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 guide[1] 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)	*m*-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	*m*-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, *m*-cresol, formic acid
Urethanes	Phenol, *m*-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
N-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**.

Reference: Polymer Properties

Polymer Solutions: Solvents and Solubility Parameters (continued)

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 ($\delta_{polymer}$) and solvent ($\delta_{solvent}$), 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, ($\delta_{polymer}$ - $\delta_{solvent}$), 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 below[2] or other references for a more detailed explanation of δ values.

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

Solvent	δ (cal/cm³)F	H-Bonding Strength[3]	Solvent	δ (cal/cm³)½	H-Bonding Strength[3]
Acetone	9.9	m	Dioctyl 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) monomethyl ether	9.3	m
Benzene	9.2	p	Dipropyl phthalate	9.7	m
Butyl acetate	8.3	m	Ethyl acetate	9.1	m
Butyl alcohol	11.4	s	Ethyl amyl ketone	8.2	m
Butyl butyrate	8.1	m	Ethyl *n*-butyrate	8.5	m
Carbon disulfide	10.0	p	Ethylene carbonate	14.7	m
Carbon tetrachloride	8.6	p	Ethylene dichloride	9.8	p
Chlorobenzene	9.5	p	Ethylene glycol	14.6	s
Chloroform	9.3	p	Ethylene glycol diacetate	10.0	m
Cresol	10.2	s	Ethylene glycol diethyl ether	8.3	m
Cyclohexanol	11.4	s	Ethylene glycol dimethyl ether	8.6	m
Diamyl ether	7.3	m	Ethylene glycol monobutyl ether (Butyl Cellosolve®)	9.5	m
Diamyl phthalate	9.1	m	Ethylene glycol monoethyl ether (Cellosolve®)	10.5	m
Dibenzyl ether	9.4	m	Furfuryl alcohol	12.5	s
Dibutyl phthalate	9.3	m	Glycerol	16.5	s
Dibutyl sebacate	9.2	m	Hexane	7.3	p
1,2-Dichlorobenzene	10.0	p	Isopropyl alcohol	8.8	m
Diethyl carbonate	8.8	m	Methanol	14.5	s
Di(ethylene glycol)	12.1	s	Methyl amyl ketone	8.5	m
Di(ethylene glycol) monobutyl ether (Butyl Carbitol®)	9.5	m	Methylene chloride	9.7	p
Di(ethylene glycol) monoethyl ether (Carbitol®)	10.2	m	Methyl ethyl ketone	9.3	m
Diethyl ether	7.4	m	Methyl isobutyl ketone	8.4	m
Diethyl ketone	8.8	m	Propyl acetate	8.8	m
Diethyl phthalate	10.0	m	1,2-Propylenecarbonate	13.3	m
Di-*n*-hexyl phthalate	8.9	m	Propylene glycol	12.6	s
Diisodecyl phthalate	7.2	m	Propylene glycol methyl ether	10.1	m
N,N-Dimethylacetamide	10.8	m	Pyridine	10.7	s
Dimethyl ether	8.8	m	1,1,2,2-Tetrachloroethane	9.7	p
N,N-Dimethylformamide	12.1	m	Tetrachloroethylene (perchloroethylene)	9.3	p
Dimethyl phthalate	10.7	m	Tetrahydrofuran	9.1	m
Dimethylsiloxanes	4.9-5.9	p	Toluene	8.9	p
Dimethyl sulfoxide	12.0	m	Water	23.4	s
Dioctyl adipate	8.7	m			
Dioctyl phthalate	7.9	m			

[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.**

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

Reference: Polymer Properties

Polymer Solutions: Solvents and Solubility Parameters (continued)

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

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

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

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Polymer Solutions: Solvents and Solubility Parameters (continued)

Table IV: Solubility Parameters for Homopolymers[5]

Repeating Unit	δ(cal/cm³)½
(Alphabetical Sequence)	
Acrylonitrile	12.5
Butyl acrylate	9.0
Butyl methacrylate	8.8
Cellulose	15.6
Cellulose acetate (56% Ac groups)	27.8
Cellulose nitrate (11.8% N)	14.8
Chloroprene	9.4
Dimethylsiloxane	7.5
Ethyl acrylate	9.5
Ethylene	8.0
Ethylene terephthalate	10.7
Ethyl methacrylate	9.0
Formaldehyde (Oxymethylene)	9.9
Hexamethylene adipamide (Nylon 6/6)	13.6
n-Hexyl methacrylate	8.6
Isobornyl acrylate	8.2
1,4-*cis*-Isoprene	8.0
Isoprene, natural rubber	8.2
Isobutylene	7.8
Isobornyl methacrylate	8.1
Isobutyl methacrylate	7.2
Lauryl methacrylate	8.2
Methacrylonitrile	10.7
Methyl acrylate	10.0
Methyl methacrylate	9.5
Octyl methacrylate	8.4
Propyl acrylate	9.0
Propylene	9.3
Propylene oxide	7.5
Propyl methacrylate	8.8
Stearyl methacrylate	7.8
Styrene	8.7
Tetrafluoroethylene	6.2
Tetrahydrofuran	9.4
Vinyl acetate	10.0
Vinyl alcohol	12.6
Vinyl chloride	9.5
Vinylidene chloride	12.2

Repeating Unit	δ(cal/cm³)½
(Increasing δ Value Sequence)	
Tetrafluoroethylene	6.2
Isobutyl methacrylate	7.2
Dimethylsiloxane	7.5
Propylene oxide	7.5
Isobutylene	7.8
Stearyl methacrylate	7.8
Ethylene	8.0
1,4-*cis*-Isoprene	8.0
Isobornyl methacrylate	8.1
Isoprene, natural rubber	8.2
Lauryl methacrylate	8.2
Isobornyl acrylate	8.2
Octyl methacrylate	8.4
n-Hexyl methacrylate	8.6
Styrene	8.7
Propyl methacrylate	8.8
Butyl methacrylate	8.8
Ethyl methacrylate	9.0
Butyl acrylate	9.0
Propyl acrylate	9.0
Propylene	9.3
Chloroprene	9.4
Tetrahydrofuran	9.4
Methyl methacrylate	9.5
Ethyl acrylate	9.5
Vinyl chloride	9.5
Formaldehyde (Oxymethylene)	9.9
Methyl acrylate	10.0
Vinyl acetate	10.0
Methacrylonitrile	10.7
Ethylene terephthalate	10.7
Vinylidene chloride	12.2
Acrylonitrile	12.5
Vinyl alcohol	12.6
Hexamethylene adipamide(Nylon 6/6)	13.6
Cellulose nitrate (11.8% N)	14.8
Cellulose	15.6
Cellulose acetate (56% Ac groups)	27.8

[5]Values 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.