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Abstract

Using a mean-field model, the segmental interaction parameters of various polymer blends based on styrene and 2,6-dimethyl-phenylene oxide derivatives are revised using new experimental results and the 'best fit values' are established. The predictive qualities of the model are shown and suggestions about group-contribution method are made. Calculations based on the revised segmental interaction parameters are in excellent agreement with the experimental data. © 1997 Elsevier Science B.V.

Keywords: Polymer blends; Miscibility; Mean-field model; Segmental interaction parameters

1. Introduction

Over the years, there has been a strong interest to understand the principles governing the miscibility and phase domain formation of multicomponent polymer systems. Simple models that provide a useful framework for describing blends with controlled phase behavior have emerged, among which the Flory–Huggins equation [1,2] and the empirical Flory–Huggins χ models [3–5] have been the most popular.

It is known that miscibility in polymer blends is strongly dependent on the chain microstructure. Composition and sequence distribution in a copolymer, stereo-configuration, branching and cross-linking are structural features affecting local environments, whereas the size (molecular weight) and shape of molecules (chain flexibility) have long-range effects. The effect of molecular size on

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miscibility is clearly described [6]: with increasing molecular weight, miscibility decreases. The combinatorial part in the Flory–Huggins theory [2,3] accounts for this effect.

More than a decade ago, a simple mean-field theory of random copolymer blends based on a mixture of polymer segment concept was introduced [7–9]. It was shown that using the mean-field approach, phase behavior of blends can be described by pair interactions between all segments in the blends. This theory provided also a general explanation for the effect of chemical composition on miscibility.

In our studies of polymer–polymer miscibility (see for example Vuković et al., [10,11]) the mean-field model [7,8] was applied. The model is reliable and a fast method for correlating experimental results and describing the phase behavior of polymer blends. It has become widely used in the description of miscibility/immiscibility phenomena.

In this study, the mean-field model is comprehensively tested by using a collected database, involving various polymer blends based on styrene (S) and 2,6-dimethyl-1,4-phenylene oxide (PO) derivatives. Most of these experimental data have been obtained in our laboratory. Presently our computerized database contains data for 80 binary polymer systems. Since new experimental data has become available, it has been possible to revise some of earlier parameter values based on limited information and to establish their ‘best fit values.’ The aim of the present paper is to report the new estimated segmental interaction parameters, and to give examples of the predictive capability of the model.

2. Experimental data

As already indicated, in this study we will concentrate on the miscibility and phase behavior of various polymer systems mainly based on styrene polymer derivatives, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and partially sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO), i.e., random copolymers which are assumed to consist of varied content of sulfonylated and unsulfonylated 2,6-dimethyl-1,4-phenylene oxide repeating units and can be symbolized as poly(PO-co-SPO) for the sake of clarity. Homopolymer–homopolymer, homopolymer–random copolymer systems and blends of two random copolymers and alternating and random copolymers will be considered.

It should be mentioned that there is an overall paucity of available information on the thermodynamic properties of polymer blends, specially if one of the components is a copolymer. In many cases the copolymers are not fully characterized. The type of data for different polymer systems varies considerably in quantity, quality and in the nature of the experimental information provided, and that makes tabulation of the data difficult. The information usually available is copolymer composition in mole or weight percent, the number average and/or the weight average molecular weight. For nearly all systems considered in this study, experimental values of the specific volumes at given conditions are not available.

The studied polymer systems together with the experimental data references are summarized in Table 1.

For each polymer blend, the computerized database contains the following information: component codes or identification numbers, system type code (homopolymer–homopolymer, homopolymer–copolymer or copolymer–copolymer), composition code of the constituents for the copolymers,

Table 1

References of the experimental data used for segmental interaction parameters determination

System	References	System	References
PS/PPO	[12–14]	SPPO/PpMS	[15]
PS/BrPPO	[7]	SPPO/P(S-co-oFS)	[16]
PS/SPPO	[17,15]	SPPO/P(S-co-pFS)	[16]
PS/PoFS	[18]	SPPO/P(S-co-oCIS)	[19]
PS/PoCIS	[20]	SPPO/P(S-co-pCIS)	[19]
PS/PAMS	[21]	SPPO/P(S-co-oBrS)	[22]
PS/P(S-co-oBrS)	[23]	SPPO/P(S-co-pBrS)	[22]
PS/P(S-co-pBrS)	[23]	SPPO/P(S-co-oMS)	[15]
PS/P(S-co-AMS)	[24]	SPPO/P(S-co-pMS)	[15]
PS/P(oCIS-co-pCIS)	[25,26]	SPPO/P(S-co-AN)	[16]
PPO/PpIS	[27]	SPPO/P(S-co-MAN)	[28]
PPO/PoMS	[15]	SPPO/P(oFS-co-oCIS)	[10]
PPO/PpMS	[15,29]	SPPO/P(oFS-co-pCIS)	[10]
PPO/PAMS	[30]	SPPO/P(pFS-co-oCIS)	[11]
PPO/P(S-co-oFS)	[8,31]	SPPO/P(pFS-co-pCIS)	[11]
PPO/P(S-co-pFS)	[8,31,32]	SPPO/P(oFS-co-oBrS)	[33]
PPO/P(S-co-oCIS)	[8]	SPPO/P(oFS-co-pBrS)	[33]
PPO/P(S-co-pCIS)	[8,34]	SPPO/P(pFS-co-oBrS)	[33]
PPO/P(S-co-oBrS)	[8,23]	SPPO/P(pFS-co-pBrS)	[33]
PPO/P(S-co-pBrS)	[8,23]	SPPO/P(oFS-co-pFS)	[35]
PPO/P(S-co-oMS)	[15]	SPPO/P(oCIS-co-pCIS)	[36]
PPO/P(S-co-pMS)	[15]	SPPO/P(oBrS-co-pBrS)	[37]
PPO/P(S-co-AMS)	[30]	SPPO/P(oMS-co-pMS)	[15]
PPO/P(S-co-AN)	[38]	SPPO/P(AMS-alt-MAN)	[28]
PPO/P(S-co-MMA)	[39]	SPPO/P(AMS-alt-MMI)	[40]
PPO/P(oFS-co-oCIS)	[41]	SPPO/P(AMS-alt-PhMI)	[40]
PPO/P(oFS-co-pCIS)	[8,41]	SPPO/P(PhVEE-alt-PhMI)	[42]
PPO/P(oFS-co-pBrS)	[43]	SPPO/P(PhVBE-alt-PhMI)	[42]
PPO/P(oFS-co-pFS)	[44]	PAMS/P(S-co-AMS)	[24]
PPO/P(oCIS-co-pCIS)	[45]	PMMA/P(S-co-AN)	[46–49]
PPO/P(oMS-co-pMS)	[15]	P(S-co-AN)/P(S-co-MAN)	[9,50–54]
PPO/P(pMS-co-AN)	[55]	P(S-co-AN)/P(S-co-MMA)	[56,57]
PPO/BrPPO	[7]	P(S-co-AN)/P(S-co-PhMI)	[50]
BrPPO/PpMS	[58]	P(S-co-AN)/P(MMA-co-AN)	[56,59]
SPPO/SPPO	[16]	P(S-co-AN)/P(MMA-co-BMA)	[60]
SPPO/PoFS	[61]	P(S-co-MMA)/P(S-co-MMA)	[62]
SPPO/PpFS	[61]	P(S-co-MMA)/P(S-co-MAN)	[63,57]
SPPO/PpCIS	[61]	P(S-co-MMA)/P(MMA-co-AN)	[56]
SPPO/PpBrS	[61]	P(S-co-MMA)/P(MMA-co-MAN)	[59]
SPPO/PoMS	[15]		

composition of the blend, number of data points, data type code—such as miscibility/immiscibility behavior of the blend at a given temperature, and finally the data themselves. In addition, the relevant literature references are included. The system used in building up the database makes provision for an easy update.

3. Theoretical model

Based on a lattice theory, the Flory–Huggins expression for the Gibbs energy [1,2] of a mixture of two polymers can be written as:

$$\frac{\Delta G^M}{RT} = \underbrace{\frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2}_{\text{combinatorial term}} + \underbrace{\chi_{\text{blend}} \Phi_1 \Phi_2}_{\text{residual term}} \quad (1)$$

where N_1 and N_2 are the number of lattice cells occupied by polymers 1 and 2, Φ_1 and Φ_2 their volume fractions calculated on the basis of lattice occupancy, and χ_{blend} is a dimensionless overall interaction parameter for the polymer–polymer system. In practice, the χ_{blend} parameter exhibits considerable variation with temperature, pressure and blend composition. The combinatorial contribution of Eq. (1) to the Gibbs energy of mixing is due to the differences in the sizes of molecules, while the residual contribution is essentially due to the energetic interaction.

The mean-field theory [7,8] provided the evaluation of χ_{blend} parameter in a group contribution framework, in terms of segmental interactions, where segments are usually defined as the monomer repeating units. This is an arbitrary assignation and implies that χ_{blend} parameters must be functions of the segmental definition. In this model, a polymer molecule is assumed to consist of a given number of segments, while a polymer blend is a mixture of these segments. Further, it is assumed that each segment occupies one lattice site. The excluded volume effect is taken into account by a single site occupancy requirement. The residual term of Eq. (1) assumes that the molecular segments are randomly mixed on the lattice. The model neglects free volume contributions to the Gibbs energy of mixing and it does not take into account any possible directional interactions.

For the most general case of mixtures of two random copolymers of the type $(A_{1-x}B_x)_{N_1}/(C_{1-y}D_y)_{N_2}$, the overall interaction parameter χ_{blend} can be expressed as a linear combination of the segmental interaction parameters, χ_{ij} :

$$\chi_{\text{blend}} = (1-x)(1-y)\chi_{AC} + (1-x)y\chi_{AD} + x(1-y)\chi_{BC} + xy\chi_{BD} \\ - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (2)$$

where the definition of the respective χ_{ij} parameters is obvious from their subscript, and copolymer compositions x and y should be expressed on the basis of lattice sites occupancy. The first four terms on the right-hand side of Eq. (2) define additive intermolecular interactions between the nonbonded component monomers in the mixture of two copolymers, weighted according to the copolymer compositions, whereas the remaining two terms define the intramolecular forces between the two different monomers comprising each of the copolymers.

In Eq. (2), x and y should be in terms of volume fractions, but very often weight or mole fractions are used. Furthermore, it was pointed out by Nishimoto et al. [54] and Salomons et al. [18] that in many papers in which Eq. (2) has been used, the authors failed to report the basic segmental units.

In the present work, the calculation employed volume fractions based on Bondi's van der Waals volumes [64,65] which may be considered as the best expression for the lattice occupancy.

The basic criterion for miscibility of blends is that χ_{blend} must be less than a critical value $\chi_{\text{blend}}^{\text{crit}}$,

Table 2

Van der Waals volumes of the repeating units, as calculated using increments proposed by Bondi [64,65]

Repeating unit	V_w (cm ³ mol ⁻¹)
S	62.85
PO	68.82
SPO	132.44
AMS	73.07
<i>o</i> (<i>m,p</i>)MS	74.00
<i>o</i> (<i>m,p</i>)FS	66.13
<i>o</i> (<i>m,p</i>)CIS	72.33
<i>o</i> (<i>m,p</i>)BrS	75.45
<i>o</i> (<i>m,p</i>)IS	79.97
MAN	39.52
MI	43.46
MMI	53.38
PhMI	85.55
AN	31.71
MMA	56.10

which for monodisperse polymers may be calculated on the basis of the number of lattice cells occupied [66]:

$$\chi_{\text{blend}}^{\text{crit}} = 0.5(N_1^{-0.5} + N_2^{-0.5})^2 \quad (3)$$

where N_1 and N_2 are the number of lattice cells occupied by a molecule of polymers 1 and 2, respectively.

Eq. (3) may be interpreted as defining N_1 and N_2 as the degrees of polymerization or the number of repeating units of polymers, if the molar volumes of all repeating units have similar values. It turns out that for many polymer systems, this is a valid approach, and that for many cases $\chi_{\text{blend}}^{\text{crit}}$ calculated from the number of repeating units is quite satisfactory. In the present work, in spite of differences between the van der Waals volumes of the repeating units (see Table 2), $\chi_{\text{blend}}^{\text{crit}}$ is calculated using the number of repeating units of polymers. This interpretation of the Flory model will find its final and empirical justification in the obtained results presented below. However, it is obvious that the segmental interaction parameters depend on the $\chi_{\text{blend}}^{\text{crit}}$ and on the van der Waals volumes used.

The boundary between miscibility and immiscibility domains for copolymer–copolymer system is described by a function expressed in terms of x and y , such that:

$$f(x, y) = \chi_{\text{blend}} - \chi_{\text{blend}}^{\text{crit}} = 0 \quad (4)$$

4. Estimation of the segmental interaction parameters

First, the van der Waals volumes of the repeating units have been calculated using the structural increments proposed by Bondi [64,65]. Their values are given in Table 2. Then, the experimental data for copolymer compositions given in different units (molar or weight fractions) along the authors are

Fig. 1. Miscibility of 50:50 wt.% blends of poly(S-co-oBrS) and SPPO copolymers. Volume fraction scales. (○) one phase; (●) two phases; (▲) intermediate situation; (—) correlated miscibility/immiscibility boundary.

converted in volume fractions on the basis of these van der Waals volumes, as required by the model. As an example, for the system SPPO/poly(S-co-oBrS) at 473 K, the experimental phase diagram with copolymer compositions in volume fractions is shown in Fig. 1. The homogeneous blends are represented by open circles, the heterogeneous blends by full circles, and the blends in intermediate situations by triangles. It has been shown [35] that such blends are at or near the critical point.

It is obvious from Fig. 1 that the state of the system depends strongly on the two copolymer compositions, i.e., the content of oBrS (x) and of SPO (y). It is therefore necessary to correlate the χ_{blend} parameter with these variables. The compositions corresponding to the intermediate situations and to the boundaries separating the homogeneous and heterogeneous regimes have been considered as belonging to blends in the critical state, for which Eq. (4) should be verified.

In the present work, the experimental data of 80 binary polymer blends have been selected for the estimation of the segmental interaction parameters.

The objective function for the parameter estimations may be defined in many ways. We tried different functions, and we chose to estimate the parameters by minimization of the following expression:

$$F = \sum_n \left(\frac{\chi_{\text{blend}}^{\text{crit}} - \chi_{\text{blend},n}}{\chi_{\text{blend}}^{\text{crit}}} \right)^2 \quad (5)$$

where the sum is extended to a set of points with coordinates x_n and y_n located at the miscibility/immiscibility boundary, and $\chi_{\text{blend}}^{\text{crit}}$ is calculated by using Eq. (3). The conformational entropic term $\chi_{\text{blend}}^{\text{crit}}$ is molecular-weight-related and calculated from the number of repeating units of the respective blend components. In most cases $\chi_{\text{blend}}^{\text{crit}}$ is in the range 0.002 to 0.006. The optimization algorithm

used in the parameter estimation program (see Bogdanić and Berg [67]) is a modified Levenberg–Marquard algorithm [68]. The problem of fitting the mean-field equation to experimental data is thereby reduced to finding the values of χ_{ij} parameters that will predict miscibility/immiscibility boundaries which in best agreement with the experimental one. Since the mean-field model is a group-contribution model, the same values of segmental interaction parameters enter in the calculations for various systems, and the minimization of the objective function is made simultaneously on several systems.

For the SPPO/poly(S-co-oBrS) system chosen above as an example, the value of the objective function depends on six intersegmental parameters, and by minimization of the objective function given by Eq. (5), their best values have been determined. The initialization of the parameter values was obtained from the miscibility limits of homopolymer–copolymer systems, such as for example blends of PS/poly(S-co-oBrS) and PPO/poly(S-co-oBrS), as well as from interaction parameters obtained from previous papers. When the best values of the parameters are obtained, the curve

Table 3
Segmental interaction parameters at 473 K

Segment pair	χ_{ij}	Segment pair	χ_{ij}
S,PO	-0.043	SPO,pFS	0.046
S,SPO	0.22	SPO,oClS	0.175
S,oFS	0.0025	SPO,pClS	0.009
S,pFS	0.06	SPO,oBrS	0.15
S,oClS	0.005	SPO,pBrS	0.01
S,pClS	0.055	SPO,oMS	0.18
S,oBrS	0.013	SPO,pMS	0.17
S,pBrS	0.048	SPO,AMS	0.505
S,pIS	0.09	SPO,MAN	0.81
S,oMS	0.0025	SPO,PhMI	0.39
S,pMS	0.003	SPO,AN	0.20
S,MAN	1.85	oFS,pFS	0.04
S,PhMI	0.29	oFS,oClS	0.064
S,AN	0.98	oFS,pClS	0.07
S,MMA	0.04	oFS,oBrS	0.042
PO,SPO	0.25	oFS,pBrS	0.108
PO,oFS	0.005	pFS,oClS	0.11
PO,pFS	0.057	pFS,pClS	0.043
PO,oClS	0.021	pFS,oBrS	0.12
PO,pClS	0.034	pFS,pBrS	0.11
PO,oBrS	0.047	oClS,pClS	0.09
PO,pBrS	0.055	oBrS,pBrS	0.10
PO,pIS	0.097	oMS,pMS	0.01
PO,oMS	0.006	pMS,AN	0.91
PO,pMS	0.005	AMS,MAN	0.152
PO,AMS	0.11	AMS,PhMI	1.22
PO,MAN	1.68	MMA,AN	0.50
PO,PhMI	0.90	MMA,MAN	1.20
PO,AN	1.23	AN,MAN	0.04
PO,MMA	0.21	AN,PhMI	0.07
SPO,oFS	0.176		

Table 4
Correlation of miscibility boundaries. Mean relative deviations (%), $\Delta\%$

System	Number of data sets	$\chi_{\text{blend}}^{\text{crit}} (10^{-3})$	$\Delta\%$
SPPO/P(S-co-oFS)	9	4	8.4
SPPO/P(S-co-oClS) ^a	11	4	0.1
SPPO/P(S-co-pClS) ^b	18	4	3.0
SPPO/P(S-co-oBrS) ^c	10	4	0.8
SPPO/P(S-co-pBrS)	19	4	2.1
SPPO/P(S-co-oMS)	8	4	11.5
SPPO/P(S-co-pMS)	9	4	7.4
SPPO/P(S-co-AN)	8	3	34.3
SPPO/P(oFS-co-pFS)	18	2	13.2
SPPO/P(oFS-co-oCS)	10	3.5	0.2
SPPO/P(oFS-co-pClS)	19	3.5	0.1
SPPO/P(oFS-co-oBrS)	11	4.3	0.1
SPPO/P(oFS-co-pBrS)	17	4	1.4
SPPO/P(pFS-co-oClS) ^d	18	3.5	0.3
SPPO/P(pFS-co-pClS)	16	3.5	0.4
SPPO/P(pFS-co-oBrS)	19	4	0.6
SPPO/P(pFS-co-pBrS)	17	4	1.3
SPPO/P(oBrS-co-pBrS)	16	4	1.1
SPPO/P(oMS-co-pMS) ^e	10	5	0.3
P(S-co-MMA)/P(S-co-MAN)	8	2	14.6
P(S-co-AN)/P(MMA-co-AN)	8	2	13.3
P(S-co-AN)/P(S-co-MAN)	9	4	4.3
SPPO/P(oClS-co-pClS) ^f	16	3	0.6
SPPO/P(S-co-pFS) ^g	15	4	4.0
P(S-co-AN)/P(S-co-MMA) ^h	11	2	0.6
Overall deviation			3.8

^aSee Fig. 1; ^bsee Fig. 2; ^csee Fig. 3; ^dsee Fig. 4; ^esee Fig. 5; ^fprediction, see Fig. 6; ^gprediction, see Fig. 7; ^hprediction, see Fig. 8.

corresponding to Eq. (4) may be drawn. However, while the parameter determination is going on, for new systems, the number of parameters to be determined decreases, as it is usual in any group-contribution method, and may be reduced to one or two parameters (see for example references [10,11]). In the volume fraction coordinates, this curve is a part of an ellipse or a hyperbola, limited to the physical range of the variables x and y ($0 \leq x \leq 1$ and $0 \leq y \leq 1$), as discussed by Ueda and Karasz [69] and as shown on Fig. 1.

Based on the experimental miscibility/immiscibility data for blends containing segments i and j , 61 χ_{ij} parameters that best fit the data have been obtained. These segmental interaction parameters calculated at 473 K are presented in Table 3.

To give an idea of the correlation capabilities of the approach, we present in Table 4 for several systems the number of data sets (n_{obs}) included in χ_{ij} parameter estimation, the values of the $\chi_{\text{blend}}^{\text{crit}}$ calculated from Eq. (3) and the mean relative deviations (%) defined by the relation:

$$\Delta = 100 \sqrt{\frac{F}{n_{\text{obs}}}} \quad (6)$$

where F is given by Eq. (5). In Table 4 some difficult systems are included, as for example SPPO/poly(S-co-AN), together with three predicted systems. For the whole data set the mean deviation is 4%.

5. Results and discussion

The purpose of this section is to present an evaluation of the mean-field theory capability for correlating and predicting miscibility of polymer blends. We do so by showing examples of calculations for several systems included in Table 1. The phase diagrams will be shown using the original units (i.e., either mole fraction or weight fraction). Examples have been chosen to illustrate the influence of the chemical structure of the components of the blends.

Figs. 1–5 compare correlated miscibility domains with experimental data for binary polymer blends of the following random copolymers: poly(S-co-*o*BrS), poly(S-co-*o*CIS), poly(S-co-*p*CIS), poly(*p*FS-co-*o*CIS) and poly(*o*MS-co-*p*MS), all in blends with SPPO.

In Figs. 6–8, we used Eq. (2) in terms of χ_{ij} as a predictive method. The obtained results show that it is possible (as in other group-contribution methods) to apply the same parameters to systems which have not been included in parameter estimation. The required six χ_{ij} parameter values have been obtained from subsidiary experiments on phase boundaries of other homopolymer–copolymer or copolymer–copolymer combinations which include the necessary segment pairs. As an example, for the blend of poly(S-co-AN) with poly(S-co-MMA) shown on Fig. 8, the miscibility domain is a function of the interactions between three possible binary segmental pairs, i.e., interactions between S and AN, S and MMA, and MMA and AN monomer units. The values of the respective segmental interaction parameters $\chi_{S,AN}$, $\chi_{S,MMA}$ and $\chi_{MMA,AN}$, respectively, have been previously determined by simultaneous correlation of experimental data for the: PMMA/poly(S-co-AN), poly(S-co-AN)/poly(S-co-MAN), poly(S-co-AN)/poly(MMA-co-AN), poly(S-co-MMA)/poly(S-co-MMA), poly(S-co-MMA)/poly(S-co-MAN) and poly(S-co-MMA)/poly(MMA-co-AN) blend systems.

As can be seen from Figs. 1–8, comparison of correlations as well as predictions with experimental phase behavior usually shows very good agreement, and confirms the general validity of describing interactions in terms of the χ_{ij} parameters.

The influence of chemical structure on polymer–polymer miscibility has been extensively discussed in a recent paper [70]. Here we limit ourselves to three aspects only: the influence of the nature of the substituent on the aromatic ring, the intramolecular repulsion effect and the influence of the position (*ortho*, *para*) of the substituent.

Figs. 2, 4 and 7 show the miscibility domains of blends of SPPO with three copolymers: poly(S-co-*o*CIS), poly(*p*FS-co-*o*CIS) and poly(*p*CIS-co-*o*CIS), respectively. In these examples, the *o*CIS monomer unit is common to all copolymers. By changing the other monomer unit (S or *p*FS or *p*CIS), the miscibility domain is expanded as is shown in these figures. For this reason the role of interaction parameters $\chi_{S,SPO}$, $\chi_{SPO,pFS}$ and $\chi_{SPO,pCIS}$ in inducing miscibility is of interest. It can be seen from Figs. 2, 4 and 7 and Table 3 that miscibility for the mentioned systems increases as values of the interaction parameters decrease, i.e., $\chi_{S,SPO} > \chi_{SPO,pFS} > \chi_{SPO,pCIS}$. The experimental results, as well as the results obtained by the mean-field model show that the ability of the halogen substituent to increase miscibility in these blends is given by $pCIS > pFS > S$.

Fig. 2. Miscibility of 50:50 wt.% blends of poly(S-co-oCIS) and SPPO copolymers. (○) one phase; (●) two phases; (—) correlated miscibility/immiscibility boundary.

We will now consider blends of SPPO with four copolymers which include the styrene monomer unit, i.e., poly(S-co-oBrS), poly(S-co-oCIS), poly(S-co-pCIS) and poly(S-co-pFS), represented by Figs. 1–3 and 6. The miscibility domain necessarily includes the point ($x = 0$, $y = 0$), corresponding

Fig. 3. Miscibility of 50:50 wt.% blends of poly(S-co-pCIS) and SPPO copolymers. (○) one phase; (●) two phases; (▲) intermediate situation; (—) correlated miscibility/immiscibility boundary.

Fig. 4. Miscibility of 50:50 wt.% blends of poly(*p*FS-co-*o*CIS) and SPPO copolymers. (○) one phase; (●) two phases; (—) calculated miscibility/immiscibility boundary.

to the miscibility of homopolymers PS and PPO, as a consequence of the attractive interactions between S and PO monomer unit. PPO is not miscible with styrene halogen-substituted homopolymers containing, i.e., with poly(*o*BrS), poly(*o*CIS), poly(*p*CIS) or poly(*p*FS), and PS is not miscible

Fig. 5. Miscibility of 50:50 wt.% blends of poly(*o*MS-co-*p*MS) and SPPO copolymers. (○) one phase; (●) two phases; (▲) intermediate situation; (—) correlated miscibility/immiscibility boundary.

Fig. 6. Miscibility of 50:50 wt.% blends of poly(S-co-pFS) and SPPO copolymers. (○) one phase; (●) two phases; (▲) intermediate situation; (—) predicted miscibility/immiscibility boundary.

with highly sulfonylated PPO. The miscibility domains for these blends are bounded by the intercept on the axis $x = 0$, that corresponds to the partial miscibility of PS with SPPO and by the intercept on the axis $y = 0$, that corresponds to the partial miscibility of PPO with the considered copolymers. It

Fig. 7. Miscibility of 50:50 wt.% blends of poly(pCIS-co-oCIS) and SPPO copolymers. (○) one phase; (●) two phases; (▲) intermediate situation; (—) predicted miscibility/immiscibility boundary.

Fig. 8. Miscibility of 50:50 wt.% blends of poly(S-co-AN) and *p*(S-co-MMA) copolymers. (○) one phase; (●) two phases; (—) predicted miscibility/immiscibility boundary.

should also be underlined that PS is not miscible with poly(*o*BrS), poly(*o*ClS), poly(*p*ClS) or poly(*p*FS) homopolymers, and that the intersegmental interaction parameters between S and the corresponding monomer units are positive. By applying Eq. (2), these parameters appear between the last two terms and contribute to the value of the miscibility limits on the axis $y = 0$. PPO is also not miscible with highly sulfonylated PPO [16], and the intersegmental interaction parameter between PO and SPO is positive. By applying Eq. (2), this parameter appears also between the last two terms, and contributes to the value of the miscibility limits on the axis $x = 0$. As mentioned earlier, these two terms represent the intramolecular repulsion effect.

For SPPO/poly(*p*FS-co-*o*ClS) (Fig. 4) blends, miscibility occurs also due to the intramolecular repulsion in copolymers. It can be seen that poly(*p*FS) is not miscible neither with PPO, nor with highly sulfonylated PPO (more than 70 mole % of sulfonylation), but is miscible in a large composition range of the sulfonylation degree (20 mole % < y < 70 mole %). This is accounted for by the large and positive value of the $\chi_{\text{PO,SPO}}$ segmental interaction parameter.

For the system SPPO/poly(*p*ClS-co-*o*ClS) (Fig. 7), miscibility domains appear on both axes, in spite of the immiscibility of any homopolymer pairs. This is again due to the $\chi_{\text{PO,SPO}}$ value, but also to the value of the $\chi_{\text{oClS,pClS}}$ parameter.

In a general way, for copolymer–copolymer blends miscibility may arise through the last two terms in Eq. (2). In all the present examples, the only negative parameter is related to the $\chi_{\text{S,PO}}$ segmental interaction parameter ($\chi_{\text{S,PO}} = -0.043$) and this value cannot explain the large miscibility observed, which requires negative value in χ_{blend} . This internal repulsion effect was specifically pointed out by ten Brinke et al. [8] and more recently, for vapor–liquid equilibria, by Gupta and Prausnitz [71].

Figs. 2 and 3 show miscibility maps for SPPO/poly(S-co-*o*ClS) and SPPO/poly(S-co-*p*ClS) blends. It appears clearly that the miscibility regime is much larger when the chloro-substituent is in

the *para* position. This observation can be confirmed by many other examples which are not presented here. Table 3 shows that the repulsion of the *ortho*-substituted styrene with the SPO unit ($\chi_{\text{SPO},o\text{CIS}}$) is much greater than that of the *para*-substituted styrene ($\chi_{\text{SPO},p\text{CIS}}$). We thus consider that a steric effect influences, to some extent, the miscibility behavior of SPPO/poly[S-co-*o*(*p*)CIS] systems. This effect must be taken into account for any group-contribution method.

6. Conclusion

By summarizing the results of our studies on the miscibility of a large group of polymer blends based on styrene and 2,6-dimethyl-1,4-phenylene oxide derivatives, it is evident that there is a remarkable agreement between the miscibility/immiscibility boundaries obtained experimentally and those calculated using the mean-field model and revised parameters. It has been shown that the interaction parameters derived and listed in Table 2 are sufficiently quantitative to be of predictive value for copolymer systems studied in this work, but not used in their estimation. By using this procedure, the experimental work for the study of new blends containing the same segment pairs, may be reduced to some extent.

List of symbols

Variables

F	objective function [see Eq. (5)]
ΔG^M	Gibbs energy of mixing
N_i	number of lattice cells occupied by polymer <i>i</i>
R	gas constant
T	temperature
V_w	van der Waals volume
x	volume fraction of B in copolymer $A_{1-x}B_x$
y	volume fraction of D in copolymer $C_{1-y}B_y$

Greek letters

Δ	mean deviation [see Eq. (6)]
χ_{blend}	overall interaction parameter of a blend
$\chi_{\text{blend}}^{\text{crit}}$	critical value of the overall interaction parameter of a blend
χ_{ij}	interaction parameter between segments <i>i</i> and <i>j</i>
Φ_i	volume fractions of polymer <i>i</i>

Superscript

crit	critical value
------	----------------

Subscripts

i	polymer segment i
j	polymer segment j
n	number of experimental points

Abbreviations

-alt-	alternating copolymer
-co-	random copolymer
<i>m</i> -	<i>meta</i>
<i>o</i> -	<i>ortho</i>
<i>p</i> -	<i>para</i>
P	poly

Repeating units

AMS	α -methylstyrene
AN	acrylonitrile
BrPPO	brominated poly(2,6-dimethyl-1,4-phenylene oxide)
MAN	maleic anhydride
MI	maleimide
MMA	methyl methacrylate
MMI	methyl maleimide
MS	methylstyrene
<i>o</i> BrS	<i>o</i> -bromostyrene
<i>o</i> ClS	<i>o</i> -chlorostyrene
<i>o</i> FS	<i>o</i> -fluorostyrene
<i>o</i> MS	<i>o</i> -methylstyrene
<i>p</i> BrS	<i>p</i> -bromostyrene
<i>p</i> ClS	<i>p</i> -chlorostyrene
<i>p</i> FS	<i>p</i> -fluorostyrene
<i>p</i> IS	<i>p</i> -iodostyrene
<i>p</i> MS	<i>p</i> -methylstyrene
PO	2,6-dimethyl-1,4-phenylene oxide
PhMI	phenyl maleimide
S	styrene
SPO	sulfonylated 2,6-dimethyl-1,4-phenylene oxide repeating unit in SPPO

Homopolymers

PAMS	poly(α -methylstyrene)
P <i>m</i> ClS	poly(<i>m</i> -chlorostyrene)
P <i>m</i> MS	poly(<i>m</i> -methylstyrene)
P <i>o</i> BrS	poly(<i>o</i> -bromostyrene)
P <i>o</i> ClS	poly(<i>o</i> -chlorostyrene)

P _o FS	poly(<i>o</i> -fluorostyrene)
P _o MS	poly(<i>o</i> -methylstyrene)
P _p BrS	poly(<i>p</i> -bromostyrene)
P _p ClS	poly(<i>p</i> -chlorostyrene)
P _p FS	poly(<i>p</i> -fluorostyrene)
P _p IS	poly(<i>p</i> -iodostyrene)
P _p MS	poly(<i>p</i> -methylstyrene)
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PS	polystyrene

Copolymers

P(AMS-alt-MAN)	poly(α -methylstyrene-alt-maleic anhydride)
P(AMS-alt-MMI)	poly(α -methylstyrene-alt-methyl maleimide)
P(AMS-alt-PhMI)	poly(α -methylstyrene-alt-phenyl maleimide)
P(MMA-co-AN)	poly(methyl methacrylate-co-acrylonitrile)
P(MMA-co-BMA)	poly(methyl methacrylate-co- <i>n</i> -butyl methacrylate)
P(MMA-co-MAN)	poly(methyl methacrylate-co-maleic anhydride)
P(<i>o</i> BrS-co- <i>p</i> BrS)	poly(<i>o</i> -bromostyrene-co- <i>p</i> -bromostyrene)
P(<i>o</i> ClS-co- <i>p</i> ClS)	poly(<i>o</i> -chlorostyrene-co- <i>p</i> -chlorostyrene)
P(<i>o</i> FS-co- <i>o</i> BrS)	poly(<i>o</i> -fluorostyrene-co- <i>o</i> -bromostyrene)
P(<i>o</i> FS-co- <i>o</i> ClS)	poly(<i>o</i> -fluorostyrene-co- <i>o</i> -chlorostyrene)
P(<i>o</i> FS-co- <i>p</i> BrS)	poly(<i>o</i> -fluorostyrene-co- <i>p</i> -bromostyrene)
P(<i>o</i> FS-co- <i>p</i> ClS)	poly(<i>o</i> -fluorostyrene-co- <i>p</i> -chlorostyrene)
P(<i>o</i> FS-co- <i>p</i> FS)	poly(<i>o</i> -fluorostyrene-co- <i>p</i> -fluorostyrene)
P(<i>o</i> MS-co- <i>p</i> MS)	poly(<i>o</i> -methylstyrene-co- <i>p</i> -methylstyrene)
P(<i>p</i> FS-co- <i>o</i> BrS)	poly(<i>p</i> -fluorostyrene-co- <i>o</i> -bromostyrene)
P(<i>p</i> FS-co- <i>o</i> ClS)	poly(<i>p</i> -fluorostyrene-co- <i>o</i> -chlorostyrene)
P(<i>p</i> FS-co- <i>p</i> BrS)	poly(<i>p</i> -fluorostyrene-co- <i>p</i> -bromostyrene)
P(<i>p</i> FS-co- <i>p</i> ClS)	poly(<i>p</i> -fluorostyrene-co- <i>p</i> -chlorostyrene)
P(PhVBE-alt-PhMI)	poly(phenylvinyl sec-butyl ether-alt-phenyl maleimide)
P(PhVEE-alt-PhMI)	poly(phenylvinyl ethyl ether-alt-phenyl maleimide)
P(PO-co-SPO)	SPPO
P(S-co-AMS)	poly(styrene-co- α -methylstyrene)
P(S-co-AN)	poly(styrene-co-acrylonitrile)
P(S-co-MAN)	poly(styrene-co-maleic anhydride)
P(S-co-MMA)	poly(styrene-co-methyl methacrylate)
P(S-co- <i>o</i> BrS)	poly(styrene-co- <i>o</i> -bromostyrene)
P(S-co- <i>o</i> ClS)	poly(styrene-co- <i>o</i> -chlorostyrene)
P(S-co- <i>o</i> FS)	poly(styrene-co- <i>o</i> -fluorostyrene)
P(S-co- <i>o</i> MS)	poly(styrene-co- <i>o</i> -methylstyrene)
P(S-co- <i>p</i> BrS)	poly(styrene-co- <i>p</i> -bromostyrene)
P(S-co- <i>p</i> ClS)	poly(styrene-co- <i>p</i> -chlorostyrene)
P(S-co- <i>p</i> FS)	poly(styrene-co- <i>p</i> -fluorostyrene)

P(S-co-PhMI)	poly(styrene-co-phenylmaleimide)
P(S-co- <i>p</i> MS)	poly(styrene-co- <i>p</i> -methylstyrene)
SPPO	partially sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide); random copolymer = poly(PO-co-SPO)

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