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Solubility parameters of ethene/1-octene random copolymers

R.-D. Maier, J. Suhm, J. Kressler, R. Mülhaupt

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 21, D-79104 Freiburg, Germany

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Summary

Random copolymers of ethene with 1-octene were investigated by means of pressure-volume-temperature (PVT) measurements. Solubility parameters were calculated from the thermal expansion coefficients and isothermal compressibilities. While expansion coefficients are virtually independent of 1-octene content, compressibilities decrease with increasing 1-octene incorporation. The solubility parameters varied between 17.3 and 15.2 MPa$^{1/2}$ when 1-octene incorporation was varied between 2 and 100 wt%. In the framework of the solubility parameter concept copolymers containing less than 95 wt% 1-octene were shown to be immiscible with isotactic poly(propene).

Introduction

In contrast to conventional multi-site Ziegler-Natta catalysts, modern single-site metallocene-based catalysts give excellent control of molar mass, molar mass distribution, stereo- and regioregularities as well as comonomer incorporation. Comonomers, e. g., 1-olefins, cycloolefins, styrene, and 1,5-dienes, are randomly distributed in the poly(ethene) backbone. Steric irregularities and comonomer incorporation control superstructure formation during crystallization and blend formation (1). Ethene copolymers with 1-octene can be prepared covering the entire feasible composition range without sacrificing high molecular weights and high catalyst activities. Both half sandwich titanocene (2) and ansa-metallocenes (3) have been applied successfully to produce poly(ethene-co-1-octene), abbreviated as E-co-O. Such ethene copolymers, e. g. semicrystalline linear low density poly(ethene) and rubber-like copolymers with high comonomer content exceeding 20 wt% offer attractive potential as blend components together with isotactic poly(propene), abbreviated as i-PP (4).

Since morphology and macroscopic properties of polymer blends are strongly dependent on the thermodynamic interactions of the blend components, it is of interest to study how copolymer composition governs thermodynamic interactions. Graessley and coworkers examined in detail the thermodynamics of mixing of a variety of (model) polyolefin blends (5-8). They obtained information on blend interactions by means of solubility parameters which were determined using small angle neutron scattering (5,6) and pressure-volume-temperature (PVT) measurements (5,7,8). Solubility parameters of random copolymers were reported for poly(ethene-co-1-butene) made by hydrogenation of anionically polymerized polybutadiene precursors (5,6,8) and for metallocene poly(ethene-co-propene) (7,8). Objective of this research has been to examine the influence of 1-octene content on solubility parameters of E-co-O, which cover the composition ranging from poly(ethene) to poly(1-octene), abbreviated as PO. The solubility parameter approach should allow conclusions with respect to miscibility of i-PP with E-co-O.

Theoretical Background

A simple concept of predicting miscibility of binary systems of liquids of low molar mass has been proposed by Hildebrand and Scott (9) based upon the Flory-Huggins (FH) theory (10). Later, the concept has been extended to polymer mixtures. The FH interaction parameter, χ, was expressed by the solubility parameters, δ, of the two blend components

$$\chi_{12} = V_r\left(\delta_1 - \delta_2\right)^2 / RT \tag{1}$$

where V_r is the reference volume. The solubility parameter of a component is defined as

$$\delta = \left(U / V\right)^{1/2} \tag{2}$$

with the internal energy U of vaporization per unit volume V of the component. Using the thermal expansion coefficient, $\alpha=V^{-1}(dV/dT)_p$, and the isothermal compressibility, $\kappa=-V^{-1}(dV/dp)_T$, both being accessible through PVT measurements, Eq. 2 can be rewritten as follows

$$\delta = \left(\alpha T / \kappa\right)^{1/2} \tag{3}$$

It should be mentioned that it is also possible to calculate solubility parameters by means of equation-of-state theories (11,12).

The application of Eqs. 1-3 has several limitations. The most important restriction is the claim for strict absence of any specific interaction between the blend components. This requirement is met for a number of polyolefin blends. According to Krishnamoorti et al., the mixing behavior of blends of this kind is classified as ‘regular’ (8). Although most polyolefin blends mix regularly, for some of them, especially for blends containing poly(isobutene), irregular mixing was found (5,13), i. e. the prediction of the phase behavior using Eqs. 1 and 3 fails. There is no physical explanation for the occurence of irregular mixing, but in terms of equation-of-state theories there are large differences in the blend components’ characteristic temperatures (8).

Experimental

Polymer Characterization:

1-Octene contents of E-co-O were determined by ^{13}C-NMR spectroscopy using a Bruker ARX 300. The spectra were taken at 400 K using $C_2D_2Cl_4$. The frequency was 75.4 MHz, with a 30° pulse angle, 2s delay time and at least 8000 scans. E-co-O's and i-PP's molar masses and molar mass distributions were determined by size exclusion chromatography (SEC). Measurements were taken on Shodex columns at 140°C in 1,2,4-trichlorobenzene using an IR detector and poly(ethene) and poly(propene) standards for E-co-O and i-PP, respectively. Melting temperatures and melting enthalpies were determined by means of differential scanning calorimetry (DSC) with a Perkin Elmer Series 7. E-co-O melting temperatures and enthalpies were taken from the second heating run at a heating rate of 10°C/min, after the samples had been cooled from the melt with a cooling rate of 10°C/min.

Materials:

Table 1 lists the E-co-O, i-PP, and their properties. E-co-O-9, -11, -17, -39, -55, -64, and PO were synthesized in our laboratory (14). E-co-O-2, -8, -10, -12, -14, and -25 were obtained from Dow Chemicals, Europe.

Density and PVT measurements:

Polymer densities were measured at 25°C and atmospheric pressure using a Micropycnometer (Quantachrome) (see Table 1). The changes in density as a function of temperature and pressure were obtained with a Gnomix PVT apparatus (Boulder, CO) (15). The sample cell contained about 1g of polymer and mercury as a confining fluid. The measurements were performed in the isothermal mode, i. e. the sample was held at a certain temperature, and the pressure was continuously raised from 10 MPa to 200 MPa with pressure, volume, and temperature being recorded in steps of 10 MPa. The specific volume corresponding to atmospheric pressure was extrapolated by the Tait equation using the PVT software. Subsequently, this procedure was repeated for temperatures between 30 and 270°C in steps of approximately 10°C. For the evaluation of the expansion coefficients and compressibilities, only the melt data of the respective polymer were taken into account. It should be mentioned that PVT properties of polymers are independent on molar mass, as long as the molar masses exceed approximately 5000 g/mol (7,16).

Table 1 Properties of E-co-O and i-PP

polymer	$W_{1\text{-Octene}}$	M_n [g/mol][c]	M_w/M_n[c]	T_m [°C][d]	ΔH_m [J/g][d]	ρ [g/cm^3]
E-co-O-2	0.02[a]	35200	2.1	128.0	161.9	0.935[a,e]
E-co-O-8	0.075[a]	36400	2.4	119.2	134.4	0.915[a,e]
E-co-O-9	0.086[b]	252200	2.3	114.0	130.4	0.906[e]
E-co-O-10	0.095[a]	31400	3.1	112.4	112.7	0.908[a,e]
E-co-O-11	0.113[b]	230100	2.6	108.9	113.6	0.898[e]
E-co-O-12	0.12[a]	34100	2.4	104.9	91.1	0.902[a,e]
E-co-O-14	0.14[a]	30200	3.0	102.8	108.2	0.898[a,e]
E-co-O-17	0.174[b]	205600	2.7	97.2	93.4	0.890[e]
E-co-O-25	0.25[a]	41400	2.1	89.2	76.9	0.875[a,e]
E-co-O-39	0.394[b]	123400	2.2	52.9	22.0	0.863[e]
E-co-O-55	0.55[b]	105100	2.1	-	-	0.853[e]
E-co-O-64	0.64[b]	82400	2.4	-	-	0.855[e]
PO	1[b]	35000	2.4	-	-	0.850[e]
i-PP	-	118500	2.3	n. d.	n. d.	0.904[e]

a specifications given by Dow, Europe
b weight fraction of 1-octene incorporation, determined by ^{13}C-NMR
c determined by high temperature SEC
d determined by DSC, heating rate 10°C/min
e density at 25 °C

Results and discussion

In Figure 1, the solubility parameters of selected E-co-O are plotted versus the temperature using temperatures ranging between 150 and 250°C. They were calculated according to Eq. 3 from the expansion coefficients and compressibilities at atmospheric pressure. For all copolymers, a strong decrease of the solubility parameters as a function of temperature is observed. It is also clearly visible that, at fixed temperatures, the numerical values of the solubility parameters of E-co-O decrease drastically with increasing comonomer incorporation. This is depicted in Table 2 where solubility parameters, calculated at 200°C, as well as the corresponding expansion coefficients and compressibilities are listed.

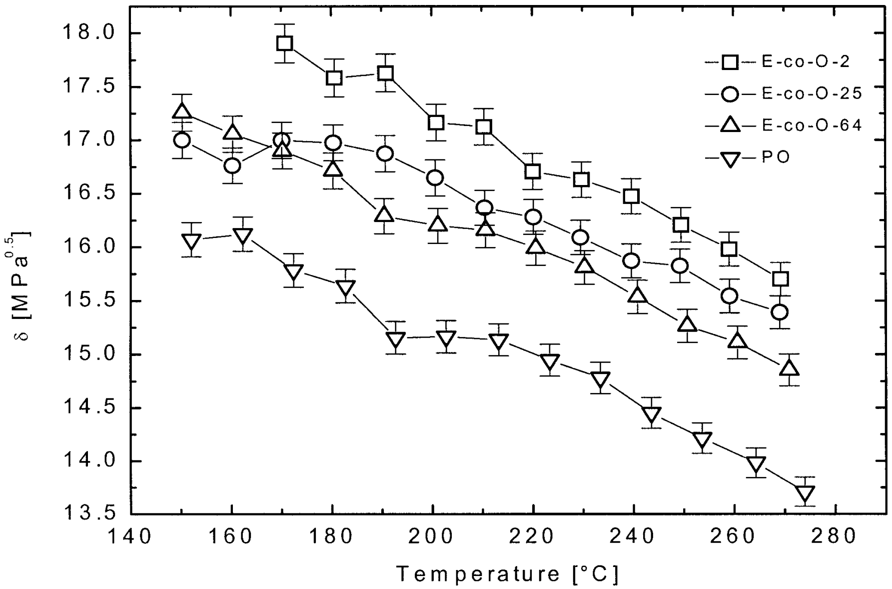

Figure 1 Solubility parameters of selected E-co-O as a function of temperature

Table 2 Expansion coefficients, α, compressibilities, κ, and solubility parameters, δ, of E-co-O and i-PP at 200°C and atmospheric pressure

Polymer	α [10^{-4} K^{-1}]	κ [10^{-4} MPa^{-1}]	δ [$MPa^{1/2}$]
E-co-O-2	7.66	12.21	17.2
E-co-O-8	7.57	12.96	16.7
E-co-O-9	7.44	12.70	16.6
E-co-O-10	7.52	12.71	16.7
E-co-O-11	7.48	12.76	16.6
E-co-O-12	7.54	13.01	16.5
E-co-O-14	7.53	12.65	16.7
E-co-O-17	7.63	12.81	16.7
E-co-O-25	7.53	12.85	16.5
E-co-O-39	7.39	12.98	16.4
E-co-O-55	7.50	13.27	16.3
E-co-O-64	7.93	14.01	16.3
PO	7.70	15.50	15.2
i-PP	7.41	15.02	15.3

Disregarding deviations for E-co-O-64, the expansion coefficients of the E-co-O apparently do not depend on 1-octene incorporation, whereas the slight decrease of the compressibilities with increasing comonomer content accounts for the decrease of the solubility parameters. This is in accord with equation-of-state analyses, showing that the characteristic pressure of model ethene / 1-butene copolymers and metallocene ethene / propene copolymers (5) as well as of metallocene ethene / 1-octene copolymers (14), which strongly depends on the compressibility, is sensitive to comonomer incorporation. The characteristic temperature, into which the expansion coefficient enters, but not the compressibility, is reported to experience only very slight changes upon increasing comonomer incorporation.

The solubility parameters of E-co-O (at 200°C) range from 17.3 and 15.2 $Mpa^{1/2}$. The solubility parameter of i-PP is 15.3 $Mpa^{1/2}$. The maximum difference in the solubility parameters of two components, allowing miscibility at molar masses of $M \approx 10^5$ g/mol and temperatures of $T \approx 200°C$, is approximately 0.3 $Mpa^{1/2}$, provided that regular mixing prevails (8). In Figure 2, the solubility parameters (200°C, atmospheric pressure) of the E-co-O are plotted versus the weight fraction of 1-octene incorporation. The numerical value of the solubility parameter decreases drastically at relatively low 1-octene incorporation ($W_{1\text{-octene}} < 0.4$) caused by the increasing compressibility (cf. Eq. 3) as a result of the larger amount of short chain branching in the copolymers. On the other hand, already relatively low amounts of ethene incorporation into PO may reduce the compressibility and thus increase the numerical value of the solubility parameter.

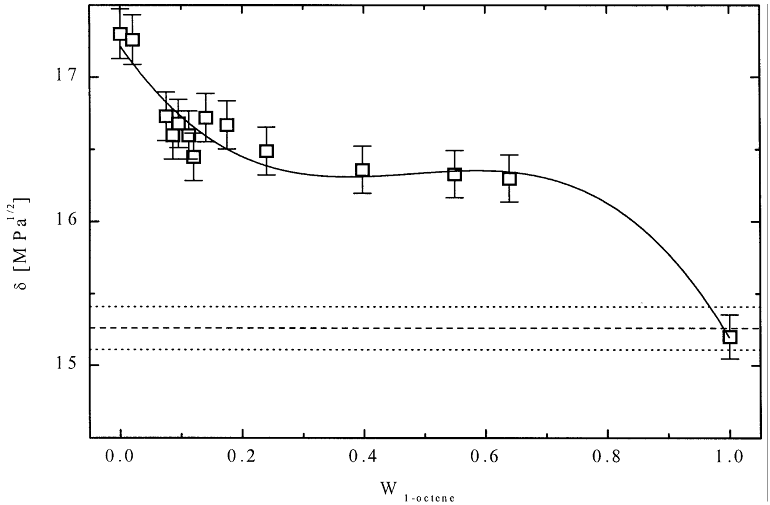

Figure 2 Solubility parameters of E-co-O as a function of weight fraction of 1-octene (200°C and atmospheric pressure). The solid line represents a third order polynomial fit and is drawn to guide the eye. The dashed line represents the solubility parameter of i-PP, and the dotted lines the error associated with it.

Before an estimation of the miscibility of E-co-O with i-PP is given, the viability of the solubility parameter concept should be addressed. It was found that most polyolefin blends mix regularly (5,8,13). Also the phase behavior of blends of poly(propene) with different stereoregularities was described successfully using the concept of regular solutions (17). However, a significant number of blends was found to mix irregularly. Although a physical explanation could not be found, an empirical classification in terms of equation-of-state theories was given (8). Here, two polyolefins are found to mix regularly when only small differences of the characteristic temperatures of two blends components exist. Mixing irregularities are encountered when either at small differences in the characteristic pressures large differences in the characteristic temperatures prevail, or when the differences both in characteristic pressures and temperatures are large. In the case of i-PP blends with E-co-O, regular mixing can be assumed since only small differences in characteristic temperatures of all E-co-O (14) and i-PP exist. This is also reflected by small differences in the expansion coefficients, as depicted in Table 2. The phase behavior is governed by the differences in the compressibilities of the respective E-co-O on the one side, and of i-PP on the other side, as discussed above.

Conclusion

Thus assuming regular mixing and the validity of the solubility parameter concept in E-co-O / i-PP blends, immiscibility is predicted for i-PP with E-co-O having 1-octene incorporation below approximately 95 wt% ($W_{1\text{-octene}} < 0.95$), provided that a difference in the components' solubility parameters of 0.3 $\text{Mpa}^{1/2}$, as discussed above, is sufficient to cause phase separation. The exact location of the critical 1-octene content, below which immiscibility with i-PP results, would require the synthesis of additional copolymers in the range between 64 and 100 wt% 1-octene and the investigation of their miscibility behavior. According to the solubility parameter concept, isotactic poly(propene) and poly(ethene-co-1-octene) should be miscible when 1-octene content exceeds 95 wt%. Typical linear low density poly(ethene-co-1-octene) with 1-octene content < 25 wt% are immiscible.

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