Study on Segmental Interaction Parameter Between Ethylene and Vinyl Acetate Monomer Units of EVA by Inverse Gas Chromatography

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ABSTRACT: A method of analysis of inverse gas chromatography (IGC) measurements on copolymers to calculate segmental interaction parameters was proposed. Poly-(ethylene-co-vinyl acetate) (EVA), poly(vinyl acetate) (PVAc), and dotriacontane (C32) were studied at 120°C with eight different probes of varying polarities by IGC. The value of the segmental interaction parameter between ethylene units and vinyl acetate units in EVA was found to be 1.18, which is consistent with the literature values. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 693–698, 1999

Key words: segmental interaction parameter; inverse gas chromatography; miscibility; EVA; Flory–Huggins theory

INTRODUCTION

Miscibility in polymer-polymer blends is a subject of theoretical as well as of practical interest. It is generally agreed that the thermodynamic basis for the miscibility is an exothermic heat of mixing because of the very small combinational entropy in high molecular weight polymer blend systems. It is suggested that specific intermolecular interactions, such as hydrogen bonding, are responsible for the exothermic heat of mixing. But recently it was demonstrated that systems consisting of a homopolymer and a copolymer may be miscible for a certain range of copolymer composition even though the combination of their corresponding homopolymers is immiscible.^{1,2} For example, poly(methyl methacrylate) (PMMA) is not miscible with either polystyrene or polyacrylonitrile but is miscible with poly(styrene-co-acrylonitrile) within a certain copolymer composition

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range.^{3,4} These systems have no exothermic interaction between the different monomer units. It has been proposed that such a "miscibility window" is due to repulsion between the two different monomer units composing the copolymer. In a mean-field approach, the overall Flory-Huggins interaction parameter between the two polymers can be simply expressed in terms of the respective segmental interaction parameters.¹⁻⁷ Therefore, the data of segmental interaction parameters can be used to predict the miscibility of copolymers. But the experimental measurement of the segmental interaction parameter is difficult. Most data were estimated from experimental miscibility maps.^{4,6,7} The availability of a simple technique for characterizing segmental interaction parameters in copolymers would be of great value.

Inverse gas chromatography (IGC) is an extension of conventional gas chromatography (GC) in which a nonvolatile material to be investigated is immobilized within a GC column. This stationary phase is then characterized by monitoring the passage of the volatile probe molecules of known properties as they are carried through the column via an inert gas.⁸

The applications of IGC in various areas have been reviewed.⁸ Among other applications, IGC has been most widely used to characterize the solid surface and to determine the polymer-polymer interaction parameters. When the retention of the probe is due to equilibrium adsorption on the surface of the stationary phase, IGC is able to generate adsorption isotherms and to evaluate the surface properties⁹ and acid/base interactions for specified adsorbate-adsorbent pairs.¹⁰ The illustrations of IGC as a source of data for the surface and interface characterization of silica, illites, kaolinites, cork, and nylon 66 were given by Papirer and coworkers^{11,12} and Tate Ruetsch.¹³ When the probe can penetrate the polymer in the stationary phase and the retention is predominantly due to the equilibrium bulk sorption of the polymer, IGC can be applied to the interaction thermodynamics of the polymerprobe and polymer-polymer systems. The thermodynamic characterization of binary polymer blends by IGC was reviewed by Mandal et al.¹⁴

IGC is one of the most useful techniques for characterizing the interaction parameter χ_{23}' for a polymer-polymer pair. Because of its simplicity and rapid data collection, IGC has been used for many polymer systems.¹⁴ The theoretical base of the normal determination of χ'_{23} by IGC is the Flory–Huggins expression for the change of the free enthalpy in mixing, which was extended to three-component systems.^{15–17} The calculation of χ'_{23} from the IGC results is available, strictly speaking, only for homogeneous systems where the components are distributed randomly at the segmental level. However, the two homopolymers corresponding to the monomer units of a copolymer having segmental repulsion must be incompatible. It is impossible to characterize the interaction parameter of a blend incompatible by the classical IGC procedure because of the phase separation in the system. The purpose of this article was to show how the segmental interaction parameter between ethylene and vinyl acetate monomer units of poly(ethylene-co-vinyl acetate) (EVA) can be obtained by using a modified procedure of IGC.

THEORY

Guillet and coworkers first applied the gas-liquid chromatography technique to systems in which

the stationary phase is a polymer.¹⁸ The thermodynamics of the solvent–solute interaction for the case of a polymeric solvent with a volatile solute (probe) of infinite dilution was considered in their articles.¹⁹ By combination of the Flory–Huggins theory with routine chromatographic calculations, the expression for the interaction parameter of the probe and the polymer, χ_{12} , was given as^{14,16,20}

$$\chi_{12} = \ln(RTv_2/V_gV_1P_1^0) - 1 + V_1/M_2v_2 - (B_{11} - V_1)P_1^0/RT \quad (1)$$

where V_1 and P_1^0 are the probe molar volume in the liquid phase and the saturated vapor pressure, respectively; B_{11} , the second virial coefficient of the probe in the gas phase; v_2 , the specific volume of the polymer at the experimental temperature; R and T, the gas constant and the absolute temperature, respectively; M_2 , the molecular weight of the polymer; and V_g , the specific retention volume of a probe on a gas chromatographic column. Equation (1) has been routinely used for the calculation of χ_{12} from IGC experiments.

In the case of a copolymer investigation by IGC, a similar analysis on the copolymer column yields the analogous parameter $\chi_{\text{copolymer}}$, and

$$\Delta G_{\text{mix}} = RT \left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{\text{copolymer}} \right) \quad (2)$$

where $\chi_{\text{copolymer}}$ is the Flory–Huggins interaction parameter between the probe and the copolymer. Subscripts 1 and 2 denote the probe and the copolymer, respectively. ϕ_i is the volume fraction. n_i is the number of moles of the component.

In a mean-field approach for a binary mixture of a random copolymer and a probe, the $\chi_{copolymer}$ can be expressed in a manner similar to the Brinke et al.¹ treatment of a binary blend of a copolymer and a homopolymer:

$$\chi_{\text{copolymer}} = y\chi_{1C} + (1 - y)\chi_{1D} - y(1 - y)\chi_{CD} \quad (3)$$

where y is the copolymer $(C_y D_{1-y})_n$ composition expressed in a volume fraction. χ_{1C} and χ_{1D} are the interaction parameters between the probe and the segments of different monomer units. χ_{CD} is the segmental interaction parameter between monomer units C and D in the copolymer. If the composition y and the parameters χ_{1C} , χ_{1D} , and $\chi_{\text{copolymer}}$ are known [e.g., from IGC experiments

	VAc Content	Molecular	v_2 at 120°C	T_{g}	T_m	
Sample	(wt %)	Weight	(cm^{3}/g)	(°C)	(°C)	Source
PVAc	100	$1.52 imes10^5$	0.891	31	_	Shanghai Petrochemical Ltd., Shanghai, China
EVA-1	48.5	$2.2 imes 10^5$	1.080	—	84.0	Levapren500, Bayer, Lever Kusen
EVA-2	15.4	$1.1 imes10^4$	1.191	_	81.5	DuPont, Wilmington, DE
C32	0	450.5	1.336		69	Aldrich Chemical Co., Milwaukee

Table I Materials and Their Characteristics

on homopolymer C, homopolymer D, and copolymer $(C_y D_{1-y})_n$, respectively], χ_{CD} may be calculated from eq. (3) as the only unknown.

EXPERIMENTAL

Materials

Details of the poly(vinyl acetate) homopolymer (PVAc), ethylene-vinyl acetate copolymers (EVA), and dotriacontane (C32) used are listed in Table I. The vinyl acetate contents of EVA-1 and EVA-2 shown in Table I were calculated from the element analysis results. The M_w 's of EVA-1 were determined by GPC in tetrahydrofuran, relative to polystyrene standards, and the polydispersity index $M_{\rm w}/{\rm M_n}$ is 2.7. The ¹H-NMR spectrum was obtained on a Varian XL-300 spectrometer using tetramethvlsilane (TMS) as an internal reference. EVA was dissolved in deuterochloroform. The vinyl acetate diad and triad in EVA-1 is 20.6%, as calculated from the ¹H-NMR spectrum. EVA-2 is not soluble in solvent at room temperature; therefore, its molecular weight was calculated from the intrinsic viscosity of the solution in *p*-xylene at 75°C using the equation of polyethylene.²¹ The molecular weight of PVAc shown in Table I is nominal. The specific volumes v_2 of PVAc and C32 at 120°C were calculated from the density at 25°C and the expansion coefficients that were available from the literature.²² The specific volume v_2 of EVA was calculated from the v_2 of PVAc and C32 stoichiometrically. The melting temperature (T_m) and the glass transition temperature (T_{σ}) were measured by DSC. The chromatographic support was a 60/80 mesh White Support 102 (acid washed and treated with DCMS, Shanghai Reagents Co., Shanghai). All the probes were obtained from reputable suppliers and used as received. The

vapor pressure of the probes was obtained from their Antoine vapor-pressure coefficients; these coefficients together with other necessary constants were extracted from Dreisbach compilation and other sources.^{23,24}

Column Preparation

Packed columns were prepared from 157-cm-long strips of $\frac{1}{4}$ -in.-o.d. copper tubing. Each of the polymer samples was first weighed carefully and dissolved in about 100 mL of solvent. The solvents used were tetrahydrofuran for PVAc and EVA-1 and xylene for C32 and EVA-2. The polymer samples were then deposited onto the support in 7% column loading by employing a procedure described in Al-Saigh and Munk's work.¹⁶ Prior to any retention measurements, each new column was conditioned in the chromatograph at 120°C for 8 h.

Data Acquisition

A modified 102 GC unit (Shanghai Analytical Instruments Co.) was utilized for gathering all the elution data. High-purity nitrogen was used as the carrier gas. The experiments were performed at 120°C and a nominal flow rate of 16 mL/min. Methane served as the marker. The signal from the flame-ionization detector was converted from analog to digital and processed on a microcomputer. Retention times were measured at least in triplicate, with reproducibility of better than 3%. During the data analysis, the correction for retention of the marker and for retention by the support were performed in accordance with Munk et al.'s procedure.^{16,20,25}

	V_{σ}	V_{σ}	V_{σ}	V_{σ}
Probe	PVÅc	EVÅ-1	EVÅ-2	C32
Cyclohexane	8.70	31.55	42.82	65.07
Octane	10.52	54.93	83.32	141.36
Benzene	31.83	51.18	48.28	57.72
Toluene	52.43	98.02	95.63	120.26
Carbon				
tetrachloride	18.85	42.12	45.20	57.98
Ethyl acetate	15.92	29.61	21.09	22.80
Tetrahydrofurane	29.87	39.08	32.75	36.73
Dioxane	83.55	73.53	52.42	51.64

Table II Summary of Specific Retention Volumes of Various Probes on PVAc, EVA-1, EVA-2, and C32 at 120°C

RESULTS AND DISCUSSION

During the earlier studies on the IGC technique, Guilet et al. indicated that in the temperature region below T_g the retention volume is due to equilibrium adsorption on the polymer surface and that above $T_{\mbox{\scriptsize g}}$ the probe penetrates the polymer and bulk sorption begins to contribute to the V_g .²⁶ The relations between V_g and the thermodynamic interaction parameters [eq. (1)] are based on the bulk-sorption model. It is therefore imperative that for the evaluation of the thermodynamic qualities one should work in the region above the $T_g + 50^{\circ}$ C for a completely amorphous polymer or in the region above the T_m for a semi-crystalline polymer.¹⁴ The data of T_g and T_m for the samples are given in Table I. It is obvious that the column temperature, 120°C, used in the IGC measurements is above the T_m or above T_g + 50°C.

Although in this region the retention is predominantly due to bulk sorption, there still may be some surface adsorption, depending on the column loading, the flow rate of the carrier gas, the amount of the probe injected, and the probe size.¹⁴ According to Munk et al.,^{16,20} the effect of the surface adsorption to V_g becomes insignificant at a column loading of 7%, a flow rate of gas 16 mL/min, and a small injection of the probe, and the effect of adsorption on the support can be eliminated by direct subtraction of the support retention from the apparent specific retention of the column. To eliminate the effect of surface adsorption, the conditions and procedures of our experiments are completely consistent with what Munk et al. suggested.

A total of eight probes of varying polarities were employed. None of them was a hydrogenbonded polar substance. Specific retention volumes V_g of the probes on PVAc, EVA-1, EVA-2, and C32 at 120°C are given in Table II. The Flory–Huggins interaction parameters χ_{12} for PVAc, EVA-1, EVA-2, and C32 with various probes calculated using eq. (1) are listed in Table III. The values of the segmental interaction parameter χ_{CD} between the ethylene units and vinyl acetate units in EVA (Table IV) were calculated using eq. (3), where $\chi_{copolymer}$, χ_{1C} , and χ_{1D} were substituted by χ_{12} of EVA, PVAc, and C32, respectively.

By inspecting Table IV, one finds that the χ_{CD} value varies with the probe used, although the probe dependence is not as strong as in the determination of polymer-polymer interaction parameters χ'_{23} for the blends^{14,17,20,27} by IGC. As more studies were reported, one of the major problems with the IGC-determined interaction parameter of the blend is that its value varies with the probe, although it should be independent of the choice of the probe from the thermodynamic consideration. Numerous attempts have been reported to resolve the problem of probe-dependent interaction parameters. DiPaola-Baranyi and Degre²⁸ noted the possibility that nonrandom partitioning of the probe molecules could affect the forces acting between the molecules of the mixed stationary phases. Shi and Schreiber¹⁷ attributed the probe dependence to the difference between the bulk and the surface compositions of the stationary phase. Klotz et al.²⁹ selected probes that were thermodynamically symmetric with respect to the polymers to be evaluated. El-Hibri et al.²⁰ found a correlation to exist between the apparent B_{23} values and the Hildebrand solubility parameter of the probe. Horta et al.³⁰ developed a modified

Table III Flory–Huggins Interaction Parameters χ_{12} for PVAc, EVA-1, EVA-2, and C32 with Probes

Probe	χ_{12} PVAc	χ_{12} EVA-1	$\overset{\chi_{12}}{ ext{EVA-2}}$	χ_{12} C32
Cyclohexane	1.337	0.242	0.032	-0.058
Octane	1.911	0.451	0.130	0.025
Benzene	0.185	-0.097	0.057	0.170
Toluene	0.322	-0.111	0.011	0.097
Carbon				
tetrachloride	0.557	-0.054	-0.030	0.029
Ethyl acetate	-0.033	0.214	0.648	0.884
Tetrahydrofurane	-0.087	-0.163	0.111	0.282
Dioxane	-0.157	0.164	0.597	0.833

	Molar Volume	χ_{CD}	χ_{CD}
Probe	of Probe at 120°C	from EVA-1	from EVA-2
Cyclohexane	123.6	1.00	0.63
Octane	184.4	1.16	1.05
Benzene	101.8	1.15	1.18
Toluene	119.5	1.24	1.14
Carbon tetrachloride	110.7	1.21	1.22
Ethyl acetate	114.2	1.34	1.42
Tetrahydrofurane	97.1	1.27	1.35
Dioxane	91.3	1.21	1.33
Average		1.20	1.17

Table IV Calculated Segmental Interaction Parameter χ_{CD}

form of Flory's equation that enables one to calculate the probe-independent interaction parameter χ_{23}^{*T} . This equation takes account of the equation-of-state parameters. Chee³¹ calculated the polymer solubility parameter and the entropy contribution to the interaction parameter. Sanchez³² suggested that a full description of polymer mixture thermodynamics requires the definition of four different parameters. Farooque and Deshpande²⁷ proposed an interaction-density parameter to overcome probe-to-probe variations in χ_{23} . Iruin et al.³³ used an approach based on the lattice fluid theory in an attempt to eliminate the probe dependence of the thermodynamic parameters calculated by IGC for the blend system having a hydrogen bond. However, so far, the problem of probe dependence in the measurement of the interaction parameter with IGC has not been well solved. It is difficult to fully understand the reason behind the probe dependence in this measurement from the limited data in Table IV. An interesting observation is that the molecular size of octane is much larger than that of the others (see the molar volumes in Table IV), which may influence the penetration of the probe molecule through the whole thickness of the polymer during its passage through the column. Under such nonequilibrium conditions, V_g is perhaps underestimated, and the value of χ_{CD} from octane is less reliable, whereas the more deviations of the χ_{CD} values obtained with cyclohexane and ethyl acetate from the average value probably can be attributed to the smaller V_g and a more inaccurate estimate of χ_{12} .

All the eight probes employed were of varying polarities. Although no hydrogen bond can be developed between these probes and the polymer, the different probes are of different acidity or basicity according to Lewis' formalism. In the same manner, EVA copolymers exhibit Lewis basicity (electron donor) through their carbonyl groups. These must affect the values of the χ_{CD} derived. However, the exploration for the correlation of the χ_{CD} value measured with the characteristics of the probe needs more data and thermodynamic considerations.

The values of χ_{CD} derived from EVA-1 and EVA-2 are consistent, although the values of χ_{CD} derived from EVA-2 were scattered a little more than were the values from EVA-1 because of, probably, more error propagation in the calculation of eq. (3) resulting from the lower volume fraction of vinyl acetate units in EVA-2.

The average value of the segmental interaction parameter χ_{CD} is 1.18 (Table IV). This more positive value indicated the strong repulsion between ethylene units and vinyl acetate units in their copolymer procedure for blends . Therefore, the two homopolymers, polyethylene and poly(vinyl acetate), corresponding to the monomer units of EVA, must be immiscible. It is impossible to characterize their interaction parameter by the traditional IGC because of the phase separation in the system. Unlike the immiscible blend of the two homopolymers, the random copolymer consisting of corresponding repulsive segments is very homogeneous, and the calculation of the interaction parameter from the IGC measurement is possible.

It is also interesting to compare the value of χ_{CD} obtained from the IGC measurement with the data reported in the literature. The value of 1.01 for this system at 150°C was estimated with an uncertainty of $\pm 20\%$ by Shiomi et al.⁶ from the miscibility map. The interaction energy density B_{12} (1 = vinyl acetate, 2 = ethylene) of 11.8 cal/ cm³ at 25°C was obtained by Cruz-Ramos and Paul² using model compounds. The B_{ij} value can

be transformed into a Flory–Huggins-type parameter χ_{ij} as follows [ref. 2, eq. (4)]:

$$B_{ij} = \chi_{ij} (RT/V_{\rm ref})$$

where V_{ref} is generally chosen to be the molar volume of a repeat unit. Ramos and Paul took the average molar volume of the ethylene and vinyl acetate repeat units as 52.5 cm³/mol². Thus, the χ_{ij} value of 1.05 for this system at 25°C is derived. Compared with the literature values, the result of the segmental interaction parameter calculated from the IGC measurement is reasonable.

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