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Determination of Flory interaction parameters between polyimide and organic solvents by HSP theory and IGC

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Summary

Flory-Huggins interaction parameter χ_{12} is an important parameter used for characterizing the interaction intensity between polymer and solvent. In this work, two methods were used to calculate the χ_{12} values of a polyimide (HQDPA-DMMDA) and twelve organic solvents. One method was inverse gas chromatography (IGC) technique, another was Hansen Solubility Parameters (HSP) theory. For the IGC experiment, χ_{12} was measured with an extrapolation method for the carrier gas when the temperature was changed from 50°C to 80°C. For the HSP approach, the Beerbower group contribution method was used to calculate the HSP values of the polyimide. It was found that the χ_{12} values of the polyimide and the organic solvents calculated from the two methods were similar. Consequently, the Beerbower group contribution method can be used to calculate HSP, and the HSP can be used to rapidly estimate the Flory–Huggins interaction parameter χ_{12}.

Introduction

Polymer solution thermodynamics was firstly developed by Flory and Huggins which was used to describe the interaction intensity between polymer and solvent through a dimensionless parameter χ_{12} [1, 2]. This parameter is frequently used to predict the thermodynamic state of a polymer mixing with solvent or additive, blending with other polymer, swelled with liquid, and in many other applications where the interaction between the polymer and other components plays a significant role [3]. Miscibility occurs when χ_{12} is lower than a critical value, or lower than zero. χ_{12} is usually determined by vapor pressure lowering, osmotic pressure effect, equilibrium swelling of polymer by liquid, light scattering and inverse gas chromatography (IGC) etc. [2]. In these methods, IGC has been demonstrated as an effective tool for measuring the parameter [4–9]. Generally speaking, these methods are time-consuming. Consequently, for a polymer material, especially for a new synthetic polymer, it requires a simple and rapid method to theoretically calculate χ_{12}.

The purpose of this work is to using the Beerbower group contribution method to calculate Hansen solubility parameters (HSP) and investigating the capability of HSP for theoretically estimating χ_{12} through comparing with the result of IGC experiment.

Relation between χ_{12} parameter and Hansen Solubility Parameters

The solubility parameter was first introduced by Hildebrand and Scott in 1950 [10]. The Hildebrand solubility parameter was defined as the square root of cohesive energy density. However, Hildebrand solubility parameter was only fit for non-polar polymers and non-polar solvents. In fact, the solubility parameter theory was true not only for non-polar systems, but also for the polymer systems including permanent dipole-permanent dipole and hydrogen bonding interactions. Consequently, Charles M. Hansen extended the Hildebrand solubility parameter theory to the concept called Hansen Solubility Parameters (HSP) in 1967 [11, 12]. In the HSP theory, the total energy of vaporization is divided into three separate parts as shown in Eq (1). These parts come from the non-polar/dispersion force, E_D, the permanent dipole-permanent dipole force, E_P, and hydrogen bonding force, E_H [10–12].

$$E = E_D + E_P + E_H \tag{1}$$

Dividing E by molar volume, V, gives the respective Hansen cohesion energy parameters as in Eq (2) and Eq (3).

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \tag{2}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{3}$$

where δ is the total solubility parameter, and equals to $(E/V)^{\frac{1}{2}}$. δ_D, δ_P and δ_H are the HSP for dispersion, polar, and hydrogen bonding interactions, respectively.
Since χ_{12} can be simply used in the connection with polymer solution behavior, it would be desirable to relate χ_{12} directly with the widely used HSP for known system [11, 13]. A customary equation for calculating χ_{12} from Hildebrand solubility parameter for a non-polar solvent and a non-polar polymer is [11]:

$$\chi_{12} = \frac{\left[V(\delta_1 - \delta_2)^2\right]}{RT} + \beta \tag{4}$$

where V is the molar volume of the solvent, δ is the Hildebrand solubility parameter of the solvent (1) and polymer (2), R is the gas constant, and T is the absolute temperature, β is an empirical constant. For a polar system, calculating χ_{12} is to replacing the difference of Hildebrand solubility parameters in Eq. (4) by a corresponding HSP term, i.e., $A_{1,2}$ [11]:

$$A_{1,2} = \left[(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2\right] \tag{5}$$

χ_{12} is estimated from the following equation:

$$\chi_{12} = \frac{VA_{1,2}}{RT} \tag{6}$$

Calculating HSP by Beerbower group contribution method

Since HSP are not available for all solvents and polymers, researching a method to predict unknown HSP values of polymers is very significant. Several useful prediction methods based on molecular structures have been proposed by Van Krevelen and Hoftyzer (1976), Hoy (1985), and Beerbower (1984) [14]. In this work, the Beerbower method for calculating HSP through group contribution was applied. The equation used for this calculation is [11, 14–16]:

$$\delta_X = \left[\frac{\sum \Delta V \delta_X^2}{\sum \Delta V}\right]^{\frac{1}{2}} \qquad \textbf{(7)}$$

where ΔV is molar volume. X can be replace by D, P, H and T, representing London parameter, polar parameter, electronic transfer parameter and total parameter, respectively.

Method of determining χ_{12} by IGC

Inverse Gas Chromatography (IGC) is an extension of the conventional gas chromatography (GC). The main difference between GC and IGC is that the interested species is the polymer material acting as stationary phase in IGC column. Probe solvent with known property is injected in the column and the retention time of the probe is measured at infinite dilution. The interaction between the probe solvent and the polymer is calculated from the retention time. The principle of determining χ_{12} by IGC is as follows [2, 4–9]:

$$\chi_{12}^{\infty} = \ln\left[\frac{273.2 R \upsilon_2}{V_g^0 V_1 P_1^0}\right] - \frac{P_1^0 \left(B_{11} - V_1\right)}{RT} - 1 \qquad \textbf{(8)}$$

where R is the gas constant, P_1^0 is saturated vapor pressure of the probe solvent at the column temperature, V_1 is the molar volume of probe solvent, υ_2 is the specific volume of the polymer, $V_g{}^0$ is the specific retention volume, T is the column temperature, and B_{11} is the second virial coefficient of the probe solvent which is calculated by Eq. (9) [2, 4–9]:

$$\frac{B_{11}}{V_C} = 0.430 - 0.886\frac{T_C}{T} - 0.694\left(\frac{T_C}{T}\right)^2 - 0.0375(n-1)\left(\frac{T_C}{T}\right)^{4.5} \qquad \textbf{(9)}$$

where n is the carbon atom number of the probe solvent, T_C is the critical temperature of the probe solvent, and V_C is critical volume of the probe solvent.

Soluble polyimide (HQDPA-DMMDA)

Polyimides are a series of high performance materials developed in the last several decades. Generally speaking, they have many unique properties, such as high thermal stability, low dielectric constants, good insulation characteristic, long-term stability and high permeation for gas [17]. Consequently, polyimides have been widely used in aerospace and aircraft, automobile, microelectronics and optoelectronics, gas-separation membranes [18], capacitance humidity sensors [19] and photoacid generator [20]. Although hundreds of polyimides with different structures have been synthesized, the number of soluble polyimides is small. Compared with insoluble polyimides, soluble polyimides can be easily processed by solvent dissolving method, so they are paid more attentions. HQDPA-DMMDA is a kind of soluble polyimide synthithzed in 1990s. It is an excellent polymer membrane material used widely to the dehumidification of compressed air, ethanol dehydration, separation of methanol/MTBE and concentration of benzylpenicillin sodium etc. [21–23]. In this work, we choose it to research the methods described early.

Experimental

Materials

HQDPA-DMMDA was purchased from Changchun Institute of Applied Chemistry, China. Figure 1 shows the chemical structure of HQDPA-DMMDA. It is soluble in *N*, *N*-dimethylformamide, chloroform, *N*-methylpyrrolidone, dichloromethane and *N*, *N*-dimethylacetamide. The weight average molar mass (M_w) was 0.5×10^5 to 3.5×10^5, and molar mass distribution (M_w/M_n) was 1.7–1.9. Its density was 1.296 g/cm^3 and T_g was 233°C [24]. Chromosorb 101 (80–100 mesh) was purchased from Shanghai Chemical Plant, China. Pentane was used as the non-interacting probe for calculating the net retention time of other probe solvents in this experiment because the absolute retention time of pentane was the shortest. Ethanol, propanol, isopropanol, butanol, pentanol, hexanol, benzene, cyclohexane, toluene, ether, carbon tetrachloride and tethyl acetate were used as probe solvents. They were analytical grade solvents, purchased from Tianjin Kermel Chemical Reagents Development Centre, China. Some parameters of the solvents are listed in Table 1.

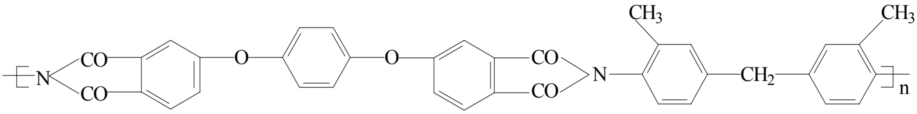

Figure 1. Chemical structure of HQDPA-DMMDA

IGC instrument and procedures

The instrument was a GC–900A gas chromatograph equipped with a flame ionization detection (FID) system, which was purchased from Shanghai TianPu Analytical Instrument Ltd., China. Nitrogen was used as the carrier gas. The probe solvents were injected manually, using a 1.0 µL Hamilton syringe. The injection volumes were 0.1 µL. The column was a stainless steel tube (0.5m length, 2.56 mm i.d.). It was washed with acetone prior to use. The stationary phase of HQDPA-DMMDA was prepared as follows: 0.2159g HQDPA-DMMDA was dissolved by NMP at ambient temperature, then 1.6941g Chromosorb was added to this solution and stirred. The solvent was removed by continuous stirring and heating. After evaporating the solvent, the prepared stationary phase was packed into the column. The column was conditioned at 90°C and fast carrier gas flow rate for twelve hours prior to measuring. For the IGC measurements, the injector and FID were heated to 130°C. The temperatures of oven were 50, 60, 70, and 80°C. Generally speaking, the column temperature for measuring χ_{12} should be higher than the glass transition temperature of the polymer since bulk sorption retention is needed. However, for some high performance polymers (such as polysulfones), bulk sorption can appear at the glassy state [25] because high performance polymers generally have large free volumes. In addition, bulk sorption retention can be achieved through an extrapolation by changing the flow rate of the carrier gas as described in Ref. [6]. In this IGC experiment, the extrapolation method was adopted although HQDPA-DMMDA was a high performance polymer with large free volume. Three flow rates: 3.8, 8.8 and 15.2 ml/min were used to extrapolate to zero flow rate to obtain the bulk retention volumes. The flow rates were measured from the end of the column with a soap bubble flow meter.

Table 1. Parameters of probe solvents

Name	Molecule weight	T_C (K)	V_C (cm^3/mol)
Ethanol	46.07	516.25	163
Propanol	60.69	509.65	218
Isopropanol	60.69	535.55	220
Butanol	74.12	562.95	274
Pentanol	88.15	586.15	326
Hexanol	102.17	610.15	381
Benzene	78.11	562.35	259
Cyclohexane	84.16	553.40	308
Toluene	92.13	591.85	316
Ether	74.12	466.75	280
Carbon tetrachloride	153.84	561.40	276
Ethyl acetate	88.1	523.25	286

Results and discussion

Table 2 lists the specific retention volume V_g^0 of ethanol for different carrier gas flow rates, which were used to extrapolate the values of zero flow rate as shown in Figure 2. For the other solvents, the same method was applied. Then, χ_{12} of HQDPA-DMMDA and the probe solvents were calculated by using Eq (8).

Table 2. The specific retention volume V_g^0 of ethanol (ml/g)

Temperature (ºC)	50	60	70	80
3.8 (ml/min)	45.31	30.78	21.73	14.95
8.8 (ml/min)	31.87	23.51	18.04	12.69
15.2 (ml/min)	10.68	8.38	7.24	6.58
0 (ml/min)	53.69	33.63	21.70	15.19

Table 3 lists the parameters for the HSP calculation of HQDPA-DMMDA and the results calculated by Eq (7). The HSP of HQDPA-DMMDA and some other polymers are summarized in Table 4.

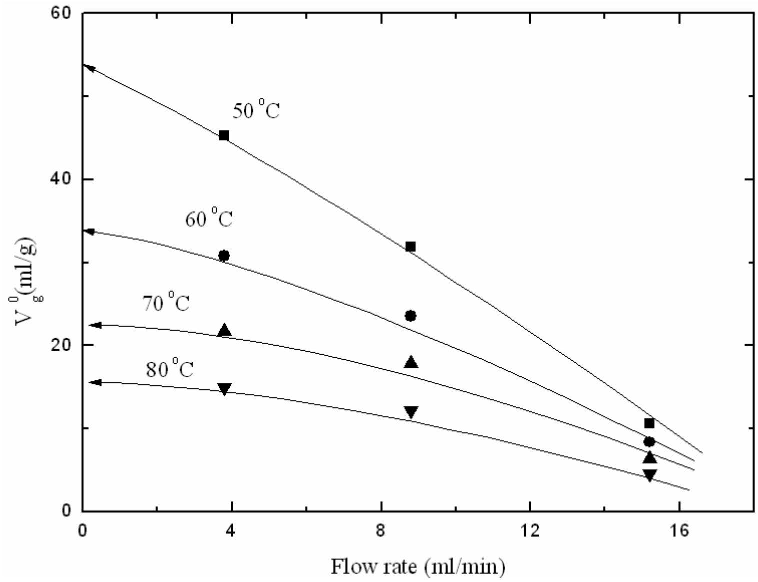

Figure 2. V_g^0 of ethanol at different temperatures

Table 3. HSP calculation for HQDPA-DMMDA using the Beerbower method [11, 14–15]

Structural Groups	No. groups (N)	N* Δ V (cm^3/mol)	N* Δ V δ_D^2 (J/mol)	N* Δ V δ_P^2 (J/mol)	N* Δ V δ_H^2 (J/mol)	N* Δ V δ_T^2 (J/mol)
$-CH_3$	2	67	9414	0	0	9414
$=CH-$	16	216	58576.0	1205.0	12050.0	71831.0
$=C<$	14	-77	46860.8	3514.6	10543.7	60919.1
$>C=O$	4	43.2	39329.6	16736.0	1388.0	57454.4
$>CH_2$	1	16.1	4937.1	0	0	4937.1
$>N-$	3	13.5	14434.8	1255.2	9419.0	25104.0
$-O-$	2	7.6	0	3765.6	10041.6	13807.2
SUM		286.4	173552.3	26476.4	43438.1	243466.8
			δ_D (MPa)$^{1/2}$	δ_H (MPa)$^{1/2}$	δ_H (MPa)$^{1/2}$	δ_T (MPa)$^{1/2}$
		HSP	24.6	9.6	12.3	29.2

Table 4. The HSP of HQDPA-DMMDA and some other polymers (MPa$^{1/2}$)

Polymer	Dispersion δ_D	Polarity δ_P	Hydrogen Bonding δ_H	Total δ_T	Reference
HQDPA-DMMDA	24.6	9.6	12.3	29.2	this work
Polycarbonate	18.6	8.4	6.0	21.3	[11, 14]
Poly(amide 6,6)	17.2	9.9	16.5	25.8	[11, 14]
Poly(ether imide)	17.3	5.4	6.3	19.2	[11, 14]
Poly(ether sulfone)	18.7	10.3	7.7	22.7	[11, 14]
Poly(methyl methacrylate)	17.9	9.7	5.5	21.1	[11, 14]

Compared with other polymers, HQDPA-DMMDA has stronger dispersion force and hydrogen bonding force, so the value of δ_T is quite large. Table 5 lists the HSP of the probe solvents. It is interesting that the HSP of polymers (such as in Table 4) are generally higher than the HSP of these organic solvents [11].

Table 5. HSP of organic solvents [11]

Name	Dispersion δ_D (MPa)$^{1/2}$	Polarity δ_P (MPa)$^{1/2}$	Hydrogen Bonding δ_H (MPa)$^{1/2}$
Ethanol	15.8	8.8	19.4
Propanol	16.0	6.8	17.4
Isopropanol	15.8	6.1	16.4
Butanol	16.0	5.7	15.8
Pentanol	15.9	5.9	13.9
Hexanol	15.9	5.8	12.5
Benzene	18.4	0	2.0
Cyclohexane	16.8	0	0.2
Toluene	18.0	1.4	2.0
Ether	15.2	6.1	5.7
Carbon tetrachloride	16.1	8.3	0
Ethyl acetate	15.8	5.3	7.2

The calculated χ_{12} values from Hansen Solubility Parameters (listed in Tables 3 and 5) by using Eq (5) and (6), and the measured χ_{12} values by IGC are listed in Table 6. The χ_{12} between HQDPA-DMMDA and organic solvents are bigger than the χ_{12} between other polymers and organic solvents. It means that HQDPA-DMMDA and organic solvents have weak interactions, so HQDPA-DMMDA is more difficult to be dissolved by organic solvents than other polymers.

Table 6. χ_{12} between HQDPA-DMMDA and organic solvents

Name	50°C		60°C		70°C		80°C	
	HSP	IGC	HSP	IGC	HSP	IGC	HSP	IGC
Ethanol	1.998	1.968	1.958	1.924	1.942	1.894	1.908	1.855
Propanol	2.308	1.884	2.269	1.855	2.229	1.790	2.203	1.760
Isopropanol	2.393	2.670	2.345	2.524	2.319	2.439	2.275	2.287
Butanol	2.801	3.098	2.748	2.884	2.706	2.837	2.663	2.653
Pentanol	3.274	3.746	3.220	3.699	3.155	3.685	3.117	3.575
Hexanol	3.779	3.862	3.689	3.763	3.641	3.649	3.561	3.477
Benzene	3.021	3.238	2.964	3.013	2.919	2.778	2.872	2.637
Cyclohexane	5.032	4.819	4.940	4.721	4.869	4.632	4.790	4.516
Toluene	3.526	3.727	3.453	3.586	3.414	3.323	3.345	3.109
Ether	4.093	4.341	4.049	4.264	3.995	4.184	3.973	4.099
Carbon tetrachloride	4.066	4.380	4.000	4.301	3.930	4.160	3.917	4.012
Ethyl acetate	3.361	3.489	3.310	3.144	3.263	2.972	3.221	2.718

From Table 6, for hydrogen bonding test solvents (such as ethanol, propanol etc.), χ_{12} values are considerably lower than other solvents, which reflect that stronger interactions exist between HQDPA-DMMDA and the solvents because HQDPA-

DMMDA has a large hydrogen bonding force. It is obvious that the values of the two methods are similar. However, the values calculated from HSP are usually lower than the corresponding values measured from IGC. In general, the interaction parameter depends on temperature, concentration and molecular mass of polymer and so on [25]. Therefore, the values of the two methods should not be completely same. These differences may vary from several to several tens percents. Since IGC is a precise technique, the differences between the two groups of χ_{12} values may be derivative from the method used to calculate the HSP. At this stage, accurate prediction method of solubility parameters from the chemical structure is still difficult because the interaction of different structural groups producing overall polar and hydrogen-bonding properties do not obey the simple rules [11]. Therefore, although there are differences between the absolute magnitudes of χ_{12} determined from HSP theory and IGC, the relative magnitude of the parameters is expected to be reliable. Consequently, the method of using Hansen Solubility Parameters to calculate χ_{12} can be used to rapidly predict the χ_{12} between polymer–organic solvent, aiding for the selection of solvents for polymer solution. Compared with other classical techniques used to determine χ_{12}, the advantages of the method are direct, easily processing and not needed expensive instrument.

Conclusions

For the polyimide (HQDPA-DMMDA) and twelve organic solvents, the Flory–Huggins interaction parameter χ_{12} measured by inverse gas chromatography (IGC) technique and calculated from Hansen Solubility Parameters (HSP) are similar. The differences of χ_{12} values between IGC and HSP methods are acceptable. Consequently, the Beerbower group contribution method can be used to calculate Hansen solubility parameters, and the HSP can be used to rapidly estimate χ_{12}.

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