

Reference: Polymer Properties

Polymer Solutions: Solvents and Solubility Parameters

Various applications require the selection of a polymer-solvent or polymer-plasticizer system. Dissolving a polymer is unlike dissolving low molecular weight compounds because of the vastly different dimensions of solvent and polymer molecules. Dissolution is often a slow process. While some polymers dissolve readily in certain solvents resulting in a true solution, others may require prolonged periods of heating at temperatures near the melting point of the polymer. Network

polymers do not dissolve, but usually swell in the presence of solvent. Table I is a quantitative guide¹ for selecting solvents to dissolve or swell polymers. The polymer is composed of the stated Repeating Unit. Representative homopolymers from each of the main polymer classes were selected. Since polymer solubility is a complex function of many variables including but not limited to molecular weight, degree of crystallinity, extent of branching, and temperature, the solubility may vary greatly within a given polymer class.

Table I: Solvents for Representative Homopolymers from Selected Polymer Classes

Repeating Unit	Solvents
Acetylene	Isopropylamine, aniline
Acrylamide	Morpholine, water
Acrylate esters	Aromatic hydrocarbons, chlorinated hydrocarbons, THF, esters, ketones
Acrylic acid	Alcohols, water, dilute aqueous alkali
Acrylonitrile	Phenylenediamines, ethylene carbonate, sulfuric acid
Alkyl vinyl ethers	Benzene, halogenated hydrocarbons, methyl ethyl ketone
Amic acids	DMF, DMSO, tetramethylurea
Aryl sulfonates	DMF
Butadiene	Hydrocarbons, THF, higher ketones
ϵ -Caprolactam (Nylon 6)	<i>m</i> -Cresol, chlorophenol, formic acid
Cellulose	Trifluoroacetic acid, aqueous solutions of cupriethylenediamine
Cellulose ethers	Aqueous alkali
Cellulose triacetate	Methylene chloride, THF, ethylene carbonate
Chloroprene	Benzene, chlorinated hydrocarbons, pyridine
Ethylene	Above 80°C: halogenated hydrocarbons, higher aliphatic esters and ketones
Ethylene phthalamide	Sulfuric acid
Ethylene terephthalate	Trichloroacetaldehyde hydrate, phenol, chlorophenol
Ethylene oxide	Chloroform, alcohols, esters
Formaldehyde	At elevated temperature: phenol, aniline, ethylene carbonate
Hexamethylene adipate (Nylon 6/6)	Trichloroethanol, phenols, sulfuric acid
Isobutene	Chlorinated hydrocarbons, THF, aliphatic ethers
Isoprene	Hydrocarbons, THF, higher ketones
Lactic acid	Chloroform, dioxane
Maleic anhydride	Dioxane, ethers, ketones
Methacrylate esters	Benzene, methylene chloride, methyl ethyl ketone
Methacrylic acid	Alcohols, water, dilute aqueous sodium hydroxide
1,4-Phenylene ethylene	Biphenyl, phenyl ether
Phenylene sulfone	Methylene chloride, DMSO
Phenyl glycidyl ether	Xylene (hot), 1,2-dichlorobenzene (hot)
Propylene	Above 80°C: halogenated hydrocarbons, higher aliphatic esters and ketones
Propylene oxide	Benzene, chloroform, ethanol
Pyromellitimides	<i>m</i> -Cresol, conc. sulfuric acid
Siloxanes	Aromatic and chlorinated hydrocarbons, esters
Styrene	Benzene, chlorinated aliphatic hydrocarbons, methyl ethyl ketone, ethyl acetate
Tetrafluoroethylene	Perfluorokerosene (350°C)
Thiophenylene	Biphenyl, dichlorobiphenyl
Ureas	Phenol, <i>m</i> -cresol, formic acid
Urethanes	Phenol, <i>m</i> -cresol, formic acid
Vinyl acetal	Benzene, chloroform, THF
Vinyl acetate	Toluene, chloroform, methanol
Vinyl alcohol	Glycols (hot), water, piperazine
Vinyl butyryl	Methylene chloride, alcohols, ketones
Vinyl chloride	THF, methyl ethyl ketone
Vinyl carbazole	Chloroform, chlorobenzene, dioxane
Vinylidene chloride	THF(hot), trichloroethane
Vinylidene fluoride	Cyclohexanone, ethylene carbonate
<i>N</i> -Vinyl pyrrolidone	Chloroform, ethanol, pyridine

¹ A more extensive selection is found in "Polymer Handbook", Eds. Brandrup, J.; Immergut, E.H.; Grulke, E.A., 4th Edition, John Wiley, New York, 1999, VII /497-535. Aldrich Catalog Number **Z41,247-3**.

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Detailed studies of polymer solubilities using thermodynamic principles have led to semi-empirical relationships for predicting solubility. A comparison of the solubility parameters of the polymer (δ_{polymer}) and solvent (δ_{solvent}), where δ is a measure of the attractive strength between molecules of the material, allows prediction of miscibility. Solubility parameters for solvents and plasticizers are provided in [Table II](#) and [Table III](#) in alphabetical order and in order of increasing δ value, respectively.

The same is provided for homopolymers in [Table IV](#). As a guide, the solubility parameter difference, ($\delta_{\text{polymer}} - \delta_{\text{solvent}}$), must be small for good miscibility.

Solubility parameter values are based on heats of vaporization. The values obtained with this method give estimates of solution behavior. It is recommended that the reader consult the reference given below² or other references for a more detailed explanation of δ values.

Table II: Solubility Parameters for Plasticizers and Solvents (Alphabetical sequence)

Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength ³	Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength ³
Acetone	9.9	m	Diethyl sebacate	8.6	m
Acetonitrile	11.9	p	1,4-Dioxane	10.0	m
Amyl acetate	8.5	m	Di(propylene glycol)	10.0	s
Aniline	10.3	s	Di(propylene glycol)		
Benzene	9.2	p	monomethyl ether	9.3	m
Butyl acetate	8.3	m	Dipropyl phthalate	9.7	m
Butyl alcohol	11.4	s	Ethyl acetate	9.1	m
Butyl butyrate	8.1	m	Ethyl amyl ketone	8.2	m
Carbon disulfide	10.0	p	Ethyl <i>n</i> -butyrate	8.5	m
Carbon tetrachloride	8.6	p	Ethylene carbonate	14.7	m
Chlorobenzene	9.5	p	Ethylene dichloride	9.8	p
Chloroform	9.3	p	Ethylene glycol	14.6	s
Cresol	10.2	s	Ethylene glycol diacetate	10.0	m
Cyclohexanol	11.4	s	Ethylene glycol diethyl ether	8.3	m
Diamyl ether	7.3	m	Ethylene glycol dimethyl ether	8.6	m
Diamyl phthalate	9.1	m	Ethylene glycol monobutyl ether		
Dibenzyl ether	9.4	m	(Butyl Cellosolve®)	9.5	m
Dibutyl phthalate	9.3	m	Ethylene glycol monoethyl ether		
Dibutyl sebacate	9.2	m	(Cellosolve®)	10.5	m
1,2-Dichlorobenzene	10.0	p	Furfuryl alcohol	12.5	s
Diethyl carbonate	8.8	m	Glycerol	16.5	s
Di(ethylene glycol)	12.1	s	Hexane	7.3	p
Di(ethylene glycol) monobutyl ether (Butyl Carbitol®)	9.5	m	Isopropyl alcohol	8.8	m
Di(ethylene glycol) monoethyl ether (Carbitol®)	10.2	m	Methanol	14.5	s
Diethyl ether	7.4	m	Methyl amyl ketone	8.5	m
Diethyl ketone	8.8	m	Methylene chloride	9.7	p
Diethyl phthalate	10.0	m	Methyl ethyl ketone	9.3	m
Di- <i>n</i> -hexyl phthalate	8.9	m	Methyl isobutyl ketone	8.4	m
Diisodecyl phthalate	7.2	m	Propyl acetate	8.8	m
<i>N,N</i> -Dimethylacetamide	10.8	m	1,2-Propylenecarbonate	13.3	m
Dimethyl ether	8.8	m	Propylene glycol	12.6	s
<i>N,N</i> -Dimethylformamide	12.1	m	Propylene glycol methyl ether	10.1	m
Dimethyl phthalate	10.7	m	Pyridine	10.7	s
Dimethylsiloxanes	4.9-5.9	p	1,1,2,2-Tetrachloroethane	9.7	p
Dimethyl sulfoxide	12.0	m	Tetrachloroethylene		
Diethyl adipate	8.7	m	(perchloroethylene)	9.3	p
Diethyl phthalate	7.9	m	Tetrahydrofuran	9.1	m
			Toluene	8.9	p
			Water	23.4	s

²"Polymer Handbook", Eds. Brandrup, J.; Immergut, E.H.; Grulke, E.A., 4th Edition, John Wiley, New York, 1999, VII /675-711. Aldrich Catalog Number Z41,247-3.

³H-Bonding: p= poor; m = moderate; s = strong



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Table III: Solubility Parameters (δ) for Plasticizers and Solvents (Increasing δ value sequence)

Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength ⁴	Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength ⁴
Dimethylsiloxanes	4.9-5.9	p	Di(ethylene glycol) monobutyl ether (Butyl Carbitol®)	9.5	m
Diisodecyl phthalate	7.2	m	Chlorobenzene	9.5	p
Hexane	7.3	p	Methylene chloride	9.7	p
Diamyl ether	7.3	m	Dipropyl phthalate	9.7	m
Diethyl ether	7.4	m	1,1,2,2-Tetrachloroethane	9.7	p
Dioctyl phthalate	7.9	m	Ethylene dichloride	9.8	p
Butyl butyrate	8.1	m	Acetone	9.9	m
Ethyl amyl ketone	8.2	m	1,2-Dichlorobenzene	10.0	p
Ethylene glycol diethyl ether	8.3	m	Diethyl phthalate	10.0	m
Butyl acetate	8.3	m	Ethylene glycol diacetate	10.0	m
Methyl isobutyl ketone	8.4	m	Di(propylene glycol)	10.0	s
Methyl amyl ketone	8.5	m	Carbon disulfide	10.0	p
Amyl acetate	8.5	m	1,4-Dioxane	10.0	m
Ethyl <i>n</i> -butyrate	8.5	m	Propylene glycol methyl ether	10.1	m
Ethylene glycol dimethyl ether	8.6	m	Di(ethylene glycol) monoethyl ether (Carbitol®)	10.2	m
Carbon tetrachloride	8.6	p	Cresol	10.2	s
Dioctyl sebacate	8.6	m	Aniline	10.3	s
Dioctyl adipate	8.7	m	Ethylene glycol monoethyl ether (Cellosolve®)	10.5	m
Isopropyl alcohol	8.8	m	Pyridine	10.7	s
Diethyl carbonate	8.8	m	Dimethyl phthalate	10.7	m
Propyl acetate	8.8	m	<i>N,N</i> -Dimethylacetamide	10.8	m
Diethyl ketone	8.8	m	Cyclohexanol	11.4	s
Dimethyl ether	8.8	m	Butyl alcohol	11.4	s
Toluene	8.9	p	Acetonitrile	11.9	p
Di- <i>n</i> -hexyl phthalate	8.9	m	Dimethyl sulfoxide	12.0	m
Ethyl acetate	9.1	m	Di(ethylene glycol)	12.1	s
Diamyl phthalate	9.1	m	<i>N,N</i> -Dimethylformamide	12.1	m
Tetrahydrofuran	9.1	m	Furfuryl alcohol	12.5	s
Dibutyl sebacate	9.2	m	Propylene glycol	12.6	s
Benzene	9.2	p	1,2-Propylenecarbonate	13.3	m
Tetrachloroethylene (perchloroethylene)	9.3	p	Methanol	14.5	s
Di(propylene glycol) monomethyl ether	9.3	m	Ethylene glycol	14.6	s
Chloroform	9.3	p	Ethylene carbonate	14.7	m
Dibutyl phthalate	9.3	m	Glycerol	16.5	s
Methyl ethyl ketone	9.3	m	Water	23.4	s
Dibenzyl ether	9.4	m			
Ethylene glycol monobutyl ether (Butyl Cellosolve®)	9.5	m			

⁴H-Bonding: p = poor; m = moderate; s = strong

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Table IV: Solubility Parameters for Homopolymers⁵

Repeating Unit (Alphabetical Sequence)	$\delta(\text{cal/cm}^3)^{1/2}$	Repeating Unit (Increasing δ Value Sequence)	$\delta(\text{cal/cm}^3)^{1/2}$
Acrylonitrile	12.5	Tetrafluoroethylene	6.2
Butyl acrylate	9.0	Isobutyl methacrylate	7.2
Butyl methacrylate	8.8	Dimethylsiloxane	7.5
Cellulose	15.6	Propylene oxide	7.5
Cellulose acetate (56% Ac groups)	27.8	Isobutylene	7.8
Cellulose nitrate (11.8% N)	14.8	Stearyl methacrylate	7.8
Chloroprene	9.4	Ethylene	8.0
Dimethylsiloxane	7.5	1,4- <i>cis</i> -Isoprene	8.0
Ethyl acrylate	9.5	Isobornyl methacrylate	8.1
Ethylene	8.0	Isoprene, natural rubber	8.2
Ethylene terephthalate	10.7	Lauryl methacrylate	8.2
Ethyl methacrylate	9.0	Isobornyl acrylate	8.2
Formaldehyde (Oxymethylene)	9.9	Octyl methacrylate	8.4
Hexamethylene adipamide (Nylon 6/6)	13.6	<i>n</i> -Hexyl methacrylate	8.6
<i>n</i> -Hexyl methacrylate	8.6	Styrene	8.7
Isobornyl acrylate	8.2	Propyl methacrylate	8.8
1,4- <i>cis</i> -Isoprene	8.0	Butyl methacrylate	8.8
Isoprene, natural rubber	8.2	Ethyl methacrylate	9.0
Isobutylene	7.8	Butyl acrylate	9.0
Isobornyl methacrylate	8.1	Propyl acrylate	9.0
Isobutyl methacrylate	7.2	Propylene	9.3
Lauryl methacrylate	8.2	Chloroprene	9.4
Methacrylonitrile	10.7	Tetrahydrofuran	9.4
Methyl acrylate	10.0	Methyl methacrylate	9.5
Methyl methacrylate	9.5	Ethyl acrylate	9.5
Octyl methacrylate	8.4	Vinyl chloride	9.5
Propyl acrylate	9.0	Formaldehyde (Oxymethylene)	9.9
Propylene	9.3	Methyl acrylate	10.0
Propylene oxide	7.5	Vinyl acetate	10.0
Propyl methacrylate	8.8	Methacrylonitrile	10.7
Stearyl methacrylate	7.8	Ethylene terephthalate	10.7
Styrene	8.7	Vinylidene chloride	12.2
Tetrafluoroethylene	6.2	Acrylonitrile	12.5
Tetrahydrofuran	9.4	Vinyl alcohol	12.6
Vinyl acetate	10.0	Hexamethylene adipamide(Nylon 6/6)	13.6
Vinyl alcohol	12.6	Cellulose nitrate (11.8% N)	14.8
Vinyl chloride	9.5	Cellulose	15.6
Vinylidene chloride	12.2	Cellulose acetate (56% Ac groups)	27.8

⁵Values reported are for homopolymers of the Repeating Unit. Reported δ values vary with the method of determination and test conditions. Averaged values are given in this table.