

Relative Solubility of Tetrachlorohexafluorobisphenol-A Polycarbonate in Various Compounds

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SYNOPSIS

The relative solubility of tetrachlorohexafluorobisphenol-A polycarbonate was observed in 127 organic compounds comprising 14 different chemical classes at room temperature and up to about 225°C. The polymer is soluble in numerous esters, ketones, halocarbons, heterocyclics, and amides. It is poorly soluble in alcohols and fluorocarbons. Correlation of observed solubility with Hildebrand total solubility parameters was poor; a much better correlation was observed with Hansen three-dimensional parameters. The solubility parameter of the polymer was estimated to be $9.1 \text{ (cal/cm}^3)^{1/2}$ ($18.7 \text{ MPa}^{1/2}$) from the averages of the Hansen parameters for 26 experimentally identified solvents. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

By varying the bisphenolic moiety in polycarbonate syntheses, a wide range of polymer physical and mechanical properties can be achieved that enable properties to be tailored to specific applications. The effects of substitutions on the isopropylidene moiety and on the phenyl rings of bisphenol-A have been previously reported and analyzed.¹ Alkyl and halogen substituents on the ring tend to increase the glass transition temperature and the gamma transition. The gamma transition of polycarbonate has been cited as the source for the toughness of the polymer.² However, in Yee's work,¹ substitution on the isopropylidene linkage resulted in increases in the glass transition temperature without a corresponding increase in the gamma transition temperature. The present study focuses on a polycarbonate containing trifluoromethyl substitutions on the isopropylidene linkage and dichloro substitutions on each phenyl ring of the bisphenol-A precursor. The material is recognized by several names: tetrachlorohexafluorobisphenol-A polycarbonate, TCBAF-PC, and TCHF-PC. It is prepared from 1,1,1,3,3,3-hexafluoro-2,2-bis(4-hydroxy-3,5-di-

chlorophenyl)propane, which is also known as 4,4'-[trifluoro-1-(trifluoromethyl)ethylidene]bis[2,6-dichlorophenol] (*Chemical Abstracts* registry number 15859-48-0). The polymer has a glass transition temperature about 70–75°C higher than that of bisphenol-A polycarbonate, which could result in higher use temperatures. The fluorine in the isopropylidene moiety decreases the surface energy, thereby altering the wetting properties. The fluorine also provides a mechanism for altering the dielectric constant of the polymer.

Unfortunately, the high glass temperature of the polymer leads to melt-processing temperatures that result in thermal degradation in an air atmosphere. Solution processing of the polymer is one route to circumvent this problem. No assessment of the relative solubility behavior of this polymer is known. This article describes the relative solubility of the polymer in 127 different compounds comprising several chemical classes up to about 225°C.

EXPERIMENTAL

The polymer may be prepared by any standard interfacial or solution process. Phosgene and tetrachlorohexafluorobisphenol-A were allowed to react in methylene chloride solvent using NaOH as base and a chain terminator, such as *p-tert*-butylphenol, for molecular weight control.³

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Molecular weight enhancement may be achieved by the presence of an amine. Typically, the organic phase is extracted twice to remove residual salts followed by drying over anhydrous $MgSO_4$. The polymer is precipitated with excess heptane and vacuum-dried overnight at $100^\circ C$. The resulting fluffy white solid used in these experiments had an inherent viscosity of ~ 0.5 dL/g in methylene chloride at $25^\circ C$. The polymer density, measured with a Micromeritics helium pycnometer (AccuPyc 1330), was 1.711 ± 0.003 g/cc. The T_g was $\sim 218^\circ C$ (measured at $10^\circ C/min$).

The compounds examined were, with a few exceptions, obtained from Aldrich Chemical Co. and used as received. Mixtures weighing about 0.4–1.0 g and consisting of about 4–11% polymer were prepared in 1 dram-capacity glass vials with screw caps

containing aluminum foil liners. The samples were mixed by periodic inversion of the vials and/or by the use of mechanical rollers. The relative solubilities were visually observed as functions of temperature at room temperature and at several increments of temperature that did not exceed the boiling point of the compound or exceed about $225^\circ C$. Visual observations were recorded on each mixture after it was at the indicated temperature for at least about 40 min and often overnight. The mixtures were not necessarily at true equilibrium.

RESULTS AND DISCUSSION

The relative solubilities of the polymer in the various compounds are shown in Table I. (The "Reference"

Table I Relative Solubilities of TCHF-PC

Reference	Compound	Polymer Concn (%)	Relative Solubility		Temperature ($^\circ C$)
			At R.T.	At Temperature	
84	1-Phenyl-2-pyrrolidinone	9.0	d	PS; PS; PS	101; 151; 200
40	Tetrahydronaphthalene	9.0	c	PS; S	101; 151
28	Methyl acetate	9.4	Sa		
103	1,1,1-Trichloroethane	9.0	S		
14	1,1,3,3-Tetramethylurea	9.1	S		
6	1,2,4-Trichlorobenzene	9.5	S		
98	1-Acetylpiperidine	9.9	S		
9	1-Ethyl-2-pyrrolidinone	9.4	S		
106	4-Heptanone	9.2	S		
107	Amyl acetate (mixed isomers)	9.9	S		
100	Butyl (<i>n</i>) acetate	9.3	S		
W	Carbon tetrachloride	8.1	S		
2	Chlorobenzene	9.6	S		
A	Chloroform	7.5	S		
I	Cyclohexanone	9.9	S		
10	Cyclohexyl acetate	9.1	S		
15	Cyclopentanone	9.3	S		
103a	Diethyl carbonate	9.1	S		
G	Diethyl ketone	9.4	S		
66	Dioxane, <i>para</i>	9.3	S		
33	Dipropyl carbonate	9.3	S		
32	Ethyl acetate	10.1	S		
26	Ethyl formate	8.8	S		
O	Isophorone	9.6	S		
38	Methyl caproate	9.6	S		
36	Methyl caprylate	9.7	S		
37	Methyl enanthate	8.8	S		
E	Methyl ethyl ketone	8.9	S		
V	Methyl isobutyl ketone	9.5	S		
81	Methyl laurate	8.5	S		
17	Methylene chloride	11.7	S		

Table I (Continued)

Reference	Compound	Polymer Concn (%)	Relative Solubility		Temperature (°C)
			At R.T.	At Temperature	
46	<i>N</i> -Ethylmorpholine	9.9	S		
58	<i>N</i> -Methylcaprolactam	9.0	S		
49	Nitrobenzene	9.6	S		
27	Octyl acetate	9.2	S		
104	Perchloroethylene	8.5	S		
77	Piperidine	11.3	S		
51	Pyridine	9.4	S		
B	Tetrahydrofuran	8.9	S		
1	Trichloroethylene	9.6	S		
91	Styrene	9.0	PS?	S	101
16	1-Methyl-2-pyrrolidinone	9.6	PS	S	101
65	2,4-Dimethyl-3-pentanone	9.8	PS	PS	101
31	Acetone	11.4	PS		
89	Benzaldehyde	8.6	PS	S	101e
4	Dichlorobenzene, <i>ortho</i>	9.4	PS	S	101
104a	Dimethyl carbonate	9.5	PS		e
101	Dimethyl sebacate	8.9	PS	PS; S	101; 151
99	Methyl formate	6.6	PS		
86	Methyl iodide	6.1	PS		
8	1-Cyclohexyl-2-pyrrolidinone	9.0	MS	S	101
44	1-Formylpiperidine	9.4	MS	S	100
80	Ethylbenzene	9.3	I-PS?	PS	101
11	Ethyl benzoate	8.9	I-PS	S	101e
13	<i>N,N</i> -Dimethylacetamide	9.5	I-PS	S	101
12	<i>N,N</i> -Dimethylformamide	9.2	I-PS	PS; S	101; 125
64	1'-Acetonaphthone	8.3	I	I; PS; PS	101; 151; 200
93	1,1,1,3,3,3-Hexafluoro-2-propanol	6.9	I		
57	1,3-Dimethyl-2-imidazolidinone	9.2	I	PS; S	101; 151e
D	1,3-Dioxolane	10.4	I	PS	60
85	1-Benzyl-2-pyrrolidinone	8.6	I	PS; MS; S	101; 151; 200
88	1-Bromonaphthalene	7.2	I	PS; PS; PS	101; 151; 200
60	1-Hexanol	8.9	I	I; MS?	100; 151
90	2-Furaldehyde	7.6	I	MS; S	101; 151
47	2-Pyrrolidinone	9.2	I	I; MS; S	101; 151; 200
97	4-Acetylmorpholine	8.7	I	PS; S	101; 151e
96	4-Bromodiphenyl ether	9.1	I	I; PS; PS	101; 151; 200
43	Acetonitrile	9.5	I		
N	Acetophenone	10.0	I	PS; MS; S	86; 121; 150
3	Anisole	9.5	I	PS; S	101-125; 150
5	Benzophenone	9.2	I	PS	125-180
K	Bis(2-ethoxyethyl)ether	8.8	I	PS	185
J	Bis(2-methoxyethyl)ether; diglyme	9.3	I	PS	121-150
T	Butyl diglyme	8.7	I	PS	150-225
69	Butyl stearate	8.7	I	I; PS; S	101; 151; 200
21	Butyl(<i>tert</i>)cyclohexane	9.0	I	PS	136-156
105	Caprolactam	10.1	I	I; I; S	101; 126; 150
79	Caprolactone, epsilon	8.8	I	PS; S	101; 151
22	Cyclohexane	8.1	I	PS	76
19	Cyclohexylbenzene	9.1	I	PS; S	136-156; 185
30	Decahydronaphthalene	9.3	I	PS; S	136-145; 156
59	Diacetone alcohol	8.3	I	PS; MS?	100; 151
20	Dicyclohexyl	8.9	I	PS; S	136-156; 185

Table I (Continued)

Reference	Compound	Polymer Concn (%)	Relative Solubility		Temperature (°C)
			At R.T.	At Temperature	
48	Diethylene glycol	6.3	I	I; I; PS	101; 151; 200
102	Diiodomethane	6.4	I	I; I	101; 151
78	Dimethyl malonate	8.7	I	PS; MS	100; 151
35	Dimethyl phthalate	9.0	I	I; I; PS	100; 151; 200
108	Dimethyl sulfone	8.8	I	I; PS; PS	176; 200; 225
L	Dimethyl sulfoxide	9.4	I	MS; S	150; 185
34	Diocetyl phthalate	8.1	I	I; PS; MS	100; 151; 200
7	Diphenyl ether	9.1	I	PS	125-225
42	Docdecane	8.2	I	I; I; PS	100; 151; 200
56	Ethanol	8.6	I		
S	Ethylene carbonate	8.5	I	PS	225
61	Ethylene glycol	5.8	I	I; I	101; 151
H	Ethylene glycol diethyl ether	8.6	I	PS	121
C	Ethylene glycol dimethyl ether	8.2	I	I, S	60; 86
41	Hexadecane	8.4	I	I; I; PS	100; 151; 200
72	Hexamethylphosphoramide	8.9	I	S	100
55	Hexane	4.2	I		
53	Isopropyl alcohol	9.3	I		
18	Isopropylcyclohexane	8.6	I	PS; MS	136-145; 156
25	Methyl benzoate	9.1	I	PS; MS; S	76; 101; 136e
39	Methyl myristate	9.0	I	PS; S	101; 151
73	Methyl salicylate	8.7	I	S	100
23	Methylcyclohexane	8.2	I	PS	101
45	N-Formylmorpholine	9.4	I	PS; MS; S	100; 151; 200
82	N-Methylacetamide	9.0	I	I; I; PS	101; 151; 199
74	N-Methylformamide	9.0	I	I; MS	101; 151
50	Nitromethane	8.5	I	PS	101
70	PEG E600	6.6	I	I; I; I	101; 151; 200
71	Perfluoro(methylcyclohexane)	7.3	I		
95	Perfluoro-1,3-dimethylcyclohexane	6.7	I		
94	Perfluorohexane	6.4	I		
M	Phenetole	9.2	I	PS	86-150
75	Poly(dimethylsiloxane), 50 cs	5.2	I	I; I; I	101; 151; 200
76	Propionitrile	8.6	I		
P	Propylene carbonate	8.6	I	PS; S	185; 225
63	Styrene oxide	10.3	I	PS; S	101; 151
83	Sulfolane	6.3	I	I; PS; PS	100; 151; 200
54	Toluene	8.6	I	S	101
68	Tricresyl phosphate	8.2	I	I; I; PS	101; 151; 200
29	Triethyl orthoformate	8.8	I	I; PS	136; 145b
67	Triethyl phosphate	9.1	I	PS; MS; S	101; 151; 200
52	Triethylamine	7.9	I		e
62	Triethylene glycol	7.1	I	I; I; PS	100; 151; 200
24	Xylene	7.5	I	PS; MS	76-101; 136

R.T. = room temperature, ~ 24°C; S = completely soluble; PS = partially soluble; MS = mostly soluble; I = insoluble; a = cloudy solution, white solid precipitates with time at R.T.; b = partially soluble and cloudy at 145°C; c = swollen; d = solid at R.T.; e = possible solvent-induced crystallization.

numbers are arbitrary and for ease of referral only.) Fourteen classes of compounds are represented including esters, ketones, halocarbons, heterocyclics, alcohols, ethers, hydrocarbons, amides, amines, aldehydes, nitriles, nitro compounds, fluorocarbons, and several miscellaneous materials. Their approximate total Hildebrand-Scott solubility parameters⁴ range from about 5.6 to 16.2 (cal/cm³)^{1/2} (11.5–33.1 MPa^{1/2}).⁵ Thirty-eight compounds with solubility parameters of about 8.4–11.2 (cal/cm³)^{1/2} (17.2–22.9 MPa^{1/2}) were identified as solvents at room temperature. Seventeen compounds with solubility parameters of about 8.0–12.2 (cal/cm³)^{1/2} (16.4–24.9 MPa^{1/2}) showed intermediate solvent ability, and 72 compounds of solubility parameters about 5.6–16.2 (cal/cm³)^{1/2} (11.5–33.1 MPa^{1/2}) were nonsolvents. The designations of “solvent” and “nonsolvent” are relative only and do not take into account the rates of dissolution within the time frames of observation. The experimental observations do not distinguish between true dissolution and reaction and/or degradation followed by dissolution. The solubilities presented are relative only; the limiting solubilities, e.g., the maximum solubilities, were not determined. The compounds designated as solvents had sufficiently good solvent power to allow the polymer to be cast from their solutions. Errors due to refractive index matches and operator judgments are also possible. The advantage of the

present method is that it allows quick identification of solvents for further evaluations.

For chemical classes where at least eight representative compounds were examined at room temperature, halocarbons, ketones, esters, heterocyclics, and amides showed significant solvent activity. Similarly, alcohols, ethers, and hydrocarbons were significant nonsolvents. As expected, elevated temperatures significantly increased dissolution in most classes. No alcohols, fluorocarbons, nitriles, or amines were identified as solvents under any conditions.

Using a density of 1.711 g/cc and the group contribution tables of Hoy,⁶ the solubility parameter of TCHF-PC was calculated to be 9.55 (cal/cm³)^{1/2} (19.5 MPa^{1/2}). Using the tables of Hoy, Fedors,⁷ and Van Krevelen and Hoftyzer,⁸ an average value of 10.3 ± 0.7 (cal/cm³)^{1/2} (21.0 ± 1.3 MPa^{1/2}) was obtained. Even though these values fall in the middle of the range of values for the identified solvents mentioned above, there is large overlap of values for the three solvent classes. The use of the dispersion, polar, and hydrogen-bonding components of Hansen^{5,9} yields better correlations of compound structure with solvent ability. Figure 1 is a plot of the polar vs. hydrogen-bonding parameters^{9,10} for 73 compounds for which Hansen parameters were available. The enclosed area represents all 26 solvents and only 13 (28%) of the 46 nonsolvents. A

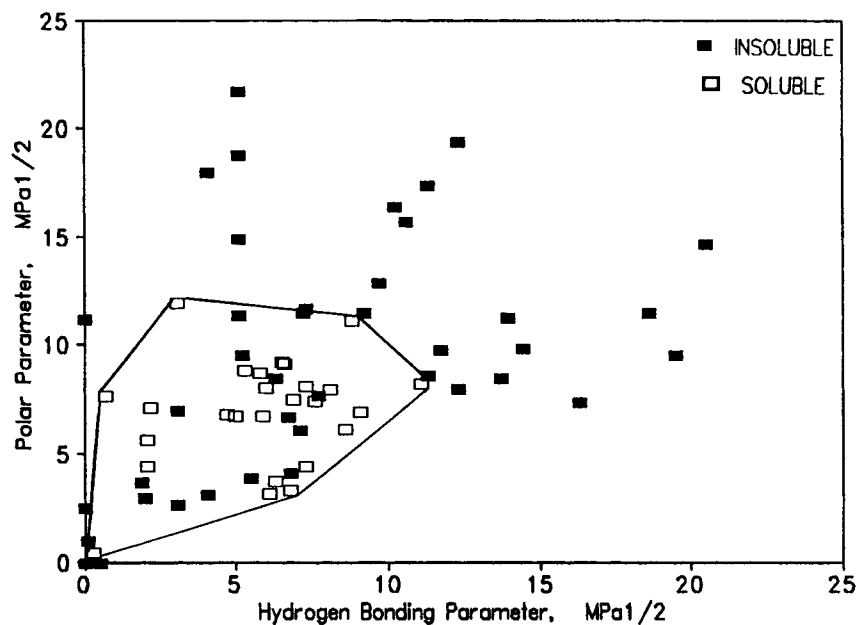


Figure 1 Solubility diagram for TCHF-PC. Hansen “P” vs. “H” components.

better correlation is also shown in Figure 2, which employs functions of all three Hansen parameters.¹¹ (F_D is 100 times the Hansen dispersion component divided by the sum of the three Hansen parameters; similar fraction contributions are calculated for the other two components.) The same relative distribution of solvent and nonsolvent points is indicated as in Figure 1. The average total solubility parameter of TCHF-PC calculated from the averages of the three Hansen parameters for the 26 experimentally identified solvents is $9.1 \text{ (cal/cm}^3)^{1/2}$ ($18.7 \text{ MPa}^{1/2}$). This is in relative good agreement with the values estimated from group contributions. It is significantly lower than a similarly obtained and corresponding value of $10.2 \text{ (cal/cm}^3)^{1/2}$ (20.8

$\text{MPa}^{1/2}$) reported for a related but nonfluorinated polymer, tetrabromobisphenol-A polycarbonate.¹²

CONCLUSIONS

Observations of the relative solubility of TCHF-PC in several classes of compounds have identified numerous solvents and nonsolvents that offer the specialist many potential preparative solution or dope compositions for the preparation of coatings, fibers, films, and other solid objects. Correlations of observed solubility with Hildebrand total solubility parameters were poor. Correlations with Hansen dispersion, hydrogen bonding, and polar parameters

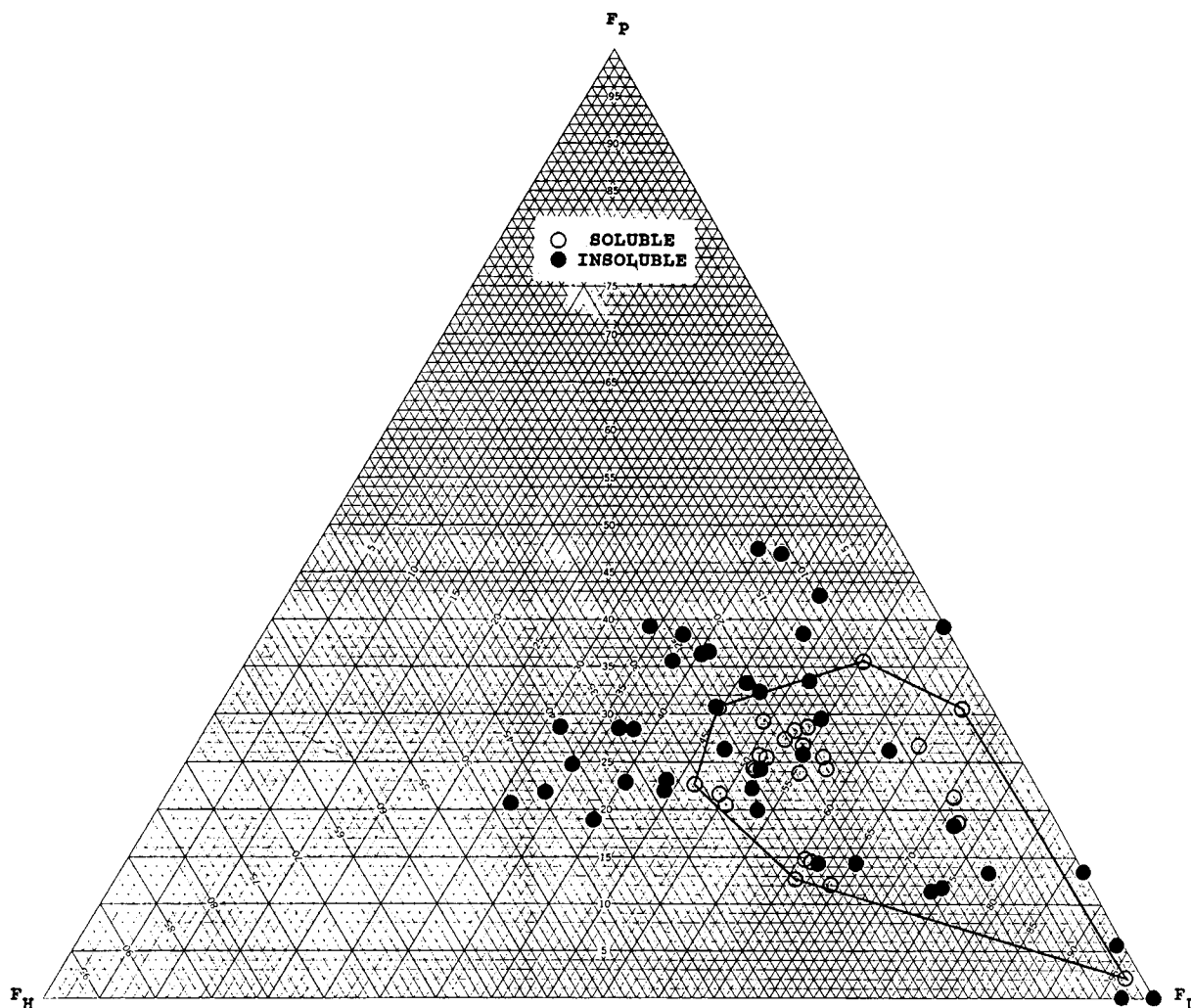


Figure 2 Solubility diagram for TCHF-PC. Graphical representation of solubility components of various liquids.

were much better; from these, a value of $9.1 \text{ (cal/cm}^3)^{1/2}$ ($18.7 \text{ MPa}^{1/2}$) is estimated for the polymer total solubility parameter.

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