

Supporting Information

The cohesive properties of a polymer can be expressed quantitatively in the cohesive energy, which is related to the internal pressure. According to Hilderbrand's theory, the square root of the cohesive energy density, which is called solubility parameter (δ), can be used as an indicator for identifying the miscibility behavior of different compounds. The chemical structure of a polymer plays an important role in its extent of solubility in different solvents. If the solvent and the polymer have a similar chemical structure, typically they should be more soluble. In other words, the solubility of the polymer and solvent is favored if their solubility parameters are equal. The solubility parameter for a given polymer is defined as the square root of the cohesive energy density in the amorphous state,

$$\delta = \left(\frac{E_{coh}}{V} \right)^{1/2} \text{ (at 298K), where } E_{coh} \text{ is the cohesive energy in a condensed state and } V \text{ is the molar}$$

volume. For low molecular weight substances E_{coh} can be calculated from the heat of vaporization, but since this method is not applicable to polymers, indirect methods such as comparative swelling or dissolution experiments in different solvents with known solubility parameters should be carried out. Different methods have been developed in order to theoretically predict the solubility parameter. Fedors, Van Krevelen, Hoy, Small and Hoftyzer-Van Krevelen have applied group contribution methods for prediction of the cohesive energy of polymers at room temperature. By using group contribution methods and calculating E_{coh} according to the tabulated values for each of the constituent structural groups of the polymer or using the molar attraction constants F , $F = (E_{coh}V)^{1/2}$ (at 298K), the solubility parameter for organic phases can be estimated. F is a useful additive quantity for both low and high molecular weight substances. It has been verified [Krevelen, 1990 #125] that each of these theoretical methods predicts the cohesive energy with a mean accuracy of about 10% relative to experiment.

A representative calculation of solubility parameters for neat PLLA is presented in **Table 4**.

Table 4

	v (cm ³ /mol)	Fedors E_{coh} (J/mol)	Small (F)	V. Krevelen (F)	Hoy (F)	H & Van (E)
-COO	18	18000	634	512	668.2	13410
-CH--	-1	3430	57	140	176	420
-CH ₃	33.5	4710	438	420	303.4	9640

sum	50.5	26140	1129	1072	1147.6	23470
δ	-----	22.75	22.36	21.23	22.72	21.56

The data for different groups are extracted from literature [Krevelen, 1990 #125].