Cresylic Soluble Polyimides

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Synopsis

Polyimides are prepared by reaction of dianhydrides with aromatic diamines under dehydrating conditions to insure conversion of the polyamic acids to polyimides. Cresylic acid solubility is observed only for cyclopentane dianhydride and benzophenone dianhydride. Most of the batches are made from BPDA, since it is the preferred dianhydride for thermal stability. Of 19 aromatic diamines only 2,4- and 2,6-diaminotoluene, 2,4-diaminoanisole, 4,5-dimethyl-1,2-phenylene diamine and 1,5-diamino-4,8-dihydroxyanthraquinone contribute a great deal toward making soluble polyimides of BPDA. 2,4-Diamino-acetanilide when used as the only diamine also gives a soluble polyimide with BPDA. The solubility of polyimides can be correlated with their solubility parameters, their symmetry, and their tendency to hydrogen bond.

INTRODUCTION

The outstanding thermal properties of polyimides are well known. Most polyimide coatings are formed from solution in *N*-alkyl substituted amides such as *N*-methyl pyrrolidone, dimethyl formamide, or dimethyl acetamide. This paper describes solutions of polyimides of 11–17% solids content in cresylic acid. Both successful and unsuccessful attempts to prepare cresylic acid-soluble polyimides from diamines and dianhydrides are reported. One of the incentives for this study is the excellent appearance of enameled copper wire prepared from cresylic acid solutions of these polyimides. Another motive is the economic advantage of cresylic acid over *N*-alkyl substituted amides as a solvent.

Although this is not an example of a cresol soluble polyimide, Holub[1] showed that benzophenone tetracarboxylic acid dianhydride reacted with *m*-phenylene diamine in cresol for 20 min at 140° to give a polyamide-acid solution. After dilution to 5% solids and application with heat to copper wire, a polyimide enamel was obtained. At higher solids in cresol or cresol–phenol mixtures this formulation[2] gave a smooth coating for glass if silicone was added. Suzuki[3] prepared a *m*-cresol-soluble linear aromatic polyimide from 3,3′-dimethyl-4,4′-diaminodiphenyl methane and benzophenone tetracarboxylic acid dianhydride. This group[4] extended their study of soluble polyimides to other substituted aromatic diamines and other dianhydrides. Reduction of the symmetry of the diamine monomers by substitution of the aromatic diamines by either alkyl, alkoxy, carboxyl, hydroxyl, or SO_3H groups improved solubility. Hosokawa[5] extended the study to include the formation of a cresol-soluble polyimide from benzophenone tetracarboxylic acid dianhydride and hexamethylene diamine. Hirota[6] found that he could make a cresol-soluble polyimide from pyromellitic dianhydride and a hydantoin containing aromatic diamine. Hosokawa[7] prepared cresylic acid soluble polyimides from benzophenone dianhydride and 4,4′- di-

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methyldiphenylmethane 3,3′-diisocyanate. An alternate[8] approach to the synthesis of a cresylic acid-soluble polyimide uses benzophenone tetracarboxylic acid dianhydride and 5(6)-amino-1-(4′-aminophenyl)-1,3,3-trimmethyl indane, blended with up to 25% methylene dianiline, to give a *m*-cresol-soluble polyimide. Cresol-soluble polyimides[9] have been prepared from oxydianiline and phenylated dianhydrides [4,4′(1,4-phenylene) bis (3,5,6-triphenyl phthalic anhydride and 4,4′, (oxydi-1,4-phenylene) bis (3,5,6-triphenyl phthalic anhydride)]. Harris and Seymour[10] have reviewed the structure solubility relationships in polyimides.

EXPERIMENTAL

The polyimides were prepared by reacting dianhydrides and diamines at approximately 30% solids in dry cresylic acid. After complete reaction the batches were reduced to approximately 15% solids with a mixture of phenol and cresylic acid. The final solvent composition was adjusted to 10 parts of phenol to 90 parts of cresylic acid.

To complete the reaction of the dianhydride with the diamine heat was applied so that the temperature rose to 170° while water was azeotroped off with toluene. The batch was thinned when the theoretical amount of water (1.8 cc for 0.05 mol of dianhydride) was obtained necessary to complete the conversion of the polyamic acid to the polyimide.

Most batches were made using 95% of the theoretical amount of diamine, assuming pure raw materials. Solids were determined by heating a 2-g sample of solution in an aluminum dish for 2 h at 200°C. Viscosity was measured by the Gardner–Holt bubble method. All batches that were soluble were stable for several months except the batch made with *o*-dianisidine which gelled in a week.

A list of dianhydrides and diamines with the code used in the table of this paper follows:

BPDA	benzophenone dianhydride Princeton 97%
BPDA 2	benzophenone dianhydride Gulf
BPDA 3	benzophenone dianhydride Aldrich 96%, mp 215–17°C, B975-0
PMDA	pyromellitic dianhydride Princeton
CPDA	cyclopentane tetracarboxylic dianhydride Aldrich 96%, mp 275–79°C, C11, 215-1
THFDA	tetrahydrofuran dianhydride Aldrich 14, 484-3
NTDA	1,4,5,8-naphthalene tetracarboxylic dianhydride, City Chem Corp., NYC
2,4 DA tol	2,4-diaminotoluol Fluka pract. F 96–99°C, 33360
2,6 DA tol	2,6 diamino toluol Fluka pract. 97%, F 102–105°C, 33370
3,4 DA tol	3,4-diaminotoluol Fluka pract. F 87–89°C, 33380
Dimetphe DA	4,5-dimethyl-1,2-phenylenediamine tech DuPont
DA anis	2,6-diaminoanisole Fluka pract. 32710
DA acet	2,4-diaminoacetanilide Fluka pract. 32690
DA benz	3,4-diaminobenzoic acid Fluka purum 32760

m-PheDA	*m*-phenylene diamine tech DuPont
MDA	4,4-diaminodiphenylmethane Fluka pract. F 89–92°C, 32950
ODA	oxydianiline Merck zur synthesis 98%, mp 188–192°C, 820948
Dianis	o-dianisidine Fluka ≥ 99%, F 135–137°C 33430
DA benzanil	3,4-diaminobenzanilide American Aniline Prod. Loch Haven, Pa.
Dibenzofur DA	3,6-dibenzofurandiamine Fluka purum 32945
DA dihydrox	3,3′-diamino-4,4′-dihydroxydiphenyl sulfone, Org. Int. Dept., Midland Yorkshiretars, Distillon Ltd., Oxlky Works
DA anthraq	1,5-diaminoanthraquinone Fluka purum 32740
DA naphth	1,8-diaminonaphthalene Fluka purum, F 62–65°, 33170
DA diphesulfide	4,4′-diaminodiphenyl sulfide Merck zur synthesis 98%, F 141–144°C, 821073
DA diphesulfone	diaminidiphenyl sulfone Merck zur synthesis 821073
DA dihydroxanthraq	1,5-diamino-4,8-dihydroxy anthraquinone

DISCUSSION

Cresylic acid-soluble polyimides can be made by reacting benzophenone dianhydride with certain diamines at a mole ratio of diamine to dianhydride of 0.95. If equimolar quanities are used, either one obtains batches of very high viscosity or gelation occurs. The solvent for the polyimides contains 10% phenol, since cresylic acid alone occasionally gives hazy solutions.

The five diamines that make polyimides soluble in cresylic acid are 2,4- and 2,6-diaminotoluene; 2,4-diaminoanisole; 4,5-dimethyl-1,2-phenylene diamine; and 1,5-diamine-4,8-dihydroxyanthraquinone. On a molar basis these five diamines seem equally effective. Batches containing 53 mol % of any of these diamines and 47 mol % methylene dianiline are soluble in cresylic acid. If only 42 mol % of any of these diamines is used with 58 mol % MDA, the polyimides are insoluble in cresylic acid. The viscosity of the solutions and toughness of films of these polyimides are similar for most of these diamines. However, the viscosity for 4,5-diamethyl-1,2-phenylene diamine containing polyimides is low, and the film is more brittle. The 1,2-location of the diamine groups can lead to a side reaction to form the imidazopyrrolone function which can act as a chain-stopper. This side reaction must have occurred also with 3,4-diaminotoluene, since it gave a low-viscosity polyimide which was clear and not smooth-flowing when examined in a viscosity tube.

Batches made with 100% 2,4-diaminoacetanilide clear up just at the end of the polymerization, but give films that are brittle.

Not all diamines can be matched with 53% 2,4-diaminotoluene to give cresylic-soluble polyimides. Those that can be used (besides MDA) are: 1,8-diaminonaphthalene; 3,4′-diaminobenzanilide; 1,5-diaminoanthraquinone; 3,6-dibenzofurandiamine; 4,4′-diaminodiphenyl sulfide; and oxydianiline.

Benzophenone dianhydrides from three different sources give similar viscosity-solids relationships using 53 mol% 2,4-diaminotoluene and 47% methylenedianiline.

TABLE I

Dianhydride	Diamine I	(%)	Diamine II	(%)	Visc	Solids	Solubility parameter
PMDA	2,4 DAtol	100	—	—	ins.		13.05
THFDA	2,4 DAtol	100	—	—	ins.		13.97
NTDA	2,4 DAtol	100	—	—	ins.		12.86
CPDA	2,4 DAtol	0	MDA	100	A	12.6	11.58
CPDA	2,4 DAtol	53	MDA	47	A	11.8	12.15
CPDA	2,4 DAtol	100	—	—	A	11.7	12.99
PMDA 50% BPDA 50%	2,4 DAtol	100	—	—	clear, gelled		12.67
BPDA	—	—	MDA	100	ins.		12.03
BPDA	2,4 DAtol	26	MDA	74	ins.		—
BPDA	2,4 DAtol	42	MDA	58	ins.		—
BPDA	2,4 DAtol	53	MDA	47	U	14.4	12.20
BPDA 2	2,4 DAtol	53	MDA	47	Y	14.3	12.20
BPDA 3	2,4 DAtol	53	MDA	47	V	15.4	12.20
BPDA	2,4 DAtol	74	MDA	26	T	13.6	—
BPDA	2,4 DAtol	100	—	—	W	14.2	12.41
BPDA[a]	2,4 DAtol	53	MDA	47	I	15.6	12.20
BPDA[b]	2,4 DAtol	53	MDA	47	Z	16.5	12.20
BPDA	2,4 DAtol	53	DAnaphth	47	D	13.1	12.43
BPDA	2,4 DAtol	53	DAbenzanil	47	U	14.5	12.35
BPDA	—	—	DAbenzanil	100	ins.		12.28
BPDA	2,4 DAtol	53	dianis	47	gelled on standing		12,13
BPDA	2,4 DAtol	53	DAanthraq	47	C	15.6	12.59
BPDA	—	—	DAanthraq	100	ins.		12.73
BPDA	2,4 DAtol	53	dibenzofur DA	47	T	14.5	12.35
BPDA	—	—	dibenzofur DA	100	ins.		12.29
BPDA	2,4 DAtol	53	dihydrox	47	ins.		13.14
BPDA	2,4 DAtol	53	DAdiphe sulfide	47	V	15.0	12.36
BPDA	2,4 DAtol	53	ODA	47	W	14.6	12.28
BPDA	2,4 DAtol	53	DAdiphe-sulfone	47	ins.		12.85
BPDA	2,4 DAtol	53	DABenz	47	ins.		12.75
BPDA	2,4 DAtol	53	*M*-PheDa	47	ins.		12.48
BPDA	2,6 DAtol	53	MDA	47	Y	16.0	12.20
BPDA	2,6 DAtol	53	MDA	47	Y	15.6	12.20
BPDA	2,6 DAtol	42	MDA	58	ins.		—
BPDA	3,4 DAtol	53	MDA	47	ins.		12.20
BPDA	3,4 DAtol	100	—	—	A	15 (not smooth)	12.41
BPDA	Dimetphe DA	53	MDA	47	C	14.9	12.14
BPDA	Dimetphe DA	42	MDA	58	ins.		—
BPDA	DAanis	53	MDA	47	U	16.1	12.21
BPDA	DAanis	42	MDA	58	ins.		—
BPDA	DAacet	53	MDA	47	ins.		12.40
BPDA	DAacet	74	MDA	26	ins.		—
BPDA	DAacet	100	—	—	N	11.7	12.83
BPDA	DAacet	100	—	—	N	17.5	12.83
BPDA	DAdihydrox-anthraq	53	2,4 DAtol	—	N	17.5	13.45
BPDA	DAdihydrox-	100	—	—	N	20.1	14.32

BPDA	anthraq *M*-PheDA	100	—	—	ins.	12.56
BPDA	Dianis	100	—	—	ins.	11.92

[a] Diamine/dianhydride ratio 0.90.
[b] Ratio 0.97.

The batch made from benzophenone dianhydride, 53 mol % 2,4-diamino-toluene, and 47 mol % *o*-dianisidine has the typical viscosity and solids of a cresylic-soluble batch, but it gels on standing. This could be due to reaction of the methoxy groups with the excess benzophenone anhydride used in the formulation, which would lead to increased molecular weight and eventually gelation.

The solubility parameters of the polyimides and the solvent are calculated by the method of Fedors.[11] His method of calculating solubility parameters requires knowing only the structural formula and not the density. His table of atomic and group contribution to the energy of vaporization and molar volume is used with the correction for molar volumes for polymers.

Values of the solubility parameter for phenol, cresol, and xylenol are 12.57, 12.13, and 11.78 respectively, using Fedors' method. The solubility parameter of cresylic acid will be close to 11.9 since its principal constituents are cresols and xylenols. Most of the soluble polymides made from benzophenone dianhydride have solubility parameters between 12.1 and 12.6. The inclusion of 10% phenol in the solvent for polyimides in this study increases the solubility parameter of cresylic, thus improving the clarity of the solution.

Sample Calculations of Solubility Parameter by Fedors' Method

The three dianhydrides (pyromellitic, tetrahydrofuran and 1,4,5,8-naphthalene) all give insoluble polyimides with 2,4-diaminotoluene because their solubility parameters are too high. Benzophenone dianhydride forms a soluble polyimide with 2,4-diaminotoluene because its solubility parameter is close to that of the solvent. Cyclopentane dianhydride forms a soluble polyimide even with methylene dianiline and with 2,4-diaminotoluene in spite of the high solubility parameter of the polyimide in the latter case. This unusual behavior may be due to the nonaromatic nature of CPDA. In most cases a necessary condition for solubility appears to be a match of solubility parameters of polyimides and solvent.

Not all polyimides that have solubility parameters close to the solubility parameter of the solvent are soluble. It appears to be also necessary that the polyimide be somewhat unsymmetrical. Diamines that give unsymmetrical polyimides and matching solubility parameters are 2,4-diaminotoluene, 2,6-diaminotoluene, and 2,4-diaminoanisole.

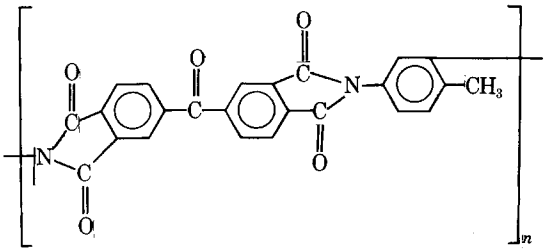
The unsymmetrical polyimides obtained from 2,4-diamionacetanilide are not as soluble as the previously mentioned polyimides because of a poorer match in solubility parameters (12.83). The unsymmetrical polyimide obtained from 3,4-diaminobenzoic acid is insoluble because of its high (13.82) solubility parameter.

It is even possible to retain solubility in cresylic acid if 47% of any of the three diamines (2,4-diaminotoluene, 2,6-diaminotoluene, or 2,4-diamino-anisole) is replaced with methylene dianiline. It is also possible to retain solubility in

cresylic acid if 47% of 2,4-diaminotoluene is replaced with several other diamines as shown in Table I as long as their solubility parameters remain close to that of the solvent.

The two diamines (diaminodiphenylsulfone and 3,3-diamino-4,4-dihy-

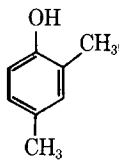
A Polyimide



	Δe_i	Δv_i
3 phenyl (trisubstituted)	3 × 7670 = 22,890	3 × 33.4 = 100.2
5 C = O	5 × 4150 = 20,750	5 × 10.8 = 54
2 —N =	2 × 2800 = 5600	2 × 5 10
5 (5- or 6-member rings)	5 × 250 1250	5 × 16 = 80
CH_3	1 × 1125 = 1125	1 × 33.5 = 33.5
	51,615	repeat unit 58
		335.2

$p = (51{,}615/335.2)^{1/2} = 12.41$

Xylenol



	Δc_i	Δv_i
1 phenyl (trisubstituted)	1 × 7630 = 7630	1 × 33.4 = 33.4
1 OH	1 × 7120 = 7120	1 × 10.0 = 10.0
2 CH_3	2 × 1125 = 2250	2 × 33.5 = 67.0
	17,000	ring 12.0
		122.4

$p = (17{,}000/122.4)^{1/2} = 11.78$

droxy-diphenylsulfone) when used as replacement 47% of 2,4-diaminotoluene give insoluble polyimides. A calculation of their solubility parameters can be made if one assumes $\Delta e_i = 2200$ and $\Delta V_i = 23.6$ for SO_2 by extrapolation of Fedors' values for SO_3 and SO_4. The high solubility parameters of 12.85 and 13.14 account for the insolubility of these two sulfone containing polyimides.

Another polyimide made by replacing 47% of 2,4-diaminotoluene with *m*-phenylene diamine was insoluble in spite of a favorable calculated solubility parameter. The insolubility of this batch is difficult to explain.

An unusual soluble polyimide is prepared from 100% 1,5-diamino-4,8-dihy-

droxyanthraquinone. This polyimide is soluble in spite of its high (14.32) solubility parameter. Perhaps its unsymmetrical structures and its tendency to hydrogen bond both ways with the solvent accounts for its solubility. The presence of the two hydroxyl groups must account for the solubility of the above-mentioned polyimide because the polyimide made from 1,5-diaminoanthraquinone is not as soluble.

To summarize: solubility parameter, symmetry, and hydrogen-bonding are all important in determining the solubility of polyimides in cresylic acid.

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