Surface Tension Measurements on Ethene−Butene Random Copolymers and Different Polypropenes

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ABSTRACT: The pendant drop apparatus is used in order to study the surface tension of ethene−1-butene random copolymer melts over the whole range of compositions, including poly(1-butene) (P-1-B) and at different temperatures. Furthermore, the surface tensions of isotactic polypropene (i-PP) and syndiotactic polypropene (s-PP) are measured. The surface tension of the melt of random copolymers decreases as a function of copolymer composition from pure polyethene (PE) to pure P-1-B in a nearly exponential manner, and the surface tensions of copolymers with a P-1-B content in the range of approximately 40 wt % match the surface tension of i-PP and s-PP. This indicates the possible existence of a window of miscibility. This result is verified by the calculation of the solubility parameters from additional sessile drop measurements on solid copolymers at room temperature and from pressure−volume−temperature data of the melts applying the Flory−Orwoll−Vrij equation-of-state theory. Also, the theory of the conformational parameter β (Bates and Fredrickson) leads to the same conclusion. All results are consistent with microscopic observations discussed in the literature.

Introduction

One possibility to improve the impact resistance of i-PP is the blending with elastomeric components such as ethen/1-olefin copolymers.[1−9] It is very important for the blending process to know the main physical properties of the blending components as viscosity, crystallinity, surface tension, etc. This leads to the question of miscibility in a thermodynamic sense or compatibility from a practical point of view. Systematic miscibility studies of polyolefins have been reported in the literature recently.[10−14] The origin of miscibility between different polyolefins has been explained by both enthalpic and entropic interactions.[15−23] The general starting point is the χ parameter of the Flory−Huggins theory in connection with the solubility parameter concept.[24−29] For the application of this theory it is necessary to determine the characteristic parameters from pressure−volume−temperature (pVT) data.[30,31] Furthermore, solubility parameters can be calculated from surface tension measurements.[32−34] Bates and Fredrickson[35,36] introduced the conformational asymmetry theory, where they used a conformational parameter β for the discussion of the miscibility of two polymers with structural differences. β is defined by

$$\beta^2 = \frac{{R_g}^2}{V} \tag{1}$$

where R_g is the radius of gyration and V is the molecular volume of a polymer segment. Both theories approach the problem of miscibility only from one molecular parameter, and thus they are limited in their application. Freed and Dudowicz combined theories into the lattice cluster theory.[37−41] They concluded that miscibility is only achieved when two polymers are nearly identical in their solubility parameter and their conformational parameter.

In several reports it has been shown that the pendant drop apparatus is a very useful tool for the determination of the surface and interfacial tension of polymer melts.[42−44] Some reports dealing with the measurement of the surface or interfacial tension of polyolefins can be found in the literature.[45−49] But there do not exist any data on the surface tension of random olefin copolymers over the whole copolymer composition range. With the metallocene catalysts technology it is possible to prepare the desired random copolymers.[50,51] In this contribution we discuss the determination of the surface tension of different random copolymers of ethene and 1-butene (P(E-*co*-B)), and based on these results, the occurrence of a miscibility window of isotactic and syndiotactic polypropene (i-PP and s-PP, respectively) with P(E-*co*-B) is studied. A possibility of a miscibility window between i-PP and P(E-*co*-B) was already described by Thomann et al. using microscopic observations of samples crystallized from the melt.[52]

Experimental Section

Materials. The metallocene polyethene (m-PE) and the P(E-*co*-B)s were synthesized by using a methylaluminoxane-activated metallocene *rac*-$Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2$ (MBI) catalyst, as described elsewhere.[50] In this study the copolymers with 48, 82, and 90 wt % 1-butene in the P(E-*co*-B) were used. The P-1-B was synthesized by using the same catalyst.[53] The commercial ethene−1-butene random copolymer A4085 (24 wt % 1-butene) was supplied by Mitsui; the HS0322 with 10 wt % 1-butene in the copolymer and the i-PP (Novolen M5) (M_w = 267 000, M_w/M_n = 2.3) were obtained by BASF AG. The s-PP (M_w = 150 000, M_w/M_n = 3) was supplied by Fina.

Sessile Drop Measurements. For the sessile drop measurements, plates of the m-PE, the P-1-B, the polypropenes, and the P(E-*co*-B)s except P(E-*co*-B48) were prepared in a hot press. The plates were stored for 24 h in an exxicator prior to measurements. P(E-*co*-B48) was spin-coated from a toluene solution on an aluminum sheet because of the adhesive behavior of this polymer. Bidistilled water, ethylene glycol, diiodomethane, α-bromonaphthalene (fresh distillated prior to

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Table 1. Specific Volumes and Surface Tensions of the Investigated Polymers

polymer	abbreviation	wt % 1-butene	specific vol from *pVT* data[a]	temp dependence of γ_{lv}[b]	range of validity [°C]
HS0322	P(E-*co*-B10)	10	$1.1536 + 7.2722 \times 10^{-4}T + 6.4865 \times 10^{-7}T^2$	$\gamma = 33.66 - 0.045T$	170–230
A4085	P(E-*co*-B24)	24	$1.1533 + 6.9785 \times 10^{-4}T + 6.9059 \times 10^{-7}T^2$	$\gamma = 33.76 - 0.054T$	150–210
	P(E-*co*-B48)	48	$1.1362 + 6.7521 \times 10^{-4}T + 7.0537 \times 10^{-7}T^2$	$\gamma = 31.99 - 0.060T$	150–190
	P(E-*co*-B82)	82	$1.1417 + 6.7631 \times 10^{-4}T + 6.3668 \times 10^{-7}T^2$	$\gamma = 34.81 - 0.076T$	130–200
	P(E-*co*-B90)	90	$1.1413 + 7.0349 \times 10^{-4}T + 5.6033 \times 10^{-7}T^2$	$\gamma = 30.32 - 0.057T$	130–210
poly-1-butene	P-1-B	100	$1.1408 + 6.6918 \times 10^{-4}T + 7.1911 \times 10^{-7}T^2$	$\gamma = 27.13 - 0.044T$	170–220
isotactic PP	i-PP		$1.1542 + 6.6463 \times 10^{-4}T + 7.2702 \times 10^{-7}T^2$	$\gamma = 31.89 - 0.058T$	210–270
syndiotactic PP	s-PP		$1.1717 + 5.7870 \times 10^{-4}T + 9.0970 \times 10^{-7}T^2$	$\gamma = 33.17 - 0.058T$	190–280

[a] This equation gives v_s in cm^3/g; the temperature used is in °C. [b] This equation gives γ_{lv} in mN/m; it is valid in the range listened in the next column; the temperature used is in °C.

Table 2. Characteristic Data of the Test Liquids Used for the Sessile Drop Measurements

test liquids	supplier	γ_{lv} [mN/m]	polarity	γ_{lv}^{d} [e] [mN/m]	γ_{lv}^{p} [f] [mN/m]	$(\gamma_{lv}^{p}/\gamma_{lv}^{d})^{1/2}$
α-bromonaphthalene[a]	Aldrich	44.60	0.0000	44.60	0.00	0.00
diiodomethane[b]	Merck	50.80	0.0453	48.50	2.30	0.22
ethylene glycol[a]	Merck	47.70	0.3522	30.90	16.80	0.74
glycerol[a]	Merck	63.40	0.4164	37.00	26.40	0.84
formamide[c]	Merck	58.20	0.5070	28.69	29.51	1.01
ethylene glycol/water = 30/70[d]	Merck	61.59	0.6672	20.50	41.09	1.42
bidistilled water[a]		72.80	0.7005	21.80	51.00	1.53

[a] Ström, G. *J. Colloid Interface Sci.* **1987**, *119*, 352. [b] Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*, 40. [c] Gebhard, K. F. *Grundlagen der physikalischen Chemie von Grenzflächen und Methoden zur Bestimmung geometrischer Grössen*; FHG IGB: Stuttgart, 1982. [d] Janczuk, B. *J. Colloid Interface Sci.* **1989**, *127*, 59. [e] γ_{lv}^{d} is calculated by $\gamma_{lv}^{d} = \gamma_{lv} - \gamma_{lv} \times$ polarity. [f] γ_{lv}^{p} is caculated by $\gamma_{lv}^{p} = \gamma_{lv} \times$ polarity.

the measurements), glycerol, and formamide were used as test liquids (see Table 2). Ten drops of each liquid were placed onto the surface of the plates. The contact angle was determined on both sides of the drop with a Krüss G40 instrument at a temperature of 20 °C. Surface tensions were calculated using the geometric mean method of Owens, Wendt, and Rabel.[54,55]

Pendant Drop Measurements. The P(E-*co*-B)s, the P-1-B, and the polypropenes were dried for 24 h at 60 °C prior to measurements. The polymers were filled into a capillary and degassed in a vacuum for 30 min prior to surface tension measurements. The capillaries are made from center calibrated KPG tubes with a 4 mm i.d. and an 8 mm o.d. At the end where the droplet is formed, the glass capillary has an o.d. of 2 mm. Surface tensions were measured by application of a pendant drop method employing digital imaging and robust shape analysis to determine the profile. The apparatus was described in detail elsewhere.[47,56,57,62] The method of selected planes of Andreas et al.[58] has been used to determine the surface tension. The profile of the pendant drop is governed by the gravitation and the surface tension. The surface tension is given by eq 2:

$$\gamma = \frac{g\Delta\rho d_e^{\,2}}{H} \tag{2}$$

where g is the gravitational acceleration, $\Delta\rho$ is the density difference between the droplet and the surrounding, d_e is the largest diameter of the drop, and H is a correction factor, which depends on the shape of the drop. Tables required for determination of $1/H$ from ratios of the drop diameters are constructed by numerical solution of the equation given by Roe, Bacchetta, and Wong.[59] The constancy of the shape correction factor was taken as an indication of equilibrium.[59] The surface tension measurements were carried out at different temperatures in steps of 10 °C. The pendant drop cell was purged with argon to prevent degradation of the polymers. Surface tension values were subsequently calculated from the shape parameters and the known densities of the polymer melts. Approximately 20 min was allowed to achieve thermal equilibrium and constant maximum drop diameter, and then data were taken as a function of time. Averaged surface tension values for every measured temperature were determined from these data. The densities were measured by using a Gnomix PVT apparatus (Boulder, CO).[60] Prior to these measurements the specific volume at ambient conditions (room temperature and atmospheric pressure) must be determined. The measurements were carried out with a Quantachrome micropycnometer, which works on the basis of helium displacement.

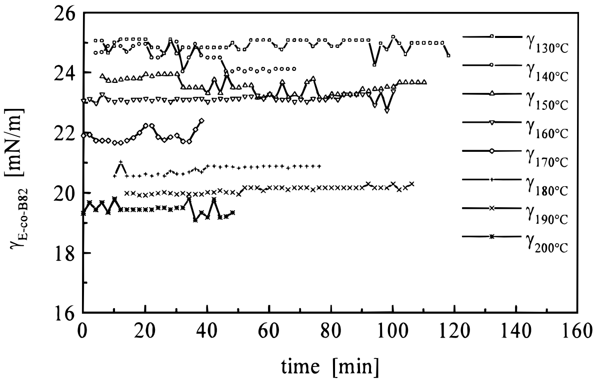

Figure 1. Scattering with time of the surface tension of the P(E-*co*-B82) with 82 wt % 1-butene ($\gamma_{P(E-co-B82)}$) at different temperatures.

Results and Discussion

It is well-known that the melt density data are very sensitive for the calculation of surface tensions of polymer melts when using the pendant drop method. Thus, the temperature dependence of the specific volumes of each P(E-*co*-B), for P-1-B, and for the polypropenes was calculated from *pVT* data. The volume data at each temperature are extrapolated to 0 MPa, and the isotherms are fitted by a polynomial of the second degree. The results are listened in Table 1. These data are used for the calculation of the surface tensions from drop shape analysis of the pendant drop. As an example for the determination of the values of the surface tension of the respective polymer melts, Figure 1 shows the scattering with time of the surface tension ($\gamma_{P(E-co-B82)}$) of the P(E-*co*-B82) with 82 wt % 1-butene at different temperatures after reaching an equilibrium shape of the droplet. The surface tension values at the respective temperatures are obtained by averaging all data points shown in Figure 1. Depending on the viscosity, the flow

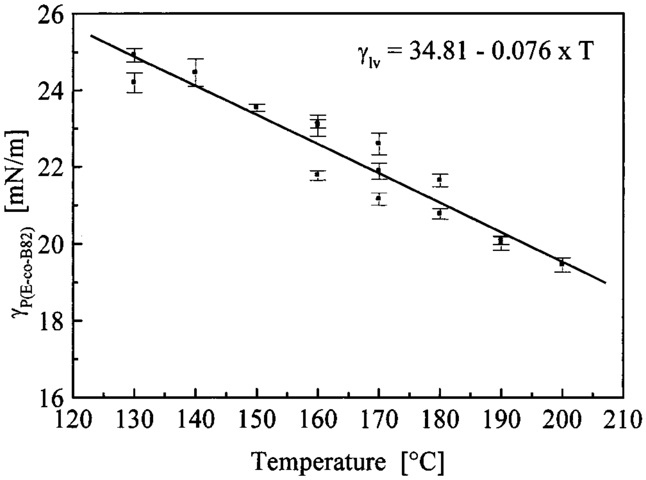

Figure 2. Surface tension as a function of temperature of the P(E-*co*-B82) with 82 wt % 1-butene.

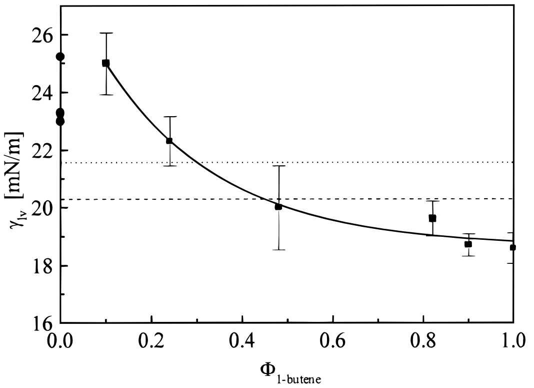

Figure 3. Surface tensions at 200 °C as functions of the 1-butene content of the P(E-*co*-B)s. A line is drawn through the surface tension values to guide the eyes. The dashed and dotted lines represent the solubility parameter of i-PP and s-PP, respectively. For the values of PE see refs 47, 61, and 62.

behavior, and the thermal stability, there is a limited range of temperature and time intervals where the surface tension can be determined, as listed in Table 1. The lowest temperature suitable for pendant drop measurements is given by the possibility to reach the thermodynamic equilibrium within reasonable time scales. The highest temperature where it was possible to measure was limited by degradation (continuous change of drop shape) and/or a low viscosity of the polymer which prevented a droplet formation; i.e., a constant mass flow is observed. Figure 2 shows the surface tension as a function of temperature of the P(E-*co*-B82). Several droplets were measured at every temperature. The results of the linear regression of the temperature dependence of the surface tensions γ_{lv} for each copolymer, for the P-1-B, and for the polypropenes are also given in Table 1.

For comparison, Figure 3 shows the surface tensions at 200 °C as functions of the 1-butene content of the P(E-*co*-B)s. Unfortunately, the surface tension of metallocene PE could not be determined. The metallocene polyethenes available to us did not form a droplet in a reasonable time scale. So values of the surface tension of polyethenes synthesized by heterogeneous catalysts are taken from the literature, and they are added to Figure 3.[47,61,62] An exponential decay for the surface tension with increasing amount of 1-butene in the random copolymer can be fitted. Negative deviations from additivity can be explained theoretically, and they are enhanced with differences of the molar volumes of the respective monomer units of the random copolymer.[63] Additionally, the dashed and dotted lines show the values of the surface tension of isotactic and syndiotactic polypropene, respectively.[64] The intersection between the surface tensions of the P(E-*co*-B)s and that of the i-PP is at a higher 1-butene content compared to the intersection with s-PP.

An identical surface tension γ_{lv} of two polymers is definitely not a sufficient criterion for miscibility. Additional sessile drop measurements and calculations from *pVT* measurements are necessary in order to discuss polymer miscibility.

Surface tensions are calculated from sessile drop measurements using the geometric mean method of Owens, Wendt, and Rabel.[54,55] They applied the Young equation $\gamma_{sl} = \gamma_{sv} - \gamma_{lv}\cos\theta$,[65] where the subscripts sv, sl, and lv refer to the solid−vapor, solid−liquid, and liquid−vapor interfaces, respectively, and θ is the contact angle formed between a pure liquid and the surface of the solid, together with the geometric mean of the γ_{sl} value defined by Good and Girifalco[66−68] (the superscripts d and p refer to the disperse and polar parts of the surface tension, respectively):

$$\gamma_{sl} = \gamma_{lv} + \gamma_{sv} - 2\sqrt{\gamma_{lv}^{d} + \gamma_{sv}^{d}} - 2\sqrt{\gamma_{lv}^{p} + \gamma_{sv}^{p}} \qquad (3)$$

This leads to eq 4:

$$\sqrt{\gamma_{sv}^{p}} \cdot \underbrace{\sqrt{\frac{\gamma_{lv}^{p}}{\gamma_{lv}^{d}}}}_{x} + \sqrt{\gamma_{sv}^{d}} = \underbrace{\frac{(1+\cos\theta)\cdot\gamma_{lv}}{2\sqrt{\gamma_{lv}^{d}}}}_{y} \qquad (4)$$

To solve this equation, the square root of the ratio of the polar part to the disperse part of the surface tension of the test liquid (marked as *x* in eq 4) can be determined by using eqs 5 and 6.

$$\gamma_{lv}^{p} = \gamma_{lv}\cdot\text{polarity} \qquad (5)$$

$$\gamma_{lv}^{d} = \gamma_{lv} - \gamma_{lv}^{p} \qquad (6)$$

Data for the polarity of the test liquids are given in Table 2. The square root of the ratio of the polar and disperse parts of the surface tension is used in the Owens, Wendt, and Rabel graphical data evaluation. This generates the value of the *x*-axis defined in eq 4 (see Table 2). The second step is to calculate the *y* value $y = (1 + \cos\theta)\gamma_{lv}/2(\gamma_{lv}^{d})^{1/2}$ for each polymer with the variable cos θ. After plotting and fitting the data by linear regression, the square of the slope $((\gamma_{sv}^{p})^{1/2})$ gives the polar part of the surface tension of the solid polymer; the extrapolated *y* value at $x = 0$ is $(\gamma_{sv}^{d})^{1/2}$. To obtain an accuracy necessary for data evaluation, six or more test liquids are measured prior to the calculation of surface tensions. The *y* values calculated from the measured contact angle for the different random copolymers and the homopolymers are listed in Table 3.

For an estimation of the solubility parameter δ_{sd} of the polymer from surface tension measurements, the following equation is used where the subscript sd refers to the method of the sessile drop:[69]

Table 3. *x* and *y* Values for the Owens, Wendt, and Rabel Evaluation of Sessile Drop Measurements

	α-bromo naphthalene	diiodomethane	ethylene glycol	glycerol	formamide	ethylene glycol/ water = 30/70	bidistilled water
$x = (\gamma_{lv}^{p}/\gamma_{lv}^{d})^{1/2}$	0.00	0.22	0.74	0.84	1.01	1.42	1.53
y m-PE	6.60	5.85	5.97	5.98	6.98	6.82	7.24
y P(E-*co*-B10)	6.03	5.69	5.93	5.89	7.01	6.95	6.76
y P(E-*co*-B24)	6.05	5.78	5.80	6.19	6.45	7.11	7.00
y P(E-*co*-B48)	6.12	5.03	5.80	5.92	6.20	7.38	7.33
y P(E-*co*-B82)	6.23	4.59	5.02	4.93	5.82	6.38	5.89
y P(E-*co*-B90)	5.83	5.06	5.84	5.47	7.55	7.93	7.75
y P-1-B	5.40	5.35	5.42	5.23	5.83	8.59	6.98
y i-PP	5.64	5.61	5.63		6.32	7.02	6.86
y s-PP	5.60	5.46	5.67		6.32	7.23	5.99

$$\delta_{sd} = \left(\frac{\gamma_{sv}}{0.75}\right)^{3/4} \tag{7}$$

It should be mentioned that these values are taken at room temperature. The data are listed together with the surface tensions and their polar as well as disperse contributions in Table 4.

Table 4. Resulting Surface Tensions from the Sessile Drop Measurements at Room Temperature

polymer	$\gamma_{sv}^{d\,(20°C)}$ [mN/m]	$\gamma_{sv}^{p\,(20°C)}$ [mN/m]	$\gamma_{sv}^{(20°C)}$ [mN/m]	δ_{sd} [J/cm^3]
m-PE	35.92	0.38	36.30	18.35
P(E-*co*-B10)	32.37	0.61	32.98	17.08
P(E-*co*-B24)	32.25	0.65	32.90	17.05
P(E-*co*-B48)	27.91	1.44	29.35	15.65
P(E-*co*-B82)	27.00	0.19	27.19	14.77
P(E-*co*-B90)	25.54	3.05	28.59	15.34
P-1-B	22.95	2.59	25.54	14.10
i-PP	29.11	0.89	30.00	15.91
s-PP	29.30	0.58	29.98	15.90

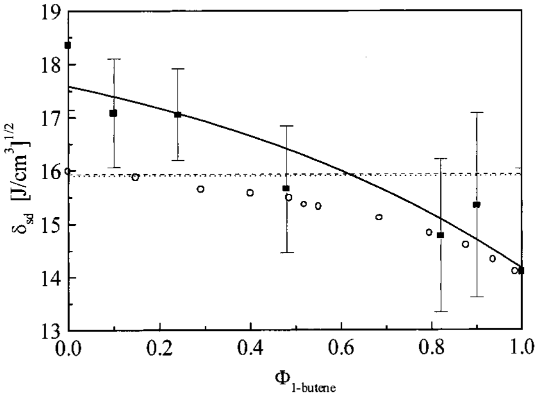

Figure 4. Solubility parameters (δ_{sd}, full squares) calculated by using the data from the sessile drop measurements as functions of the 1-butene content of the P(E-*co*-B)s. A line is drawn through the solubility parameter values to guide the eyes. The dashed and dotted lines represent the solubility parameter of i-PP and s-PP, respectively. SANS data (open circles) by Graessley et al.[22] are added. The solubility parameter of P-1-B is taken as reference value.

The comparison of the surface tension obtained by the sessile drop method with the linear extrapolation (e.g., discussed in ref 47) of the surface tensions from the pendant drop melt data to room temperature shows an identical dependence; i.e., the surface tension decreases with increasing 1-butene content in the copolymers. A larger scattering of the data obtained by sessile drop measurements may be explained by influences of the crystallization of the samples.[70]

Figure 4 shows the solubility parameters calculated from the sessile drop experiments as functions of the 1-butene content in the copolymer. The solubility parameters of the polypropenes are represented by dashed and dotted lines. Compared with the estimation from the pendant drop experiments, the miscibility window, defined by $|\delta_1 - \delta_2| \leq 0.3$ (J/cm^3)$^{1/2}$, is shifted to higher 1-butene contents in the copolymer. δ_1 and δ_2 refer to the solubility parameter of polymer 1 and polymer 2 of a polymer pair under consideration. Additionally, small-angle neutron scattering (SANS) data obtained by Graessley et al. are shown.[22] The solubility parameter of P-1-B is taken as reference value, and we assumed that this value is identical with the value obtained from our surface tension measurements. It can be seen that there is also an increase of the solubility parameter with increasing ethene content, but the increase is less pronounced. There might be several reasons for the difference. First, there is a relatively large error in our data as indicated by the error bars. Second, the SANS data for a temperature of 27 °C are obtained from extrapolation of data obtained above the melting point of crystalline samples. There is also a large uncertainty of these data.

Figure 5 shows the solubility parameters at 200 °C, calculated by using *pVT* data (see Table 5) as functions of the 1-butene content of the P(E-*co*-B)s. The following equation was used to obtain the solubility parameters δ_{pVT}:[27]

$$\delta_{pVT} = \frac{\sqrt{p^*}}{\tilde{v}} \tag{8}$$

with p^* as the reduction pressure and the reduced volume defined by $\tilde{v} = v_s/v_s^*$. The fitting of the *pVT* data is based on the Flory−Orwoll−Vrij equation.[30] The line through P(E-*co*-B)s solubility parameters crosses also the value for i-PP in the region of a high 1-butene content in the copolymer. According to the estimation used above, this indicates a miscibility window between $\phi_{1-\text{butene}} = 0.83$ and 1.00. The border of the window to higher 1-butene contents in the copolymer is not found experimentally. But the microscopic observations by Thomann et al. show definitively the immiscibility between i-PP and P-1-B.[52] Nevertheless, the borders of the window are consistent with these results. The miscibility window for the P(E-*co*-B)s with s-PP differs from the window with i-PP and is shifted to lower 1-butene contents $\phi_{1-\text{butene}} = 0.68$ and 0.91. This is in agreement with previous experiments which indicate a strong influence of the stereoregularity of polypropenes on their miscibility behavior.[60] AFM experiments do not show any evidence for a miscibility window for s-PP and the copolymers in the solid state, but there is a partial miscibility for s-PP/P(E-*co*-B52), s-PP/P(E-*co*-B70), s-PP/P(E-*co*-B82), and s-PP/P(E-*co*-B88).[71] This might be an indication for complete miscibility in the melt. This conclusion is supported by Figures 3 and 5, where the

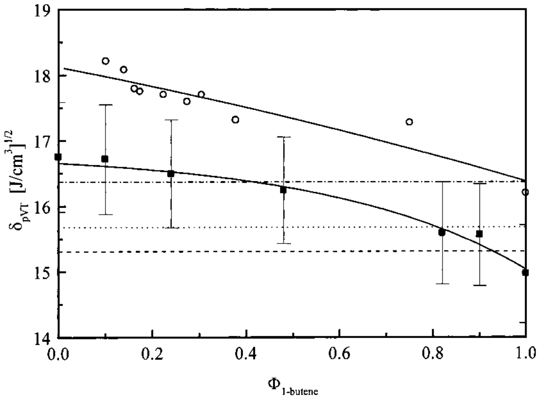

Figure 5. Solubility parameters (δ_{pVT}, full squares) for a temperature of 200 °C calculated by using *pVT* data as functions of the 1-butene content of the P(E-*co*-B)s. A line is drawn through the solubility parameter values to guide the eyes. The dashed and dotted lines represent the solubility parameter of i-PP and s-PP, respectively. For comparison the solubility parameters of Han et al. (open circles) taken at 166 °C are added (see ref 31). The dashed−dotted line represents the value for i-PP at 166 °C obtained by these authors.

Table 5. Characteristic *pVT* Data Used for Calculating the Solubility Parameter δ_{pVT}

polymer	p^* [MPa$^{1/2}$]^a	v_s [cm^3/g]^a	v^*_s [cm^3/g]^b	δ_{pVT} [(J/cm^3)$^{1/2}$]
m-PE	490	1.3243	1.002	16.75
P(E-*co*-B10)	486	1.3256	1.005	16.71
P(E-*co*-B24)	471	1.3186	1.002	16.49
P(E-*co*-B48)	456	1.2978	0.987	16.24
P(E-*co*-B82)	418	1.3025	0.993	15.59
P(E-*co*-B90)	417	1.3044	0.994	15.56
P-1-B	387	1.304	0.992	14.96
i-PP	372	1.3162	1.045	15.31
s-PP	402	1.3238	1.035	15.68

[a] Taken from the *pVT* measurement at 200 °C. [b] FOV parameter; valid for the temperature range 150−250 °C.

surface tension of s-PP in the melt crosses the line through the values for the P(E-*co*-B)s and where the solubility parameter of s-PP defines a miscibility window in the melt with the copolymers in the range between $\phi_{1-\text{butene}} = 0.68$ and 0.91. For comparison, also *pVT* data of Han[31] et al. are shown. These data are taken at 166 °C. Obviously there is an identical tendency, but the values are shifted. This is partially explained by the temperature dependence of δ. It is reasonable that δ decreases with increasing temperature. Additionally, a small systematic shift of data can be observed which might be related to the determination of the absolute density at room temperature. These data differ considerably depending on the method used. But both sets of data indicate that a possible miscibility of the P(E-*co*-B) system with polypropene can only occur in the range of very high 1-butene contents.

As already mentioned, also the concept of the conformational parameter β can be used for the estimation of the miscibility of two polymers in the absence of specific interactions. The evaluation of the small-angle neutron scattering data[12] of i-PP−atactic poly(ethylene ethylethylene) random copolymer blends shows a qualitative agreement with the conformational asymmetry theory. The conformational parameter β as a function of the 1-butene content of the P(E-*co*-B)s indicates a miscibility window in the range of higher $\Phi_{1-\text{butene}}$ values for a temperature of 180 °C (see Figure 6). For calculations the SANS data mentioned above and eq 1 are used. The R_g value for polyethene is taken from ref 34. β values for s-PP are not available.

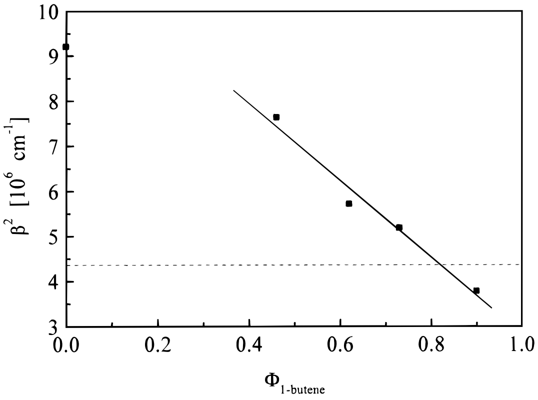

Figure 6. Conformational parameters β for a temperature of 180 °C (except for PE, $T = 175$ °C), calculated from small-angle neutron scattering data as functions of the 1-butene content of the P(E-*co*-B)s (see refs 12 and 34). A straight line is placed through the conformational parameter values to guide the eyes. The dashed line represent the conformational parameter of i-PP.

Conclusions

In this study we measured the surface tension and its temperature dependence of melts of P(E-*co*-B)s over the whole range of compositions. The surface tensions taken in the range of 200 °C of random copolymers with approximately 40 wt % 1-butene match the surface tension of i-PP and s-PP. For an estimation of the miscibility an additional determination of the polar and disperse parts of the surface tension is necessary. This is done for surface tensions measured by the sessile drop method at room temperature. The miscibility window can also be estimated by solubility parameters obtained from *pVT* measurements of polymer melts in connection with the Flory−Orwoll−Vrij equation-of-state theory. All data and theoretical data evaluations, including that of the conformational parameter β, lead to a consistent conclusion that a miscibility window of the P(E-*co*-B)s and i-PP exists at copolymer compositions between 80 and 100 wt % 1-butene in the random copolymer. The miscibility window between s-PP and P(E-*co*-B) is shifted toward lower 1-butene contents in the copolymer when compared to the miscibility window between i-PP and P(E-*co*-B).

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