

Prediction of Solubility Parameters

A Comparison of four Group
Contribution Methods



Group Contribution Models

Available Groups:

Monomer Unit		Krevelen	Hoy	Small	Fedors	CROW
Aliphatics	-CH ₃	✓	✓	✓	✓	✓
	-CH ₂ -	✓	✓	✓	✓	✓
	>CH-	✓	✓	✓	✓	✓
	>C<	✓	✓	✓	✓	✓
	=CH-	✓	✓	✓	✓	✓
	=CH ₂	✓	✓	✓	✓	✓
	>C=	✓	✓	✓	✓	✓
Aliphatic Rings	Cyclopentyl	✓	✓	✓	✓	✓
	Cyclohexyl	✓	✓	✓	✓	✓
	Cyclohexyl (di-)	✓	✓	✓	✓	✓
	Phenyl	✓	✓	✓	✓	✓
Aromatics	Phenylene (di-)	✓	✓	✓	✓	✓
	Phenylene (tri-)	✓	✓	✗	✓	✓
	-F	✓	✓	✓	✓	✓
Halogenes	-Cl	✓	✓	✓	✓	✓
	-Br	✓	✓	✓	✓	✓
	-I	✓	✓	✓	✓	✓
Alcohols	-OH	✓	✓	✗	✓	✓
Ethers	-O-	✓	✓	✓	✓	✓
Thiols	-SH	✗	✗	✗	✓	✓
Thioethers	-S-	✓	✓	✓	✓	✓
Prim. Amines	-NH ₂	✗	✓	✗	✓	✓
Sec. Amines	-NH-	✗	✓	✗	✓	✓
Tert. Amines	-N<	✗	✓	✗	✓	✓
Nitriles	-C≡N	✓	✓	✓	✓	✓
Aldehydes	-CHO	✗	✓	✗	✓	✓
Ketons	>C=O	✓	✓	✓	✓	✓
Esters	-COO-	✓	✓	✓	✓	✓
Acids	-COOH	✓	✓	✗	✓	✓
Anhydrides	-(CO) ₂ O	✓	✓	✗	✓	✓
Carbonates	-O-C(=O)-O-	✓	✓	✗	✓	✓
Amides	-C(=O)NH ₂	✗	✓	✗	✓	✓
Amides	-C(=O)NH-	✓	✓	✗	✓	✓
Urethanes	-O-C(=O)NH-	✓	✓	✗	✓	✓



A Comparison with Literature Values

Polymer	Fedors	Hoy	Krevelen	Small	CROW*	CROW	Barton**	AVG Lit.
PMMA	20.3	18.7	19.0	19.4	18.9	18.5	19.0	19.0
PMA	21.6	20.1	19.4	21.0	19.0	19.3	19.2	20.5
Pn-BMA	19.3	18.2	17.8	18.5	18.2	18.1	18.0	-
Pn-BA	20.0	19.0	18.1	19.3	18.6	18.6	18.8	18.5
PE	17.5	17.3	17.1	16.9	16.7	17.6	16.8	17.0
PTMO	18.4	19.1	18.6	18.0	17.1	18.3	17.8	18.0
PS	21.6	18.5	19.2	21.2	18.8	19.3	18.7	18.5
PVC	22.6	19.4	19.4	22.5	19.8	19.8	19.4	19.5
Nylon 6	25.4	23.4	25.6	-	-	26.5	26.6	-
PVA	21.6	20.1	19.2	21.0	19.1	19.7	19.5	20.0
PAN	29.4	24.3	29.9	29.9	26.4	25.3	25.8	26.0
PC	23.0	-	20.7	-	19.8	19.8	19.9	-
PBD	17.7	18.0	16.8	16.9	16.9	16.9	17.1	17.0

*Calculated with experimental densities of amorphous polymers, ** Recommended by Barton

Values that deviate more than one unit from recommended literature / average experimental value are marked red.



A Comparison with Barton's Recommended Values

	Accuracy of Results: $ \delta_{i, \text{calc}} - \delta_{i, \text{Barton}^{**}} ^2$					
	Fedors	Hoy	Krevelen	Small	CROW*	CROW
PMMA	1.3	0.3	0	0.4	0.1	0.5
PMA	2.4	0.9	0.2	1.8	0.2	0.1
Pn-BMA	1.3	0.2	0.2	0.5	0.2	0.1
Pn-BA	1.2	0.2	0.7	0.5	0.2	0.2
PE	0.7	0.5	0.3	0.1	0.1	0.8
PTMO	0.6	1.3	0.8	0.2	0.7	0.5
PS	2.9	0.2	0.5	2.5	0.1	0.6
PVC	3.2	0	0	3.1	0.4	0.4
Nylon 6	1.2	3.2	1.0	-	-	0.1
PVA	2.1	0.6	0.3	1.5	0.4	0.2
PAN	3.6	1.5	4.1	4.1	0.6	0.5
PC	3.1	-	0.8	-	0.1	0.1
PBD	0.6	0.9	0.3	0.2	0.2	0.2
AVG $\sqrt{ \Delta\delta^2 }$	1.86	0.82	0.71	1.35	0.28	0.33

* Calculated with experimental densities of amorphous polymers

** Recommended by Barton



A Comparison with Literature Values

	Accuracy of Results: $ \delta_{i, \text{calc}} - \delta_{i, \text{AVG Lit}} ^2$					
	Fedors	Hoy	Krevelen	Small	CROW*	CROW
PMMA	1.3	0.3	0	0.4	0.1	0.5
PMA	1.1	0.4	1.1	0.5	1.5	1.2
Pn-BMA						
Pn-BA	1.5	0.5	0.4	0.8	0.1	0.1
PE	0.5	0.3	0.1	0.1	0.3	0.6
PTMO	0.4	1.1	0.6	0.0	0.9	0.3
PS	3.1	0.0	0.7	2.7	0.3	0.8
PVC	3.1	0.1	0.1	3.0	0.3	0.3
Nylon 6						
PVA	1.6	0.1	0.8	1.0	0.9	0.3
PAN	3.4	1.7	3.9	3.9	0.4	0.7
PC						
PBD	0.7	1	0.2	0.1	0.1	0.1
AVG $\sqrt{ \Delta\delta^2 }$	1.71	0.58	0.88	1.34	0.53	0.49

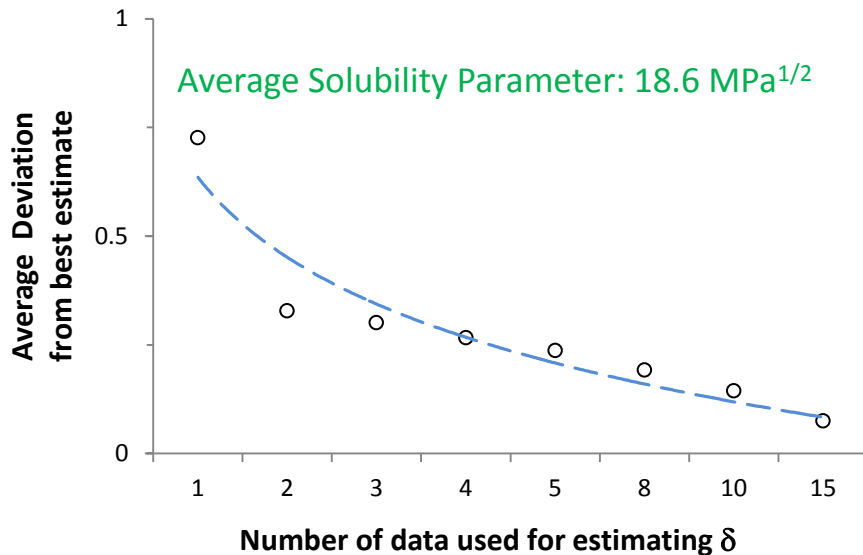
* Calculated with experimental densities of amorphous polymers



Example: Poly(isopropylphenyl methacrylate)

Hildebrand parameters from viscosity measurements and other methods, $\delta/\text{MPa}^{1/2}$:

Data Source: *CRC Handbook of Polymer-liquid Interaction Parameters and Solubility Parameters*, Allan F.M. Barton, 1990, page 569, Table 144



Average Solubility Parameter $\delta/\text{MPa}^{1/2}$	
Viscosity Measurements in Hydrocarbons	18.5
Visc. Meas. in Chlorinated Hydrocarbons	18.6
Visc. Meas. in oxygenated Liquids	18.5
Calculated with Small's GC Method	17.8
Calculated with Askadskii's AC Method	18.6
Calculated with CROW's Method	18.7

Conclusion

At least 3 - 6 independent values needed for accurate estimates of Hildebrand parameters

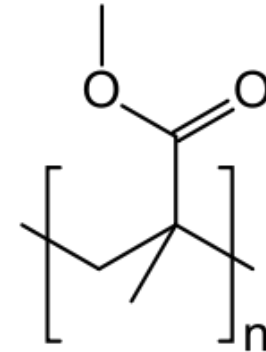


Appendix



Polymethylmethacrylate, PMMA

Property	Value
Amorphous Density @ 25°C	1.18 g/ml
Molecular Weight (Repeat Unit)	100.1 g/mole
Solubility Parameter @ 25°C	19.0 MPa ^{1/2} *
Range of Values	18.6 – 19.4 MPa ^{1/2}
Average Value	19.0 MPa^{1/2}



*Recommended by Barton

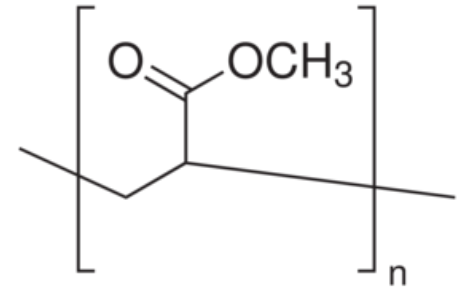
Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	20.3	18.7	19.0	19.4	18.5	18.9

1) Calculated with experimental density of the amorphous polymer

Polymethylacrylate, PMA

Property	Value
Amorphous Density @ 25°C	1.19 g/ml
Molecular Weight (Repeat Unit)	86.1 g/mole
Solubility Parameter @ 25°C	20.5 MPa ^{1/2} *
Range of Values	18.9 – 19.9 MPa ^{1/2}
Average Value	19.2 MPa^{1/2}



*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	21.6	20.1	19.4	21.0	19.3	19.0

1) Calculated with experimental density of the amorphous polymer

Polybutylmethacrylate, Pn-BMA

Property	Value
Amorphous Density @ 25°C	1.07 g/ml
Molecular Weight (Repeat Unit)	142.2 g/mole
Solubility Parameter @ 25°C	18.0 MPa ^{1/2} *
Range of Values	17.6 – 18.4 MPa ^{1/2}
Average Value	18.0 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	19.3	18.2	17.8	18.5	18.1	18.2

1) Calculated with experimental density of the amorphous polymer

Polybutylacrylate, Pn-BA

Property	Value
Amorphous Density @ 25°C	1.09 g/ml
Molecular Weight (Repeat Unit)	128.2 g/mole
Solubility Parameter @ 25°C	18.5 MPa ^{1/2} *
Range of Values	16.4 – 20.4 MPa ^{1/2}
Average Value	18.8 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	20.0	19.0	18.1	19.3	18.6	18.6

1) Calculated with experimental density of the amorphous polymer

Polystyrene, PS

Property	Value
Amorphous Density @ 25°C	1.05 g/ml
Molecular Weight (Repeat Unit)	g/mole
Solubility Parameter @ 25°C	18.5 MPa ^{1/2} *
Range of Values	18.2 – 20.2 MPa ^{1/2}
Average Value	18.7 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	21.6	18.5	19.2	21.2	19.3	18.8

1) Calculated with experimental density of the amorphous polymer

Poly(caprolactam), Nylon 6

Property	Value
Amorphous Density @ 25°C	? g/ml
Molecular Weight (Repeat Unit)	113.2 g/mole
Solubility Parameter @ 25°C Range of Values	? MPa ^{1/2} * 23.2 – 27.4 MPa ^{1/2}
Average Value	26.6 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	25.4	23.4	25.6	-	26.5	-

1) Calculated with experimental density of the amorphous polymer

Polyvinylacetate, PVA

Property	Value
Amorphous Density @ 25°C	1.19 g/ml
Molecular Weight (Repeat Unit)	86.1 g/mole
Solubility Parameter @ 25°C	19.5 MPa ^{1/2} *
Range of Values	18.2 – 20.7 MPa ^{1/2}
Average Value	19.5 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	21.6	20.1	19.2	21.0	19.7	19.1

1) Calculated with experimental density of the amorphous polymer

Polyacrylonitrile, PAN

Property	Value
Amorphous Density @ 25°C	1.15 g/ml
Molecular Weight (Repeat Unit)	53.1 g/mole
Solubility Parameter @ 25°C	26.0 MPa ^{1/2} *
Range of Values	24.3 – 27.2 MPa ^{1/2}
Average Value	25.8 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	29.4	24.3	29.9	29.9	25.3	26.4

1) Calculated with experimental density of the amorphous polymer

Polycarbonate, PC

Property	Value
Amorphous Density @ 25°C	1.21 g/ml
Molecular Weight (Repeat Unit)	254.3 g/mole
Solubility Parameter @ 25°C Range of Values	? MPa ^{1/2} * 19.2 – 20.6 MPa ^{1/2}
Average Value	19.6 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	23.0	-	20.7	-	19.8	19.8

1) Calculated with experimental density of the amorphous polymer

Polybutadiene, PBD

Property	Value
Amorphous Density @ 25°C	0.91 g/ml
Molecular Weight (Repeat Unit)	54.1 g/mole
Solubility Parameter @ 25°C Range of Values	17.0 MPa ^{1/2} * 16.5 – 17.8 MPa ^{1/2}
Average Value	17.1 MPa^{1/2}

*Recommended by Barton

Calculated Solubility Parameters (MPa^{1/2})

GC Method	Fedors	Hoy	Krevelen	Small	CROW	CROW 1)
Value	17.7	18.0	16.8	16.9	16.9	16.9

1) Calculated with experimental density of the amorphous polymer

Thank You !

