

Differential Scanning Calorimetry Study on Intermolecular Interactions in Polymer–Diluent Blends Involving Polyisoprenes and Dimethyl Terephthalate

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Synopsis

The classical expression for estimating the polymer–solvent interaction parameter χ from melting point data of the solvent is refined by considering χ to be concentration-dependent. Differential scanning calorimetry (DSC) measurements are performed on blends of *cis*-polyisoprene–dimethyl terephthalate (DMT) and *trans*-polyisoprene–DMT. It is found that the presence of DMT would not affect the DSC events of the polyisoprenes appreciably. However, in both cases, the melting point of DMT decreases, and the rate of depression increases with increasing proportions of polymer. These DSC data are analyzed by the proposed procedure. The results on the interaction energy density parameter are presented as a function of the blend concentration, and rationalized by the specific interactions between different moieties on the component molecules. The limitations of the present technique are discussed.

INTRODUCTION

The thermodynamic properties of high polymers in low molecular weight solvents or diluents are characteristically different from those predicted by Raoult's law even at low concentrations. These pronounced deviations from ideality are attributed to the considerable differences in size between the two distinct components in the systems by the classical lattice model of polymer solutions,¹ which describes the intermolecular interactions in terms of the polymer–solvent interaction parameter χ or the interaction energy density B . A number of methods has been established to determine the parameter χ (or B) of polymer solutions.^{2,3} Among them, the melting point depression method (MPDM) is of particular interest to us in the present investigation.

Kawai⁴ has reported the χ values for the solutions of polystyrene and poly(vinyl acetate) in benzene and poly(vinyl alcohol) in water obtained from the melting point depression data of the solvents. Anaguostopoulos and Coran⁵⁻⁷ have resorted to measuring the melting points of the polymers as to determine the B values of the semicrystalline poly(vinyl chloride) and polyethylene in a spectrum of diluents covering a wide variety of molecular structures. Recently, there has been an intense interest in probing the semicrystalline polymer–amorphous polymer interactions by MPDM, particularly for compatible polymer blends.⁸⁻¹¹ In this work, MPDM is applied to study the intermolecular interactions in binary blends prepared by mixing *cis*-

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and *trans*-polyisoprenes (designated respectively by CPI and TPI hereafter) with dimethyl terephthalate (DMT).

MELTING POINT DEPRESSION OF DILUENT

According to the Flory-Huggins theory of polymer solutions,¹ the free energy of mixing, ΔG_m , at temperature T is given by

$$\Delta G_m = RT(N_1 \ln v_1 + N_2 \ln v_2 + \chi N_1 v_2) \quad (1)$$

where R is the gas constant, N_1 and N_2 are numbers of moles of diluent (or solvent) and polymer, respectively, and v_1 and v_2 are their respective normalized volume fractions. It follows that the difference between the chemical potentials of the diluent in solution and in pure state is

$$\mu_1 - \mu_1^0 = RT\{\ln v_1 + (1 - 1/x)v_2 + v_2[\chi + (\partial\chi/\partial \ln v_1)_T]\} \quad (2)$$

where x is the ratio of the molar volumes of polymer and solvent. In the ensuing presentation, $1/x$ will be dropped in comparison with unity in eq. (2) for sufficiently large polymers. A unique feature of eq. (2) is the incorporation of a derivative on the right-hand side of the equation by considering χ as a function of v_1 , contrary to the conventional treatment.¹²

Thermodynamic considerations of the equilibrium melting process of diluent at T result in¹

$$\mu_1 - \mu_1^0 = \Delta \bar{H}_1^0 (T/T_{m1}^0 - 1) \quad (3)$$

where $\Delta \bar{H}_1^0$ is the molar heat of fusion of the pure diluent with melting point T_{m1}^0 . At $T = T_{m1}$, the melting point of the diluent of concentration v_1 , eqs. (2) and (3) lead to

$$\chi'_0 = \chi' + \left(\frac{\partial \chi}{\partial \ln v_1} \right)_{T_{m1}} \quad (4)$$

where

$$\chi'_0 = \left[\frac{\Delta \bar{H}_1^0}{R} \left(\frac{1}{T_{m1}^0} - \frac{1}{T_{m1}} \right) - (\ln v_1 + v_2) \right] / v_2^2 \quad (4')$$

and χ' refers to χ at T_{m1} .

The parameters χ and B are correlated by

$$\chi = B\bar{V}_1/(RT) \quad (5)$$

where \bar{V}_1 is the molar volume of the diluent. A general form of B is suggested to be given by a series as follows:

$$B = \sum_{i=0} \left(\sum_{j=0} G_{ij} T^j \right) v_1^i \quad (6)$$

where the G_{ij} 's are the empirical constants. Clearly, eq. (6) is rather intractable. Hence, in practice we assume

$$B = M + b \ln v_1, \quad v_1 > 0 \quad (7)$$

where b is an empirical constant and

$$M = \sum_{i=0} a_i (T_{m1}/T)^i, \quad T \geq T_{m1} \quad (8)$$

with all a_i 's being the empirical constants. Substituting eqs. (5), (7), and (8) into (4) yields

$$T_{m1}\chi'_0 = \frac{\bar{V}'_1}{R} \left\{ \left[a + b + \left(\frac{\partial \ln T_{m1}}{\partial \ln v_1} \right) \sum_{i=0} i a_i \right] + b \ln v_1 \right\} \quad (9)$$

where \bar{V}'_1 is the \bar{V}_1 at T_{m1} and

$$a = \sum_{i=0} a_i \quad (9')$$

It will be demonstrated that a plot of $T_{m1}\chi'_0$ against $\ln v_1$ produces a straight line. This implies that

$$\sum_{i=0} i a_i = 0 \quad (10)$$

and \bar{V}'_1 is essentially a constant over the experimental range of T_{m1} . Hence, the empirical constants a and b can be readily derived from the intercept and gradient of the foregoing linear plot, allowing one to compute the B value at T_{m1} designated by B' hereafter via

$$B' = a + b \ln v_1, \quad v_1 > 0 \quad (11)$$

However, the individual coefficients a_i 's are indeterminable herein.

EXPERIMENTAL

The CPI and TPI used were respectively a natural rubber (RRIM 600) and a synthetic rubber with their respective nominal intrinsic viscosities at 30°C in toluene equal to 6 and 3 dL/g. The latter was supplied by Dunlop Ltd. (U.K.) and had been studied in an earlier work.¹³ DMT was purchased from L. Light Co. Ltd. (U.K.) and purified by means of sublimation technique at 160°C under reduced pressure. Spectroscopy grade benzene (Merck) was dried over a molecular sieve before use.

For sample preparation, appropriate amounts of the rubber and diluent were weighed accurately into containers, where portions of 50 mL benzene were added to dissolve the solutes at room temperature. The solutions [$\sim 1\%$ (w/v)] thus prepared were then frozen with liquid nitrogen, and the benzene was subsequently sublimed under 1 mm Hg, until blends of constant weights were achieved.

A Perkin-Elmer differential scanning calorimeter (DSC), Model DSC-2, equipped with a liquid nitrogen subambient cooling accessory and a Perkin-Elmer thermal analysis data station (TADS) were used throughout these investigations. The purge gas was helium. The instrument was calibrated against cyclohexane, mercury, water, and indium at a scan rate of 10 K/min.

Blends (~ 17 mg) were encapsulated in the "high pressure" aluminum pans, and heated to 472 K at 20 K/min, held at 472 K for 2 min, and quenched to 170 K at 320 K/min. All DSC scans were performed at 20 K/min from 170 to 470 K. However, for the CPI series, the sealed samples were preannealed at $-23 \pm 3^\circ\text{C}$ for at least 5 h, before they were cooled directly to 170 K where the DSC measurements commenced.

The onset of heat capacity jump and the peak of melting curve respectively determine the glass transition temperature T_g and the melting point T_m of the sample. The area under the melting endotherm for pure DMT was recorded as the heat of fusion of diluent ΔH_1^0 . All these thermal data were estimated by the TADS standard program. They were found to be reproducible by rerunning the samples, indicating no significant thermal degradation.

The volume fraction of polymer (v_2) is given by

$$v_2 = [1 + w_1\rho_2/(w_2\rho_1)]^{-1} \quad (12)$$

where ρ_1 and ρ_2 are, respectively, the densities of DMT and polymer with their respective normalized weight fractions designated by w_1 and w_2 . Over the experimental range of T_{m1} , we estimated¹⁴ the average values of $\rho_1 = 1.193$ g/mL and $\rho_2 = 0.853$ g/mL for CPI and 0.888 g/mL for TPI. The $\Delta\bar{H}_1^0$ of DMT is 7.6 kcal/mol.

RESULTS AND DISCUSSION

Table I lists the raw data of the melting point (T_{m1}) of DMT as obtained from the DSC thermograms for the CPI–DMT and TPI–DMT blends. The values of v_2 and χ'_0 are calculated by eqs. (12) and (4') respectively. These two equations are then treated by means of variance analysis to obtain the standard deviations of v_2 and χ'_0 shown herein, based on the various errors detailed in the table. As expected, the reliability of χ'_0 estimates becomes less impressive for the extreme cases, viz. when v_2 approaches zero and unity. Hence, this particular procedure is best applied to blends of polymer volume fractions varying from ~ 0.5 to ~ 0.9 .

Figure 1 shows that the T_{m1} decreases monotonically with increasing v_2 . Apparently, the TPI is more effective in depressing the T_{m1} than the CPI, reflecting stronger interactions existing between the former and DMT. The magnitude of this deviation will be touched on later. However, the two distinct curves seem to cross at approximately $v_2 = 0.93$. This is not unexpected as the T_m of TPI is considerably higher than that of CPI.

Unlike the above findings for DMT, the thermal transition temperatures of the rubbers in the blends are virtually invariant with their compositions. The values of T_g and T_m for CPI are respectively found to be 207.8 ± 0.9 K and 303.6 ± 2.9 K, whereas the corresponding values for TPI are 201.5 ± 1.1 K and 336.9 ± 3.5 K over the range of compositions envisaged herein. Burfield

TABLE I
Thermodynamic Parameters of Blends CPI-DMT and TPI-DMT

System	No.	T_{m1} (K)	v_2	χ'_0	β
DMT	1	424.2	0.0	—	—
CPI-DMT	2	423.2	0.318 ± 0.007^a	0.43 ± 0.40^b	0.20
	3	421.7	0.612 ± 0.007	0.75 ± 0.11	0.43
	4	411.5	0.765 ± 0.006	0.69 ± 0.08	0.56
	5	407.9	0.832 ± 0.004	0.85 ± 0.07	0.63
	6	398.9	0.863 ± 0.003	0.86 ± 0.06	0.68
	7	379.9	0.934 ± 0.002	0.84 ± 0.21	0.74
	8	303.6	1.000	—	—
	TPI-DMT	9	423.0	0.309 ± 0.007	0.37 ± 0.42
10		416.3	0.602 ± 0.007	0.41 ± 0.12	0.51
11		410.6	0.758 ± 0.006	0.63 ± 0.08	0.57
12		403.4	0.827 ± 0.004	0.68 ± 0.07	0.61
13		396.4	0.876 ± 0.003	0.76 ± 0.07	0.64
14		382.0	0.931 ± 0.002	0.86 ± 0.20	0.68
15		336.9	1.000	—	—

^aStandard deviation of v_2 based on the precision of the ratio ρ_2/ρ_1 estimated to be $\pm 3\%$, and the experimental uncertainty in weight measurements of the blends equal to $\pm 1.0 \times 10^{-4}$ g.

^bStandard deviation of χ'_0 based on the experimental uncertainty in T_{m1} (and T_{m1}^0) estimated to be ± 1.2 K for $v_2 \leq 0.9$ and ± 2.5 K for $v_2 > 0.9$. The precision of $\Delta\bar{H}_1^0$ is estimated to be $\pm 3\%$.

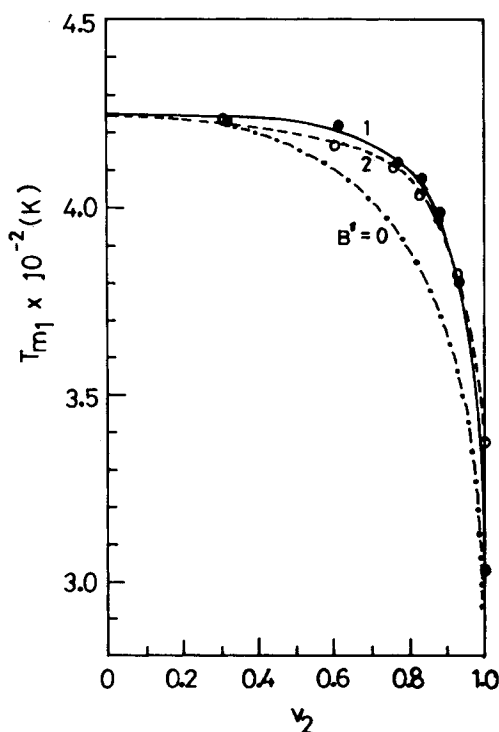


Fig. 1. Depression of the melting point of DMT at various compositions of CPI (●, curve 1) and TPI (○, curve 2). The dash-dot curve is for athermal mixing with $B' = 0$.

and Lim¹³ have quoted the T_g of the natural rubber and TPI to be 206.3 and 201.6 K, respectively, at 20 K/min. The melting points of CPI and TPI are documented¹⁵ as 301 and 338 K, respectively. The present values obtained are indeed comparable with those cited in the literature for the transition temperatures of these two polydienes. However, our foregoing T_m data from various DSC measurements are marginally inconsistent, with a standard error of $\sim 1\%$. This is not uncommon as the melting behavior of the semicrystalline polymers depends remarkably on their morphological states.^{9,16} In any event, no attempt was made to obtain the equilibrium T_m of the polymers by means of Hoffman-Weeks plot.¹⁷

The preceding findings simply suggest that specific interactions between moieties on the polyisoprenes and DMT can be realized only in the molten state. At temperatures below the melting curves shown in Figure 1, the solid DMT may just function as an inert filler which, by no means, would alter the phase transition characteristics of the polymeric matrices.

To further examine the data quantitatively, linear plots of $T_{m1}\chi'_0$ against $\ln v_1$ are constructed in Figure 2 for the two series of blends. The intercept and gradient of each of these straight lines are found by the linear least-square calculations to be, respectively, 214, -54.2 cal/mL for CPI-DMT blends and 121, -82.5 cal/mL for TPI-DMT blends. Taking $\bar{V}'_1 = 231$ mL/mol, eq. (11) becomes

$$B' \text{ (cal/mL)} = 2.31 - 0.47 \ln v_1 \quad (13)$$

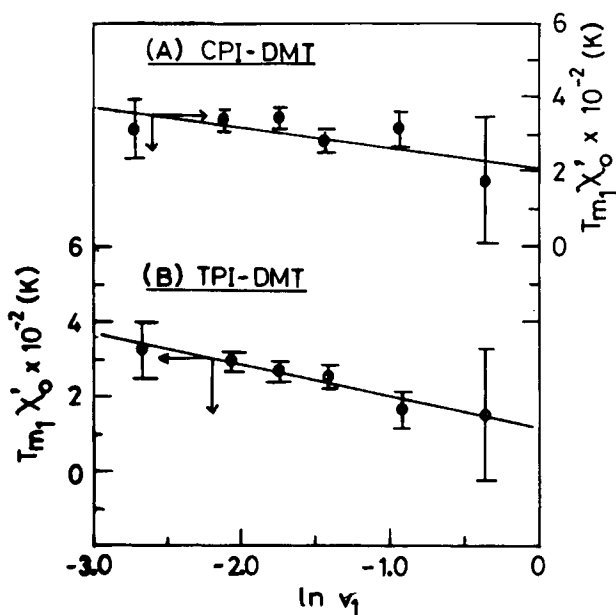


Fig. 2. Linear plots of $T_{m1}\chi'_0$ against $\ln v_1$ for blends (A) CPI-DMT (●) and (B) TPI-DMT (○). All data points have been processed by the linear least-square algorithm to produce the two straight lines shown. The error bar of each data point is indicated.

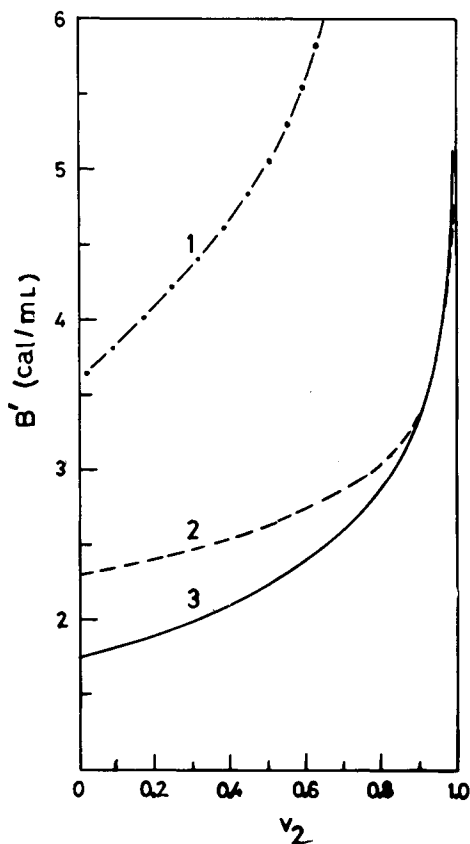


Fig. 3. Variations of b' with v_2 for blends CPI-DMT (curve 2) and TPI-DMT (curve 3) with temperature ranging from 380 to 425 K. Curve 1 is for a reference case of $T_{m1} = T_{m1}^0$.

for the former combinations, and

$$B' (\text{cal/mL}) = 1.75 - 0.70 \ln v_1 \quad (14)$$

for latter pairs.

Equations (13) and (14) are represented graphically by curves 2 and 3 respectively in Figure 3, where the hypothetical curve 1 based on $T_{m1} = T_{m1}^0$ is plotted for comparison's sake. If there are no noticeable intermolecular interactions prevailing in the systems, the T_m of DMT would not be affected by blending. On the contrary, adequate strong interactions would facilitate miscibility of molecules and eventually T_m depression. Hence, curve 1 corresponds to the critical B' , beyond which phase separation occurs. In the present context, a small B' implies enhanced interactions. On this basis, some striking features of Figure 3 are noted as follows. Since curves 2 and 3 are well below the critical curve 1, suggesting significant interactions existing between, probably, the α -hydrogens on the polyisoprenes and the carbonyl groups of the DMT. In addition, the dispersion forces between the double bonds on the polymers and the ester groups of the diluent may also play a secondary role in this connection.

At the constant temperature T_{m1} and pressure P , eqs. (1), (5), and (11) lead to

$$\left(\frac{\partial^2 \Delta G_m}{\partial N_1^2} \right)_{T_{m1}, P} = \frac{RT_{m1}}{N_1} \beta \quad (15)$$

where

$$\beta = 1 - \frac{\bar{V}_1'}{RT_{m1}} [2v_1 a - (1 - 3v_1 - 2v_1 \ln v_1) b] \quad (15')$$

The values of β for CPI-DMT and TPI-DMT mixtures are compiled in Table I. These results correspond to

$$\left(\frac{\partial^2 \Delta G_m}{\partial N_1^2} \right)_{T_{m1}, P} > 0$$

which satisfies the criterion for thermodynamic stability of an one phase mixture. This means that curves 2 and 3 represent two miscible systems resulting from the specific interactions cited above.

The parameter χ or B' may be predicted by the equation of state theory.¹² This theory expresses the thermodynamic properties of polymer solutions in terms of six characteristic parameters of the two pure components and three additional variables intimately related to the polymer-diluent pair. Unfortunately, information on all these physical parameters are not available for the present systems of interest, hence, defying the theoretical calculations of B' herein. However, the present analysis renders a practical means to estimate B' as a function of concentration.

The effects of polymer configuration on the present study are conspicuously illustrated by comparing curves 2 with 3 in Figure 3. Here, the B' value of CPI-DMT blend is higher than that of TPI-DMT mixture at any $v_2 < 0.93$. Specifically, the former is 30% higher than the latter at the infinite dilution (i.e., $v_2 \rightarrow 0$). However, this figure is greatly reduced to 6% at a higher polymer volume content of 80%. Two plausible reasons are advanced to explain these phenomena. First, the α -H in the *cis* position is less approachable than that on TPI by the DMT molecule, which is linear in shape, due to the "steric effects" resulting from the adjacent methyl group on CPI. These "steric effects" would certainly weaken the intermolecular interactions leading to higher B' . Another important contributing factor is related to the unperturbed dimensions of the polymers. The average characteristic ratios for CPI and TPI are estimated from the relevant data on the unperturbed average end-to-end distance and its temperature coefficient^{18,19} to be 5.22 ± 0.05 and 7.08 ± 0.05 , respectively, over the temperature range 100–150°C. This means that CPI chain is, in fact, considerably more compact than its *trans* counterpart. As a result, the α -H atoms on CPI would be more drastically "screened" than those on TPI by the surrounding polymer segments. Again, such "shielding effects" would definitely dampen the interactions of interest. However, the difference in degree of these effects between the two series of blends dimin-

ishes continuously with increasing concentrations of polymer until v_2 approaching 0.93 as inferred from the above observations. Beyond this critical value of v_2 , the comparison between curves 2 and 3 indeed becomes trivial, considering the gross error involved in χ'_0 determinations as noted previously.

Clearly, the CPI-DMT and TPI-DMT mixings are endothermic (i.e., $B' > 0$), a common feature of most polymer-diluent combinations.^{20,21} In contrast, blendings of compatible polymers are either athermal (or nearly so)^{8,9} or exothermic,^{10,11} depending on the strength of intermolecular interactions. The dash-dot curve in Figure 1 is plotted for a hypothetical athermal mixing using DMT as the diluent. It indicates that substantial depression of T_{m1}^0 is crucial to effect a negative enthalpy change of mixing, particularly for blends of high rubber contents.

The parameter χ may be resolved into enthalpy (χ_H) and entropy (χ_S) components,¹² i.e.,

$$\chi = \chi_H + \chi_S \quad (16)$$

Assuming \bar{V}_1 is independent of T , one can write

$$\chi_H = \chi - \frac{\bar{V}_1}{R} \left(\frac{\partial b}{\partial T} \right) \quad (17)$$

$$\chi_S = \frac{\bar{V}_1}{R} \left(\frac{\partial B}{\partial T} \right) \quad (18)$$

Since the coefficient M in eq. (7) is inaccessible by the present analysis, the composition dependencies at constant temperature of the parameters χ , χ_H , and χ_S remain undetermined. However, it can be shown that

$$\left(\frac{\partial B}{\partial T} \right)_{T_{m1}} = 0 \quad (19)$$

It follows that at $T = T_{m1}$ we have

$$\chi_S(T = T_{m1}) = 0 \quad (20)$$

$$\chi_H(T = T_{m1}) = \chi' = B'\bar{V}'_1/RT_{m1} \quad (21)$$

whose numerical values are not present in this work, however. Hence, the present procedure is meant exclusively for determining the χ_H at T_{m1} , or B' . Also, we conclude that $\chi_S = 0$ at the melting point of the diluent, at least for the types of endothermic interactions studied herein.

In summary, appreciable intermolecular interactions in the CPI-DMT and TPI-DMT blends are detected in the molten state of the diluent by means of the melting point depression method. Specifically, DMT interacts more intensely with TPI with CPI. However, such a physical affinity virtually vanishes in the glassy and rubbery states of these composites, as evidenced by their immiscibility. Moreover, these findings seem to imply that crystallization of a fully crystallizable component from the polymeric matrix is itself a phase separation process.

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