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Blends of poly(styrene-ran-2,4-dinitrostyrene) with poly(vinyl methyl ether) and poly(2,6-dimethyl-1,4-phenylene oxide)

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Phase boundaries and lower critical solution temperatures for blends of random styrene–dinitrostyrene copolymers with poly(vinyl methyl ether) and with poly(2,6-dimethyl-1,4-phenylene oxide) have been established. From an analysis of phase behaviour in terms of the overall blend interaction energy density the relevant segmental interaction energy densities have been evaluated and these have been compared with the corresponding energy densities for mononitrated copolymers. It was concluded that nitro group substitution has an adverse effect on mixing with poly(vinyl methyl ether) despite its electron withdrawing capabilities, and causes a similar effect in poly(2,6-dimethyl-1,4-phenylene oxide) mixtures for primarily structural reasons. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Over the years two particular polystyrene (PS) blends have continued to arouse interest: polystyrene with poly(vinyl methyl ether) (PVME) and polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Both form miscible blends at room temperature and, although the former shows well-defined lower critical solution demixing behaviour (l.c.s.t.) at moderately low temperatures[1], the latter blend remains single-phase until thermal degradation intervenes.

The thermodynamic drive for miscibility in both these blends involves a specific interaction between the components. In the case of PS + PVME a thermally labile donor–acceptor type interaction between ether and aromatic ring has been inferred from changes in i.r. absorption peaks of the components, both on mixing to form the single phase blend and on increasing the temperature to destabilize the blend[2,3]. N.m.r. measurements in solution have shown that the ether lone pair closely approaches (within 0.5 nm) the phenyl group[4], while in the bulk mixture the nuclear Overhauser enhancement suggests that the phenyl ring is actually closer to the ether group than its own main chain carbon atoms[5]. A similar donor–acceptor interaction has been detected from i.r. studies on PVME–poly(styrene-*co*-vinylnaphthalene) blends[6] with the larger naphthyl group acting as acceptor, and also in PVME blends with poly(2-chlorostyrene)[7]. In this latter case the details of the spectra were used as evidence for a more restricted ether group rotational environment, and this in its turn was taken to indicate the presence of a stronger ether oxygen–aromatic attraction than that in PS blends, resulting from the chlorine's electron withdrawing effects.

PS + PPO blends are found to be homogeneous on an n.m.r. spin-diffusion distance scale of a few nanometres[8]; the PS–PPO distance has been estimated as ~0.5 nm in the intimately mixed phase, though there also appear to be present heterogeneous domains on the 10 nm scale[9]. Spin relaxation measurements indicate that there is π–π conjugation interaction between the aromatic rings of PS and PPO, this being sufficiently strong to promote cooperative movement of the rings which is proposed to be the basis for the excellent impact strength of the blends[9]. Cooperative chain relaxation and orientational relaxation effects in PS + PPO blends have been observed by other techniques[10–12]. Concentration fluctuations obtained from n.m.r. measurements are found to be stronger in PS homopolymer than in PS + PPO blends, indicating that the π–π interaction is more favourable to homogeneity in the blend than in the homopolymer[13,14].

Blends of PPO and PVME with styrenic copolymers have also been the subject of attention. The behaviour of styrene–acrylonitrile, styrene–maleic anhydride and styrene–acrylic acid (SAN, SMA and SAA) copolymer

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blends are reported by Min and Paul[15] and by Wendland *et al.*[16] with respect to both l.c.s.t. behaviour and miscibility with PVME. Styrene–methyl methacrylate (SMMA) copolymers were similarly examined by Chien *et al.*[17]. In each case, and also in the poly(styrene-*co*-vinylnaphthalene) system already mentioned[6], as the comonomer concentration increases some point is reached at which the copolymers are no longer miscible with PVME. Composition-dependent miscibility limits are also observed for PPO–styrene copolymer blends, for example with acrylic and methacrylic comonomers[18], with styrene-4-chlorostyrene copolymers[19] and with SMA copolymers[20].

The phase boundary behaviour of copolymer blends as a function of copolymer composition can be described by a mean-field blend interaction parameter, B_{blend}, analagous to the Flory energy density parameter for a binary mixture[21–23]. In the particular instance of a homopolymer A blended with a statistical copolymer C_yD_{1-y} the relevant relation is[24,25]

$$B_{\text{blend}} = yB_{AC} + (1-y)B_{AD} - y(1-y)B_{CD} \qquad (1)$$

where B_{ij} characterizes the heat of mixing contribution of an i–j segmental contact. A segment is conventionally taken as a monomer repeat unit and y is the volume fraction of comonomer C in the copolymer. The negative term in equation (1) above ensures (for appropriate values of the B_{ij}) that the value of B_{blend} can be less than any individual B_{ij} value. Under these conditions miscibility is ensured even though homopolymers of A, C and D may all be mutually immiscible, hence the original adoption of the description 'repulsion' theory of copolymer miscibility[26,27]. We ourselves would prefer to regard such an 'intramolecular repulsion' term more as a consequence of the form of equation (1) since B_{ij} values are measures of the relative strengths of the forces involved.

Stable single phase blends exist when B_{blend} is less than some critical value (B_{crit}) and two-phase behaviour occurs when B_{blend} is greater than this critical value. B_{crit} for a mixture of infinite molar mass polymers is zero, otherwise it is given by the expression[21]

$$B_{\text{crit}} = 0.5RT(V_1^{-1/2} + V_2^{-1/2})^2 \qquad (2)$$

where V_1 and V_2 are the molar volumes of the two components.

Equation (1) is of course a quadratic with two solutions y_1 and y_2 which are the limits of miscibility of homopolymer A in copolymer C_yD_{1-y}. If these are experimentally determined then equations (1) and (2) can be used to evaluate any one of the three B_{ij} values provided two of them are already known. As it stands therefore, equation (1) cannot be applied to either PPO or PVME blends with styrenic copolymers, such as those described above. Since PS itself is fully miscible with both homopolymers these are systems in which only one of the miscibility limits can be experimentally realized, as is illustrated in *Figure 1*. However it has previously been demonstrated by us[24,25] that equation (1) can be combined with its derivative

$$\mathrm{d}(B_{\text{blend}})/\mathrm{d}y = B_{AC} - B_{AD} - B_{CD} + 2yB_{CD} \qquad (3)$$

to give an alternative, but useful, expression for the copolymer composition limits $y_{1,2}$

$$y_{1,2} = y_0 \pm [(B_{CD}y_0^2 - B_{AD} + B_{\text{crit}})/B_{CD}]^{0.5} \qquad (4)$$

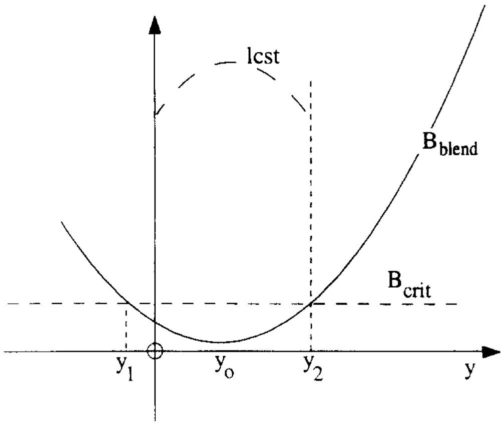

Figure 1 Schematic behaviour of B_{blend} (full line) as a function of copolymer composition y accroding to equation (1). Miscibility limit y_2 occurs in real composition space with $0 < y < 1$. Dashed line represents expected behaviour of the l.c.s.t. for miscible blends with $0 < y < y_2$

where y_0 is the minimum value taken by B_{blend}. We have applied[24,25] this relation successfully to previously unanalysed literature data and to our own data on PVME and PPO blends with styrene–nitrostyrene (SNS) copolymers and have obtained the interaction energy density for VME and PO contacts with both the *meta*-nitrostyrene (*m*NS) and the *para*-nitrostyrene (*p*NS) repeat units. In this paper we extend our investigation into the behaviour of blends of PVME and of PPO with styrene–dinitrostyrene (SDNS) copolymers in which there is a strong electron withdrawing effect from the nitro substituents and which in turn may have some detectable influence on miscibility.

Binary combinations of the same copolymer but having different compositions, C_yD_{1-y} and C_xD_{1-x}, can also be described[25] by an appropriate mean-field expression for B_{blend}. When $x = y$ the copolymers are identical and miscibility is of course assured, but at some $x \neq y$ the copolymers will no longer form single-phase blends and this condition occurs when their compositions differ by a particular composition difference δy which is given by

$$\delta y = 2(B_{\text{crit}}/B_{CD})^{0.5} \qquad (5)$$

Thus for any real copolymer, having a non-zero positive intramolecular energy density, phase separation will occur if two sufficiently disparate compositions are mixed.

EXPERIMENTAL

Homopolymer samples

The PVME sample was obtained from Polysciences (50% aqueous solution) and a fraction was isolated from toluene using petroleum ether as precipitant to reduce the polydispersity. Poly(2,6-dimethyl-1,4-phenylene oxide) (Aldrich, $T_m = 541$ K) was used without any further purification. Details are in *Table 1*.

Copolymers of styrene and dinitrostyrene

These were prepared by the vigorous nitration of polystyrene. Polystyrene (Aldrich, $\bar{M}_w = 280\,000$, 1 g) was dissolved in 17.2 cm^3 of 1,2-dichloroethane in a round-bottomed flask equipped with stirrer, thermometer and addition funnel and a 1/1 mixture of fuming nitric acid and 96% sulfuric acid was added dropwise

Table 1 Details of polymers and copolymers used

Sample code[a]	Volume fraction[b] DNS in copolymer	$10^{-3} M_n$ (g mol^{-1})	T_g (K^{-1})
PS	—	109	377
SDNS3	0.04	108	382
SDNS4	0.05	110	385
SDNS9	0.12	—	390
SDNS12	0.15	—	393
SDNS14	0.18	—	397
SDNS18	0.23	—	406
SDNS20	0.25	—	403
SDNS31	0.38	—	417
SDNS33	0.40	—	422
SDNS51	0.58	—	443
SDNS53	0.60	—	460
PVME	—	20	244
PPO	—	16	478

[a] The numbers indicate the mole fraction of dinitrostyrene in poly(styrene-ran-2,4-dinitrostyrene)

[b] Calculated from mole fraction using group additivity tables[29]

with vigorous stirring at 273 K. The reaction mixture was left stirring at room temperature for up to 30 min and then poured into an excess of chilled water. The resulting precipitate was filtered and washed with water then with methanol, redissolved in dimethylformamide (DMF) and reprecipitated in water. The polymer was filtered, washed with water then methanol and dried to constant weight at 313 K under vacuum. Nitration levels were controlled by changing the amount of nitric acid–sulfuric acid mixture.

Copolymer analysis

The copolymer samples were examined by i.r. spectroscopy as KBr discs using a Perkin–Elmer 2000 *FT* i.r. spectrometer. The spectra of the copolymers exhibited the characteristic bands of the nitro group at 1345 cm^{-1} and at 1520 cm^{-1} and a further band at 855 cm^{-1} indicated the presence of two adjacent hydrogens. The nitro group placement was established by the i.r. absorption pattern in the 2000–1600 cm^{-1} region which was characteristic for a 1,2,4-substituted benzene ring. The nitration process is assumed to be random and so these copolymers may be described as poly(2,4-dinitrostyrene-ran-styrene) (DNS-S). Further evidence for dinitration is presented below. The molar masses of two of the samples were measured in tetrahydrofuran by g.p.c. (Waters LC-150) and this showed that no measurable degradation had occurred during nitration. The degree of substitution was obtained from elemental analysis.

Blend preparation

Blends containing PVME were prepared by codissolving (co)polymer samples in DMF, casting the solution onto a slide and evaporating the solvent at room temperature. Blends containing PPO were prepared by codissolving (co)polymer samples in a 3/1 mixture of nitrobenzene and DMF and then precipitating the solution into methanol. Solids were filtered and dried at 300 K under vacuum for 2 days.

Blend behaviour

Glass transitions (T_g) were determined by d.s.c. using a Polymer Laboratories DSC-700. Samples were analysed at scan rates of 20 K min^{-1} until reproducible behaviour was obtained. The appearance of a single glass transition was taken as the criterion for blend miscibility. Further annealing of the samples at ($T_g + 25$ K) caused no further changes in phase behaviour. Where the component T_gs were too close to resolve the method of physical ageing[28] was adopted and the criterion of miscibility was then the appearance of a single enthalpy relaxation peak. The temperatures of blend demixing were determined visually for solvent-cast thin films using a programmable hot stage.

Molar volumes and B_{crit} values, and volume fraction compositions, were calculated using van Krevelin's group additivity scheme[29] and assuming that the degree of polymerization of the parent PS had remained unchanged on nitration.

RESULTS OF MISCIBILITY MEASUREMENTS

Internal miscibility of DNS-S copolymers

Provided y_0, the minimum in B_{blend}, and one B_{ij} value are known, simultaneous solution of equations (3) and (4) provides a method of determining the remaining two unknown B_{ij} values. To this end the internal miscibility of 50/50 w/w solution-cast blends of $DNS_xS_{1-x} + DNS_yS_{1-y}$ was first established, and this is shown in *Figure 2* where the one-phase and two-phase combinations of copolymers are plotted as a function of the composition variables x and y. This type of miscibility 'map' is symmetric about the diagonal which represents mixtures of copolymers with identical compositions and the two dashed lines give our best estimate of the compositional disparity $\delta y = 0.16 \pm 0.01$ that brings about immiscibility. Using an averaged copolymer molar volume of 10.6×10^4 cm^3 mol^{-1} in equation (2) identifies B_{crit} as 0.049 J cm^{-3} and equation (5) then yields a value for $B_{S\text{-}DNS}$ of 7.5 ± 1.0 J cm^{-3}.

Blends of DNS-S with PVME

Table 2 indicates that blends of PVME with DNS_yS_{1-y} are miscible from $y = 0$ to $y = 0.18$ but exhibit two-phase behaviour for $y \geqslant 0.23$. The single-phase blends all show lower critical solution temperature behaviour

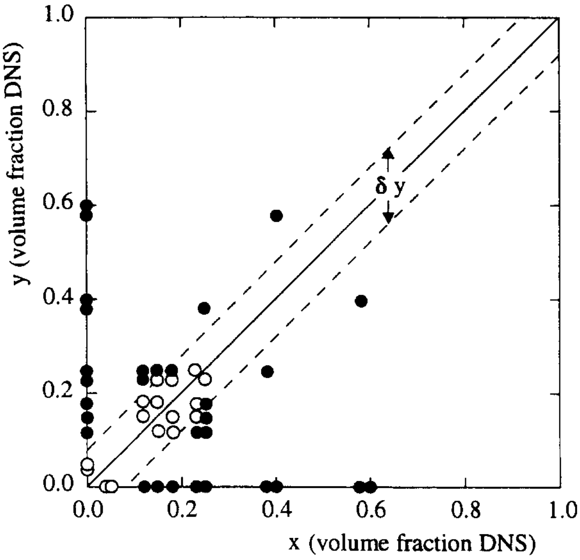

Figure 2 Miscible (open circles) and immiscible (filled circles) blends of styrene–dinitrostyrene copolymers of different compositions. x and y are the volume fractions of styrene in the copolymers

and these phase separation temperatures are plotted in *Figure 3*. If it is assumed that the temperature variation of B_{blend} is constant over this composition range then the maximum in l.c.s.t. behaviour will occur at y_0, the minimum value of B_{blend}, as indicated schematically in *Figure 1*. The maximum was located by fitting the l.c.s.t. values to the best parabola to give $y_0 = 0.085$. Now B_{crit} is $0.131\,\text{J}\,\text{cm}^{-3}$ in this blend system and, with $y_2 = 0.18$–0.23 from above, equations (3) and (4) may then be solved for both $B_{\text{S-VME}}$ and $B_{\text{VME-DNS}}$. From this analysis of the data we find that $B_{\text{S-VME}}$ lies within the range 0.03–$0.10\,\text{J}\,\text{cm}^{-3}$. This numerical uncertainty reflects the latitude in the composition limit y_2 but even so this is in very good agreement with our other values derived from phase boundary analysis[24,25]. Finally, using this present estimate for $B_{\text{S-VME}}$ gives the third interaction in the homopolymer–copolymer system, $B_{\text{VME-DNS}}$ as $6.3 \pm 1.0\,\text{J}\,\text{cm}^{-3}$.

Blends of DNS-S with PPO

The analysis of phase behaviour in this system is of necessity limited to the determination of the blend glass transitions listed in *Table 2* since all the single-T_g miscible combinations showed thermal degradation before the appearance of an l.c.s.t. Indexing this system as PPO + $\text{DNS}_y\text{S}_{1-y}$, the break between one-phase and two-phase behaviour is again between $y = 0.18$–0.23. The (negative) interaction energy density for the styrene–phenylene oxide contact has already been established[25] ($B_{\text{PO-S}} = -1.6\,\text{J}\,\text{cm}^{-3}$), as is $B_{\text{S-DNS}}$ from the analysis above, and with $B_{\text{crit}} = 0.156\,\text{J}\,\text{cm}^{-3}$ equation (1) gives $B_{\text{PO-DNS}} = 12.3 \pm 1.0\,\text{J}\,\text{cm}^{-3}$.

All the B_{ij} data are collected in *Table 3* along with data previously reported from analysis of blends of PVME and PPO blends with S*m*NS and S*p*NS copolymers.

Table 2 Glass transition temperatures and l.c.s.t. values for all blends

Sample code	Blend with PVME T_g (K^{-1})	l.c.s.t. (K^{-1})	Blend with PPO T_g (K^{-1})
PS	260	368	415
SDNS3	261	398	417
SDNS4	263	403	415
SDNS9	258	403	416
SDNS12	261	388	420
SDNS14	260	353	419
SDNS18	244 + 390	—	420 + 464
SDNS20	247 + 399		402 + 475
SDNS31	248 + 410	—	415 + 478
SDNS33	245 + 414	—	427 + 465
SDNS51	247 + 436	—	
SDNS53	249 + 443		

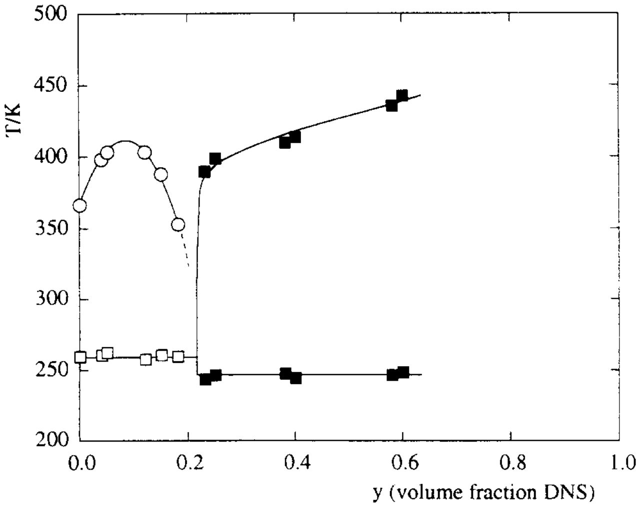

Figure 3 T_g values for PVME + S-DNS blends. Open squares are single-phase blends, filled squares are two-phase blends. The open circles are the l.c.s.t. values for the single-phase blends

DISCUSSION

Prior to discussing the B_{ij} values the T_g–composition behaviour of the three sets of styrene–nitrostyrene copolymers is presented in *Figure 4*. The markedly divergent compositional trend observed for the nitrated polystyrene samples prepared by the technique described in the Experimental section provides convincing additional evidence for the dinitration of the parent polystyrene. The progressive increase in T_g with structure is reasonably to be expected from the combined effects of changes in polarity as well as greater steric effects. The T_g for the hypothetical fully dinitrated polystyrene (PDNS) is probably in the region of 500 K.

The interaction between PS and PVME has been investigated by many groups of workers employing a variety of techniques. The three $B_{\text{S-VME}}$ entries in *Table 3* are all based on the analysis of phase boundaries

Table 3 Summary of interaction parameter values

i j	B_{ij} ($\text{J}\,\text{cm}^{-3}$)	Ref.
S-VME	0.14	24
S-VME	−0.05	25
S-VME	0.07	This work
S-*m*NS	3.6	24
S-*p*NS	4.2	25
S-DNS	7.5	This work
VME-*m*NS	2.8	24
VME-*p*NS	3.0	25
VME-DNS	6.3	This work
PO-S	−1.6	12
PO-*p*NS	6.2	25
PO-DNS	12.3	This work

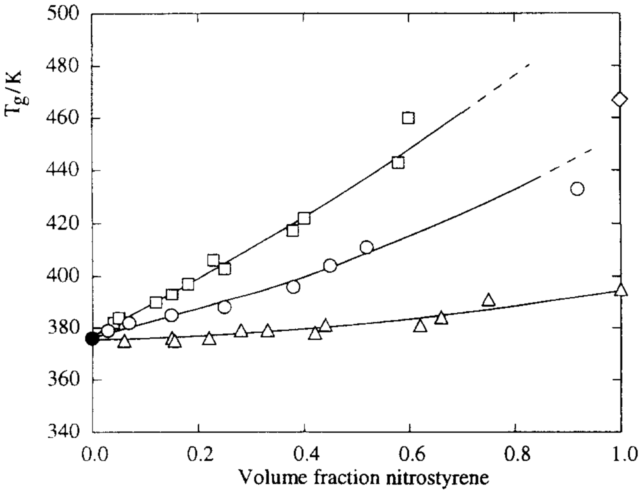

Figure 4 T_g values for S-DNS copolymers (squares), S-*p*NS copolymers (circles) and S-*m*NS copolymers (triangles) plotted against volume fraction of the nitro comonomer. The filled circle is the T_g of polystyrene. The diamond is the suggested T_g for P*p*NS from ref. 43

and average out at a small positive value of $\sim 0.05\,\mathrm{J\,cm^{-3}}$, in close agreement with other 'solvent-free' measurements[30–32]. Data from solution techniques[33,34] on the other hand tend to suggest a negative, although still small, value for $B_{\text{S-VME}}$ which may have a small tacticity dependence[35]. We have reviewed this interaction before[24] and the present result does not contradict a general conclusion—that PS + PVME is best regarded as an example of an athermal mixture in which a weak specific interaction counteracts the effect of the unlike contact dispersive forces.

On a simplistic solubility parameter argument the response of PVME + PS to the replacement of styrene by another comonomer, such as in the blends referred to in the Introduction, should be either (a) a gradual reduction in miscibility with a composition limit at which two-phase blends occur or (b) miscibility across the whole composition range; the latter occurring when the complementary homopolymer is itself miscible with PVME and the former when it is not. Examples of this latter behaviour appear to be absent in the literature, poly(2-chlorostyrene) is fully miscible with PVME with perhaps an even more favourable specific interaction than for PS itself[7], and so copolymers with styrene should likewise exhibit miscibility. This argument requires caution since styrene-4-vinylbenzene phosphonic acid copolymers, with enhanced (proton) donor abilities, become immiscible with PVME at compositions with greater than ~ 13 mol% acid[36]. This may however be due to the competing self-association of the copolymer in this case.

PVME + DNS belongs the former group, exhibiting immiscibility at some definite copolymer composition. The l.c.s.t. behaviour in this system (*Figure 3*), that of S-*m*NS and S-*p*NS blends[24,25] and blends of PVME with SAN, SMMA and SMA[15,17] copolymers all provide a convincing basis for the application mean field arguments [equation (1)] rather than solubility parameter arguments. These predict monotonic changes in mixing thermodynamics, as opposed to enhanced miscibility at some intermediate composition. Even so, the introduction of the electron withdrawing nitro groups appears to have had little beneficial effect on mixing here as can be seen by comparing the appropriate B_{ij} values in *Table 3*. The somewhat unfavourable interaction energy densities $B_{\text{VME-mNS}}$ and $B_{\text{VME-pNS}}$ were previously ascribed to steric constraints on the close approach of the π system and the ether link. The effect of essentially steric impositions alone is best given by the behaviour of PVME blended with styrene–methylstyrene copolymers. In all cases, *ortho*-, *meta*- and *para*-methyl substitution cause the l.c.s.t. values to decrease[37], interestingly in this case without going through an apparent maximum. Steric arguments are *a fortiori* applicable to PVME + S-DNS, the even more adverse outcome ($B_{\text{VME-DNS}} = 6.3\,\mathrm{J\,cm^{-3}}$) is obvious despite a possibly stronger π electron withdrawal. Dinitration appears to have brought about reduced miscibility from steric effects as evidenced by the interaction energy densities and also the decreased l.c.s.t. values compared with S-*m*NS and S-*p*NS blends.

Table 3 also shows that the intramolecular interaction between styrene and nitrostyrene becomes distinctly more unfavourable on introduction of the second nitro group, i.e. the value of $B_{\text{S-DNS}}$ is larger than the corresponding interaction energy densities for styrene with *meta*-nitrostyrene and with *para*-nitrostyrene, $B_{\text{S-mNS}} = 3.6\,\mathrm{J\,cm^{-3}}$ and $B_{\text{S-pNS}} = 4.2\,\mathrm{J\,cm^{-3}}$ respectively. These latter values are quite similar and indicate that in mononitrated copolymers the actual position of the nitro group has a minor effect on the magnitude of B_{ij}. The much increased interaction resulting from dinitration is then best explained by the greater polarity differences between styrene and its mono- and disubstituted analogues respectively although the packing or correlation requirements[38] of the phenyl rings must also be severely disrupted.

The last set of interactions listed in *Table 3* involves PPO. The molecular basis for the negative phenylene oxide–styrene interaction are favourable van der Waals forces arising from the possible coplanar arrangements of π systems in their mixtures. Similar intramolecular coplanar π–π interactions contribute to relatively favourable all-*trans* low energy conformational arrangements in polystyrene itself[39]. The possibilities for energy lowering by this mechanism are absent in combinations of phenyl units where these geometric arrangements are impeded, and a potentially favourable negative contribution to the mixing thermodynamics is similarly absent. This is evidently the case in the immiscible mixtures of *ortho*- and *para*-chlorostyrene[40] homopolymers with PPO. Clorostyrene–styrene copolymers are also immiscible with PPO[19,20,41] unless the styrene content of the copolymer is relatively high.

The possibility of coplanar interactions between phenyl units and nitrophenyl units is similarly absent as indicated intramolecularly by the limited internal miscibility of these copolymers and the consequent positive values of $B_{\text{S-mNS}}$, $B_{\text{S-pNS}}$ and $B_{\text{S-DNS}}$. The same is true intermolecularly in their PPO blends from the values for $B_{\text{PO-pNS}}$ and $B_{\text{PO-DNS}}$ shown in *Table 3*. This last interaction energy density is in fact relatively large and invites some further comment in terms of the alternative interpretation of interaction energy density which incorporates the combined effects of purely enthalpic interactions and free volume differences between the components. This aspect of B_{ij} has been addressed in the context of repulsion theory[42] for blends of PVME with styrene copolymers[15,17] but it is impossible to treat quantitatively in the present case in the absence of the necessary equation of state data. However, since relative T_g values are an approximate guide to the relative free volume of two polymers we suggest that here the adverse PO–DNS interaction is primarily due to the significant structural disparity between the segments, i.e. to extremely unfavourable van der Waals interactions, rather than originating in a free volume disparity since both these polymers have comparable glass transitions.

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