

Solubility Characteristics of Poly(Etheretherketone) and Poly(Phenylene Sulfide)

H. N. BECK

Central Research & Development—Walnut Creek, The Dow Chemical Company, Walnut Creek, California 94598

SYNOPSIS

The crystalline high-performance polymers poly(etheretherketone) (PEEK) and poly(phenylene sulfide) (PPS) are generally considered to be highly resistant to dissolution in most common solvents. This article reveals numerous compounds that dissolve in excess of 25 wt % of each polymer at elevated temperatures. Typical binary-phase diagrams depicting the minimum solubility temperature vs. concentration are also presented for several representative polymer-solvent mixtures for both PEEK and PPS. The phenomenon of the solvent-induced crystallization of PEEK is presented. The importance of these polymer-solvent systems for the preparation of permselective membranes is discussed.

INTRODUCTION

Poly(oxy-*p*-phenyleneoxy-*p*-phenylenecarbonyl-*p*-phenylene), also known as poly(etheretherketone) (PEEK), is a prime potential candidate for the preparation of permselective membranes. Its desirable features include (1) a relatively high glass temperature of about 144°C, (2) a high crystalline melting point of about 334°C, (3) excellent thermal stability, (4) a high resistance to common solvents, and (5) readily commercial availability. Poly(phenylene sulfide) (PPS) is another engineering thermoplastic that also is a candidate for membrane utility for essentially the same reasons. Its high crystalline melting point of about 286°C and its good solvent resistance make it particularly attractive.

The preparation of useful homogeneous or asymmetric permselective membranes for liquid or gas separations frequently involves the extrusion or casting of a polymer from its solution in a suitable solvent or solvent-nonsolvent mixture. The concentration of polymer in such solutions must be high enough to ensure sufficient physical integrity for processing. Concentrations in excess of 10 wt % and preferably in the range of 25–50% are often required. Membrane formation from essentially amorphous

polymers such as polysulfone or polyethersulfone is generally readily achieved because such polymers usually are readily soluble in numerous common solvents at near-ambient temperatures. An additional energy barrier to dissolution exists in semi-crystalline polymers in the form of the crystalline moieties. Such polymers, for example, polyethylene, polypropylene, and cellulose triacetate, require more severe conditions for dissolution; these include higher boiling and more thermally stable solvents and elevated temperatures to affect *significant* dissolution. PEEK and PPS fall into this class of semi-crystalline polymers.

The literature reveals few solvents for PEEK (Chemical Abstracts registry number 31694-16-3). Included are diaryl sulfones, such as diphenyl sulfone, 1-chloronaphthalene, and benzophenone. Elevated temperatures were necessary to affect dissolution, e.g., diphenyl sulfone dissolved about 70% polymer at 380–390°C.¹ The solvent abilities of the other two solvents are somewhat restricted by their relatively low boiling points. More solvents have been reported for PPS (Chemical Abstracts registry numbers 9016-75-5, 9036-11-7, and 25212-74-2). Over 40 references have mentioned the use of “solvents” in the synthesis of the polymer; they include hot aprotic polar organic solvents, peralkylated cyclic ureas, *N*-alkyllactams, such as *N*-methyl-2-pyrrolidinone, *N,N*-diethylbenzamide, *N,N*-diethyltoluamide, *N,N*-dimethylethylene urea, *N,N*-di-

methylacetamide, hexamethylphosphoramide, or *N*-methylcaprolactam. It is not clear from the abstracts if these compounds are truly solvents for the polymer or if they are only solvents for the reactants and are also behaving as dispersive and/or heat transfer media from which the polymer precipitates.

1-Cyclohexyl-2-pyrrolidinone and 1-chloronaphthalene have been used as solvents for viscosity measurements; such solutions are most likely dilute. The only class of compounds found that was reported to be a solvent is chlorinated diphenyl ethers.² For example, a 16.7% solution of PPS was prepared in *p*-chlorodiphenyl ether at 230°C. Some strongly acidic materials such as concentrated sulfuric acid may also "dissolve" these polymers, but such "solvent" action more likely reflects reaction with the polymer rather than true dissolution.

This article documents numerous additional effective, thermally stable, high-temperature solvents for both PEEK and PPS. Included are binary-phase diagrams representing the minimum solubility temperature vs. concentration for several representative polymer-solvent systems.

EXPERIMENTAL

PEEK, grades 150P and 380G, were obtained from ICI Americas, Inc. Grade 150P was used for solubility screenings. Grade 380G was used for phase diagram determinations; it melted and froze at $341.2 \pm 1.0^\circ\text{C}$ and $298.7 \pm 0.8^\circ\text{C}$, respectively, at a differential scanning calorimetry (DSC) rate of $10^\circ\text{C}/\text{min}$. PEEK was dried at 150°C for 17 h and subsequently stored over Drierite. Poly(phenylene sulfide) was obtained from Aldrich Chemical Company and was used as received; it melted and froze at $280.8 \pm 0.7^\circ\text{C}$ and $239.4 \pm 1.2^\circ\text{C}$, respectively, when scanned at $10^\circ\text{C}/\text{min}$. Solvents were obtained from a variety of sources, mostly from Aldrich Chemical Company, and were used as received. Over 100 compounds were screened as potential solvents for each polymer. Mixtures were observed visually by bright transmitted light from an AO universal microscope illuminator in 1- to 4-dram capacity glass vials under a nitrogen blanket at about 250, 275, 300, and 350°C , the exact temperature selected being determined by the apparent polymer solubility and the boiling and/or decomposition temperature of the particular compound. Mixtures were subjected to the elevated temperatures for at least 2 h with intermediate mixing by shaking, inversion, and/or rotation of the vials.

Phase diagrams were prepared on mixtures containing 10–70 wt % polymer. Complete dissolution and homogeneity on PEEK mixtures were ensured by heating the mixtures at 350°C for 4 h with periodic inversion of the vials. PPS mixtures were similarly prepared at $270\text{--}280^\circ\text{C}$. The homogeneous solutions were cooled below their solidification temperature. Resolution was then visually observed by slowly heating each sample in an air-circulating oven in 1° Centigrade increments while allowing *at least* 15–20 min between temperature changes. Oven temperatures were estimated to be precise to $\pm 0.5^\circ\text{C}$. The temperature of dissolution was recorded when the specimen was *completely* clear by bright transmitted light. The completely dissolved mixtures were usually deep red.

RESULTS AND DISCUSSION

Polymer Solvents

Solubility parameters are frequently used as a guide for selecting solvents for amorphous polymers.³ At the present time, this method has limited utility for high-melting crystalline polymers. The effects of crystallinity and elevated temperatures, as well as the necessity of using calculated solubility parameter values for both polymers and potential solvents, contribute strongly to this limitation. The alternative evaluation method used here is the "Edisonian" one, consisting of the judicious selection and screening of many compounds for their solvent ability. Solvents are limited in their utility by their inertness and vapor pressure. The high-temperature behavior of both PEEK and PPS require high-boiling thermally and chemically stable compounds for their dissolution; such compounds are generally, though not always, solids at normal room temperatures.

Tables I and II list compounds found to dissolve significant amounts of PEEK and PPS, respectively, at elevated temperatures. The approximate solubility and the corresponding temperature are not intended to be limiting values; they can serve primarily as guides for future solvent selection. It is difficult to glean any broad generalizations regarding "good" solvents for these polymers. Solvents are represented by diverse types of chemical compounds; in general, they are high-boiling, thermally stable, aromatic hydrocarbons or compounds that contain a significant aromatic content. They are also characterized by heterocyclic compounds, compounds containing nitrogen, sulfur, and/or halogens, esters, acids, ke-

Table I Solvents for PEEK

Compound	Approximate Solubility	Temperature (%)
1,2,3-Triphenylbenzene	> 50.1 wt %	349
1,2-Dibenzoylbenzene	> 50.2	349
1-Benzyl-2-pyrrolidinone	> 14.9	302
1-Phenylnaphthalene	9.9-25.0	302
1-Phenyl-2-pyrrolidinone	> 50.0	317
2,5-Diphenyloxazole	> 50.0	349
2,5-Diphenyl-1,3,4-oxadiazole	> 49.9	349
2,6-Diphenylphenol	> 50.0	349
2-Benzoylnaphthalene	> 49.9	349
2-Biphenylcarboxylic acid	> 50.1	349
3-Phenoxybenzyl alcohol	> 24.7	302
4,4'-Dibromobiphenyl	> 50.1	349
4,4'-Dihydroxybenzophenone	> 25.0	310
4,4'-Dimethoxybenzophenone	> 50.0	349
4,4'-Isopropylidenediphenol	> 50.0	318
4-Benzoylbiphenyl	> 50.1	349
4-Biphenylcarboxylic acid	> 50.1	349
4-Bromobiphenyl	5.2-24.8	302
4-Phenylphenol	> 50.0	304
9,10-Diphenylanthracene	> 50.0	349
9,9'-Bifluorene	> 50.2	327
9-Fluorenone	> 24.9	302
Anthracene	> 10.0	302
Benzil	> 10.2	302
Benzophenone	> 11.3	300
Dibenzoylmethane	> 50.4	349
Diphenyl phthalate	> 50.0	349
Diphenyl sulfone	> 50.0	349
Fluoranthene	> 50.0	349
<i>m</i> -Terphenyl	> 50.2	349
Pentachlorophenol	> 25.0	302
Pentafluorophenol	> 5.0	141
Phenanthrene	> 10.0	302
Phenothiazine	> 49.9	349
Pyrene	> 50.0	347
<i>p</i> -Terphenyl	> 50.0	349
Santowax R TM	> 60.0	347
Therminol 66 TM	> 50.1	337
Therminol 75 TM	> 50.3	332
Triphenylene	> 50.0	350
Triphenylmethane	> 50.2	349

tones, and phenols, and by organic, alkali, and/or water-soluble materials. (The solvents designated as HB-40,TM Santowax R,TM Therminol 66,TM and Therminol 75TM are products of the Monsanto Company that are hydrogenated terphenyl, mixed terphenyls, partially hydrogenated terphenyls, and mixed terphenyls and quaterphenyls, respectively.) Functional groups may be important in promoting solubility through establishment of intermolecular forces between the compound and the polymers, or

they may be simply serving to raise the boiling point, thus allowing solubility to be achieved at higher temperatures. Solvents are themselves soluble in other organic solvents. A few of the polymer solvents, e.g., caprolactam, bisphenol-A, 4-phenylphenol, 1-cyclohexyl-2-pyrrolidinone, or *o,o'*-biphenol, are water or alkali soluble. This can be important in the commercial manufacture of membranes because aqueous quench and leach solutions may be used and recycled in place of larger

Table II Solvents for PPS

Compound	Approximate Solubility	Temperature (°C)	Compound	Approximate Solubility	Temperature (°C)
1,1-Diphenylacetone	> 49.9 wt %	302	4-Phenylphenol	> 50.0 wt %	302
1,2,3-Triphenylbenzene	> 49.9	349	9,10-Dichloroanthracene	> 50.0	302
1,3-Diphenylacetone	> 49.8	302	9,10-Diphenylanthracene	> 50.0	349
1,4-Dibenzoylbutane	> 49.8	302	9,9'-Bifluorene	> 50.1	275
1-Benzyl-2-pyrrolidinone	> 50.4	302	9-Fluorenone	> 50.4	302
1-Bromonaphthalene	> 50.6	274	Anthracene	> 50.2	302
1-Chloronaphthalene	> 24.3	236	Benzil	> 50.2	302
1-Cyclohexyl-2-pyrrolidinone	> 50.2	302	Benzophenone	> 50.4	274
1-Ethoxynaphthalene	> 49.8	274	Dibenzothiophene	> 50.3	302
1-Methoxynaphthalene	> 48.9	247	Dibenzoylmethane	> 50.2	349
1-Phenyl-naphthalene	> 50.1	302	Diphenyl carbonate	> 24.9	302
1-Phenyl-2-pyrrolidinone	> 50.0	273	Diphenyl phthalate	> 24.8	349
2,4,6-Trichlorophenol	> 25.0	247	Diphenyl sulfone	> 50.0	349
2,5-Diphenyloxazole	> 50.1	349	ϵ -Caprolactam	> 25.1	242
2,5-Diphenyl-1,3,4-oxadiazole	> 50.1	349	Fluoranthene	> 50.0	349
2,6-Dimethoxynaphthalene	> 50.1	274	Fluorene	\leq 50.1	274
2,6-Diphenylphenol	> 49.9	349	HB-40 TM	> 49.4	302
2,7-Dimethoxynaphthalene	> 50.1	274	<i>m</i> -Terphenyl	> 50.2	302
2-Benzoylnaphthalene	> 50.5	349	<i>N,N</i> -Diphenylformamide	> 50.2	302
2-Biphenylcarboxylic acid	> 50.2	349	<i>o,o'</i> -Biphenol	> 49.9	302
2-Methoxynaphthalene	> 24.8	242	<i>o</i> -Terphenyl	> 49.9	302
2-Phenoxybiphenyl	> 50.5	302	Phenanthrene	> 49.9	302
2-Phenylphenol	> 50.0	274	Phenothiazine	> 50.1	349
3-Phenoxybenzyl alcohol	> 50.0	302	Pyrene	> 50.0	273
4,4'-Dibromobiphenyl	> 50.1	302	<i>p</i> -Terphenyl	> 50.0	302
4,4'-Dimethoxybenzophenone	> 50.0	349	Santowax R TM	> 50.0	273
4,4'-Diphenylbenzophenone	> 50.0	302	Tetraphenylmethane	> 25.2	349
4,4'-Isopropylidenediphenol	> 24.9	275	Therminol 66 TM	> 50.0	273
4-Benzoylbiphenyl	> 49.9	302	Therminol 75 TM	> 50.0	273
4-Biphenylcarboxylic acid	\leq 25.7	349	Thianthrene	> 50.0	302
4-Bromobiphenyl	> 50.0	258	Triphenylene	> 49.9	350
4-Bromodiphenyl ether	> 50.1	274	Triphenylmethane	> 50.0	349

quantities of potentially flammable and/or toxic organic solvents. Aliphatic hydrocarbons or compounds containing a significant aliphatic content are poor solvents or nonsolvents for both polymers. Steric effects are important; for example, 1,2,3-triphenylbenzene dissolves over 50 wt % PEEK while 1,3,5-triphenylbenzene dissolves less than 10%.

Obviously, PPS is a more soluble polymer than PEEK. Temperatures generally in excess of about 300°C and about 240°C are necessary to achieve any significant dissolution of PEEK and PPS, respectively. The T_m of each polymer apparently must be approached or exceeded for significant initial dissolution to occur. Most likely, the higher temperatures are necessary to destroy crystallinity; the resulting amorphous polymer is then soluble in the compound.

Phase Diagrams

Binary-phase diagrams were determined for 17 representative solvents for both polymers; the diagrams

show the minimum solubility temperature as a function of polymer concentration. Figure 1 is such a diagram showing a linear plot for mixtures of PEEK and diphenyl sulfone. Any point above the line represents a soluble one-phase mixture; any below, an insoluble multiphase composition. Linear equations representing the data for the mixtures are presented in Table III. (The coefficients are shown to one more significant figure than observed.) The correlation coefficients show a close agreement with linearity. Slightly better correlation was found using more exotic curve-fitting procedures.⁴ It is important to note that although any of the curves may be *mathematically* extrapolated the results may have little or no practical and realistic significance below about 10 and above about 90% polymer concentrations; solubility at 0 or 100% polymer concentration is, of course, a meaningless discontinuity. Although data were obtained only by heating a multiphase composition, the diagrams represent a close approach to equilibrium conditions due to the very slowness of temperature change. Greater sources of

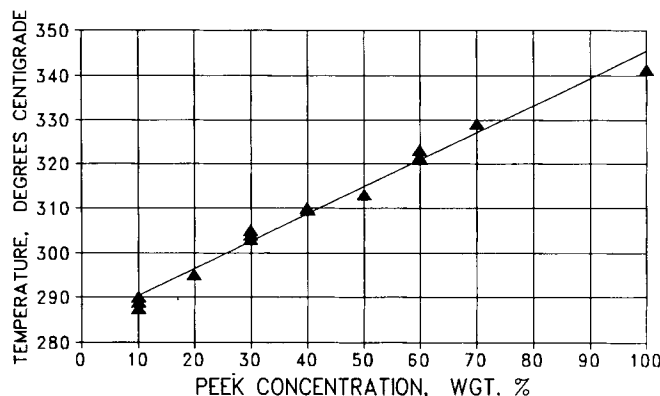


Figure 1 PEEK–diphenyl sulfone mixtures. Minimum solubility temperatures vs. concentration.

error may lie in operator judgment of complete dissolution due to smallness of particle or domain size or possible refractive index matches. The equations further reinforce the screening observations that PPS is a more soluble polymer than PEEK at similar concentrations and temperatures. For typical membrane-spinning operations that use, for example, 50 wt % polymer, melt temperatures in excess of about 308–320°C and about 249–270°C would be required to affect complete polymer dissolution for PEEK and PPS, respectively, in the solvents shown.

Solvent-Induced Crystallization of PEEK

The solvent-induced crystallization of amorphous polymers is well documented. The degree and rate of crystallization are determined by a diffusion-controlled process involving solvent, concentration, and contact time and temperature. The exposure of amorphous PEEK solid and hollow fibers at 101–115°C for 4 to 5 d to several of the solvents in Table I resulted in partial to complete crystallization. PEEK when heated in the absence of solvent ex-

Table III Equations Representing Minimum Solubility Temperature vs. Polymer Concentration^a

Polymer	Solvent	A ^a (°C)	B ^a (°C/%)	R ^{2 a}
PEEK	<i>m</i> -Terphenyl	293.8	0.5019	0.97
PEEK	Diphenyl sulfone	284.3	0.6081	0.99
PEEK	Fluoranthene	273.0	0.7627	0.97
PEEK	Pyrene	266.7	0.8173	0.97
PPS	Diphenyl sulfone	260.1	0.2065	0.94
PPS	Benzil	248.7	0.3180	1.00
PPS	<i>o,o'</i> -Biphenol	246.4	0.3547	0.99
PPS	Benzophenone	233.7	0.4805	1.00
PPS	ϵ -Caprolactam	233.2	0.4650	0.99
PPS	<i>m</i> -Terphenyl	231.9	0.5202	0.97
PPS	4-Phenylphenol	230.1	0.5190	0.99
PPS	2-Phenylphenol	227.9	0.5408	0.99
PPS	9-Fluorenone	224.6	0.5780	0.99
PPS	Fluoranthene	223.9	0.5931	0.98
PPS	1-Cyclohexyl-2-pyrrolidinone	219.9	0.6204	0.99
PPS	Anthracene	217.0	0.6482	1.00
PPS	Pyrene	216.9	0.6760	0.97

^a $Y = A + BX$, where Y = temperature (°C); X = polymer concentration, wt %; and R^2 = coefficient of determination.

hibited no significant crystallization under these conditions. The solvents inducing crystallization were, in approximate order of effectiveness, 1-phenyl-2-pyrrolidinone > benzophenone > 1-cyclohexyl-2-pyrrolidinone > *m*-terphenyl > fluoranthene > diphenyl phthalate. Solvent-induced crystallization can be of utility in the preparation and control of the asymmetric portion of certain membranes.

CONCLUSIONS

The crystalline polymers PEEK and PPS are generally considered resistant to dissolution to any significant extent in most common solvents. However, numerous thermally stable compounds of diverse chemical structure and high boiling points are very effective solvents provided the polymers' crystalline melting points are approached or exceeded. Such solvents are generally solids at room temperature. Polymer concentrations exceeding at least about 70 wt % can be readily achieved. Such concentrations are sufficient to show promise for the preparation of asymmetric or homogeneous permselective membranes from these solutions. The solvents may also

induce crystallization to occur in amorphous PEEK at least 40°C below its glass temperature; such behavior is also anticipated to occur with PPS.

The author is indebted to Drs. R. D. Mahoney and R. A. Lundgard of Central Research & Development, The Dow Chemical Company, for their inputs to and discussions of this work.

REFERENCES

1. F. N. Cogswell and P. A. Staniland, *Eur. Pat. Appl.* EP 102159 A2 (1984) (to Imperial Chemical Industries PLC); *Chem. Abstr.* **100**(26): 211107m (1984).
2. H. A. Smith, U. S. Pat. 4,118,363 (1978) (to The Dow Chemical Co.).
3. A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Inc., Boca Raton, FL, 1983.
4. Hewlett-Packard Program No. 00112-75-1 for HP Model 75C computer. Copies of these curves may be obtained from the author if desired.

Received July 15, 1991

Accepted September 4, 1991