respect to the volume fraction, ϕ_1 .

As shown in Figure 7, the combinatorial contribution accounted for about 47%–60% of the total ethylene activity, the free-volume contribution about 12%–25%, and the elastic effect about 22%–35%. It was apparent that the interactional contribution was zero, which was also true for isopentane and *n*-hexane activity. This was because the groups of these gases in a pure component were coincident with those in the corresponding gas–polymer system.

Figure 8 shows the various contributions to gas activity in DGM1820 of the volume fraction, $\phi = 0.065$, at 343 K.

According to eq. (3), the combinatorial contribution should be the same for the same gas volume

fraction. With the gas molecule size increasing, the free volume of the gas molecule decreased and closed the free volume of polyethylene, thus the free-volume contribution decreases. And the elastic contribution increased with increasing gas molecule size.

CONCLUSIONS

The solubility of ethylene, isopentane, and *n*-hexane in three types of polyethylene was obtained by a pressure-decay method in the temperature range of 333–363 K. Solubility decreased with increasing temperature at a given pressure. An absorption model was built with the UNIFAC group contribution method in conjunction with the theory that crystallinity is dependent on temperature. The model had only one adjustable parameter, δ . The relationship of the crystallinity of the polymer with temperature was very critical. The experimental data could be fitted quite well using our model.

Compared with the Flory–Huggins model and the UNIFAC–M–H method, our model was shown to fit the solubility data of alkanes, olefins, and aromatic hydrocarbons in polyethylene well, especially in the temperature range near the melting point of the

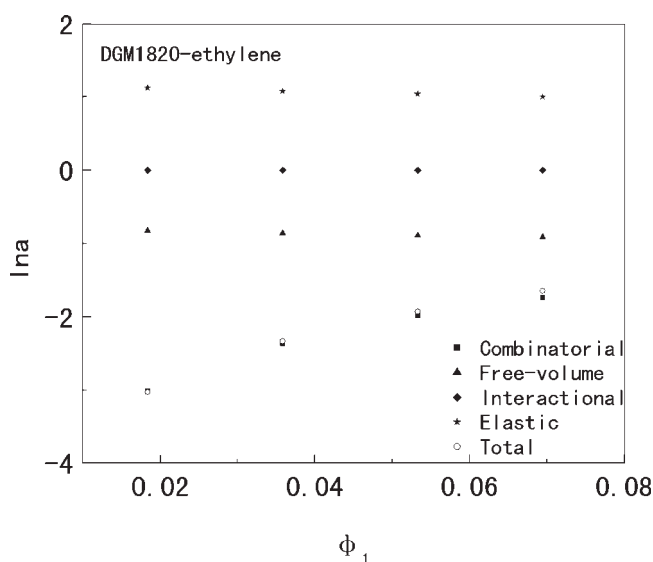


Figure 7 Various contributions to ethylene activity in DGM1820 at 333 K.

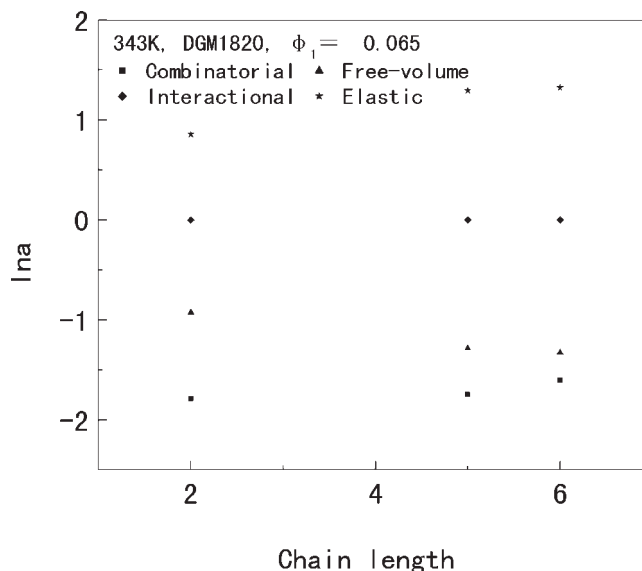


Figure 8 Various contributions to gas activity in DGM1820 at 343 K.

polymer sample. According to the four free-energy contributions to the gas activity, the effect of gas molecule size on absorption was analyzed.

We appreciate the material donations from the Qilu Petrochemical Co.

NOMENCLATURE

a_1	gas activity
a_1^c	gas activity from combinatorial contribution
a_1^{fv}	gas activity from free-volume contribution
a_1^{int}	gas activity from interactional contribution
a_1^{el}	gas activity from elastic contribution
f	fraction of elastically effective chains in amorphous region
p	probability that a crystallizable unit crystallizes on cooling
S	solubility of gas in polymer (g/g polymer)
S_{am}	solubility of gas in amorphous polymer (g/g amPE)
w_{crys}	crystallinity of semicrystalline polymer
$w_{crys,25}$	crystallinity of semicrystalline polymer at 298 K
δ	fraction of elastically ineffective chains in the whole polymer
ϕ	volume fraction of gas in mixture (%)
χ	Huggins interaction parameter
subscript 1	gas
subscript 2	polymer

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