Preparation of polyamides having 2-phenyl-4,5-imidazolediyl units in the main chain

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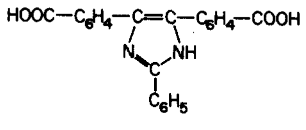
Polyamides having 2-phenyl-4,5-imidazolediyl units in the main chain were prepared from 4,4'-(2-phenyl-4,5-imidazole)dibenzoic acid and aromatic diamines. Polycondensation by a direct solution method gave high-molecular-weight polymers. The polymers are highly soluble in polar solvents and show high T_g (>290°C) and T_d (>440°C) values. Films were cast from dimethylacetamide or 1-methyl-2-pyrrolidone solutions. Mechanical properties, i.e. tensile strength, elongation at break and tensile modulus, were evaluated.

(**Keywords: polyamides; imidazole; soluble; thermostable; mechanical properties**)

INTRODUCTION

Polymers having imidazole units in the main chain reported so far are polyimidazoles[1] and a polybenzimidazole[2]. The former, prepared from 1,4-bis (phenylglyoxaloyl)benzene and aromatic dialdehydes, were of low molecular weight ($\eta_{inh} = 0.1$–$0.5\,dl\,g^{-1}$) and soluble in polar solvents. The latter, prepared from diphenyl 4,5-imidazoledicarboxylate and 3,3'-diaminobenzidine, was only partially soluuble in concentrated sulphuric acid. The inherent viscosity of the soluble portion was as low as $0.16\,dl\,g^{-1}$. Since soluble high-molecular-weight polymers having imidazole rings in the main chain have not been prepared successfully, the effects of the imidazole units on the physical properties of the polymers obtained have not been clearly elucidated.

Recently, we prepared heteroaromatic dibenzoic acids, i.e. 4,4'-(2,3-quinoxaline)dibenzoic acid[3] and 4,4'-(1,2,4-triazine-5,6-diyl)dibenzoic acid[4], from an α-diketone-containing dibenzoate, diethyl 4,4'-benzildicarboxylate. The polyamides prepared from these dibenzoic acids were thermally stable and soluble in polar solvents. In the present study, we prepared a new dibenzoic acid having an imidazole unit, i.e. 4,4'-(2-phenyl-4,5-imidazole) dibenzoic acid **1**, from diethyl 4,4'-benzildicarboxylate[5]. Polyamides derived from **1** are expected to be thermostable and soluble in various solvents, since the structure of the polymer chain is similar to that of polyamides having quinoxaline-2,3-diyl or 1,2,4-triazine-5,6-diyl units[3,4]. In this paper are reported the preparation of **1** and its polycondensation with aromatic diamines. The physical properties of the polymers obtained are also reported.

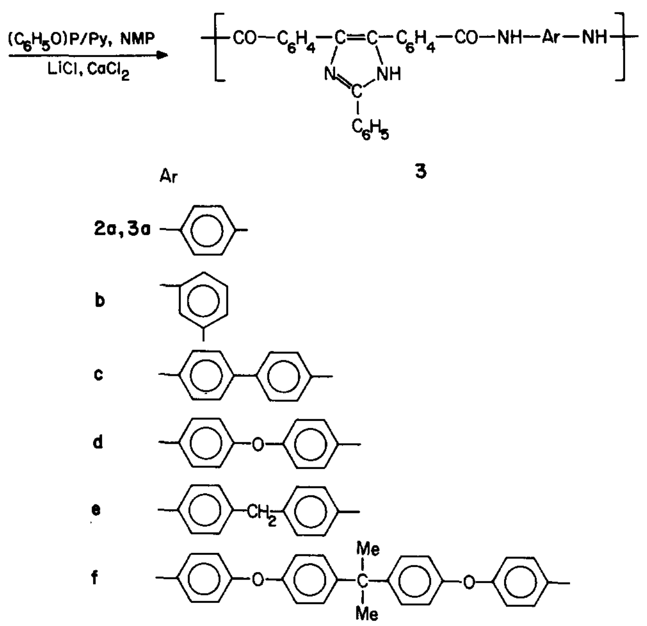


$HOOC{-}C_6H_4{-}C{=}C{-}C_6H_4{-}COOH$ (imidazole ring: N, NH, C–C_6H_5)

1

+ $H_2N{-}Ar{-}NH_2$

2



$\xrightarrow[LiCl,\ CaCl_2]{(C_6H_5O)P/Py,\ NMP} \left[CO{-}C_6H_4{-}C{=}C{-}C_6H_4{-}CO{-}NH{-}Ar{-}NH \right]$ (imidazole ring: N, NH, C–C_6H_5)

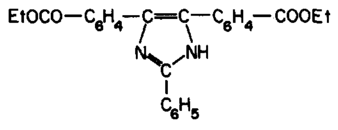
EXPERIMENTAL

Materials

Diethyl 4,4'-benzildicarboxylate **4**. This was prepared according to the procedure described earlier[4]. Solvents used were dried and distilled before use. Commercially available reagents were purified by the conventional methods.

$C_2H_5OOC{-}C_6H_4{-}CO{-}CO{-}C_6H_4{-}COOC_2H_5$

4



$EtOCO{-}C_6H_4{-}C{=}C{-}C_6H_4{-}COOEt$ (imidazole ring: N, NH, C–C_6H_5)

5

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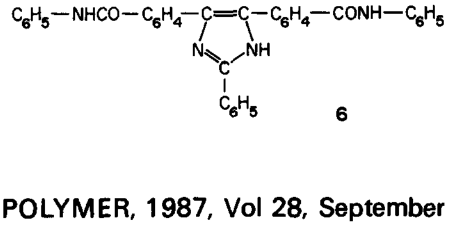
Diethyl-4,4′-(2-phenyl-4,5-imidazole)dibenzoate **5**. In a 500 ml four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet were placed 8.0 g of **4** and 280 ml of acetic acid. After **4** was dissolved under nitrogen atmosphere at 100°C, ammonium acetate (34 g) and benzaldehyde (12 ml) were added, and the solution was refluxed for 5.5 h. The reaction mixture was cooled to room temperature and poured into water. Reaction products precipitated were collected, washed with water and recrystallized from aqueous ethanol ($EtOH:H_2O = 3:1$ in volume). Yield 84%. M.p. 201–202°C (light yellow needles). I.r.(KBr):1714 (s, ester) and 1680 cm^{-1} (s, imidazole) (1210 cm^{-1} due to α-diketone disappeared). Analysis: **5**, $C_{27}H_{24}N_2O_4$ (440.5); calc. C 73.62, H 5.49, N 6.36; found C 73.60, H 5.56, N 6.30.

4,4′-(2-Phenyl-4,5-imidazole)dibenzoic acid **1**. In a 300 ml four-necked flask equipped with a reflux condenser, a mechanical stirrer and a thermometer were placed 10.8 g of **5** and 150 ml of ethanol. After 4.1 g of potassium hydroxide dissolved in 32 ml of aqueous ethanol ($EtOH:H_2O = 1:1$ in volume) was added, the reaction mixture was heated to reflux for 5 h. The mixture was cooled to room temperature and acidified with a 3 N HCl solution. The precipitates formed were collected and washed with water until the filtrate became neutral. The crude product was recrystallized from 1-methyl-2-pyrrolidone (NMP) containing 5 wt% propylene oxide. The light yellow crystallites obtained were found to be a 1:1 adduct of **1** and NMP. The adduct was heated at 170°C under reduced pressure to obtain **1** as light yellow powder. Yield 88%. M.p. >400°C (decomp.). Analysis: **1**·NMP, $C_{28}H_{25}N_3O_5$ (483.5); calc. C 69.55, H 5.21, N 8.69; found C 69.35, H 5.34, N 8.82. I.r. (KBr) of **1**: 3450 (N–H), 2800–3300 (broad, OH), 1690 cm^{-1} (s, COOH). ^1H n.m.r. ([$^2H_6$]-DMSO): 7.5–8.16 (m), 12.53 (s); intensity ratio 15:1. Analysis: **1**, $C_{23}H_{16}N_2O_4$ (384.4); calc. C 71.87, H 4.20, N 7.29; found C 71.82, H 4.28, N 7.32.

2-Phenyl-4,5-bis(4-phenylcarbamoylphenyl)imidazole (model compound) **6**. In a 50 ml four-necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen gas inlet were placed 1.2 g of calcium chloride, 0.4 g of lithium chloride and 4 ml of NMP. The mixture was heated until all the ingredients were dissolved and then cooled to room temperature. Dibenzoic acid **1** (0.769 g), aniline (0.37 ml), triphenylphosphite (1.05 ml) and an additional 5 ml of NMP were added. The reaction mixture was heated with stirring at 115°C for 2 h. The reaction mixture was then cooled to room temperature and poured into water. The crude product, obtained in 88% yield, was recrystallized three times from aqueous acetone (acetone:water = 3:1 in volume). M.p. 152°C (d.s.c.). I.r. (KBr): 3450 (H–N), 1660, 1530 cm^{-1} (amide I, II). ^1H n.m.r. ([$^2H_6$]-DMSO): 7.1–8.14(m), 10.3(s), 12.98(s); intensity ratio 23:2:1. Analysis: **6**, $C_{35}H_{26}N_4O_2$ (534.6); calc. C 78.63, H 4.90, N 10.48; found C 78.04, H 4.95, N 10.36.



$$C_6H_5\text{—NHCO—}C_6H_4\text{—}\underset{\underset{\underset{C_6H_5}{|}}{N\diagdown C\diagup NH}}{C{=}C}\text{—}C_6H_4\text{—CONH—}C_6H_5$$

6

Polycondensations

A typical procedure is as follows. In a four-necked 50 ml flask equipped with a mechanical stirrer, a nitrogen gas inlet, a reflux condenser and a thermometer were placed 1.2 g of calcium chloride, 0.4 g of lithium chloride and 15 ml of NMP. The mixture was heated with stirring until the salts were dissolved and then cooled to room temperature. Dibenzoic acid **1** (0.769 g), oxydianiline (0.400 g), triphenylphosphite (1.05 ml) and an additional 5 ml of NMP were added under a nitrogen stream. The temperature was then raised to 115°C. After 5 h, the reaction mixture was cooled and poured into aqueous methanol ($MeOH:H_2O = 1:1$ in volume). The precipitates formed were collected on a glass filter, washed with methanol and dried *in vacuo*. Yield 102%. $\eta_{inh} = 0.73$ dl g^{-1} (0.5% conc. H_2SO_4, at 30°C). Analyses: **3a**, $C_{29}H_{17}N_4O_2$ (456.5); calc. C 76.30, H 4.42, N 12.27; found C 74.09, H 4.75, N 11.48. **3b**, $C_{29}H_{17}N_4O_2$ (456.5); calc. C 76.30, H 4.42, N 12.27; found C 73.14, H 4.45, N 11.74. **3c**, $C_{35}H_{21}N_4O_2$ (532.6); calc. C 78.93, H 4.54, N 10.52; found C 76.50, H 4.90, N 10.08. **3d**, $C_{35}H_{21}N_4O_3$ (548.6); calc. C 76.63, H 4.41, N 10.21; found C 74.77, H 4.46, N 9.88. **3e**, $C_{36}H_{23}N_4O_2$ (546.3); calc. C 79.10, H 4.79, N 10.25; found C 75.94, H 4.99, N 9.54. **3f**, $C_{50}H_{38}N_4O_4$ (758.9); calc. C 79.14, H 5.05, N 7.38; found C 77.63, H 4.97, N 7.06.

Measurements

T_g was obtained as an intersection between the baseline and the extrapolated slope of the curve obtained by differential scanning calorimetry (d.s.c.) using a Rigaku Denki 8055D1 thermal analyser. T_g was also evaluated from a peak of the loss modulus curve in dynamic mechanical analysis (d.m.a.) using an Iwamoto Seisakusho VED-F dynamic viscoelastometer. T_d was evaluated as a temperature at which a 5% weight loss was recorded in thermogravimetric analysis (t.g.a.) using a Rigaku Denki 8075D1 thermobalance. Mechanical properties were examined at a strain rate of 100 mm min^{-1} using a Shimadzu AG-10TB autograph. The test specimen was of a dumb-bell type (about 30 μm thick, 40 mm x 6 mm). I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. N.m.r. spectra were obtained with a Hitachi R-600 60 MHz *FT* ^1H n.m.r. spectrometer.

RESULTS AND DISCUSSION

4,4′-(2-Phenyl-4,5-imidazole)dibenzoic acid **1** was prepared by cyclocondensation of diethyl-4,4′-benzildicarboxylate **4** and benzaldehyde in the presence of ammonium acetate, followed by hydrolysis under alkaline conditions.

$$4 + C_6H_5\text{—CHO} + AcONH_4 \longrightarrow$$

$$5 \xrightarrow[(2)HCl]{(1)KOH/EtOH} 1$$

The i.r. and n.m.r. spectra of the product indicated formation of a salt; the product was thus recrystallized from NMP containing 5 wt% propylene oxide. Elemental analysis of the light yellow needles obtained showed a lower carbon content than that calculated for **1**. Thermogravimetric analysis showed a 19.5% weight loss

Table 1 Results of polycondensation[a] of 4,4′-(2-phenyl-4,5-imidazole) dibenzoic acid and aromatic diamines

Run number	Polymer	[M] (mol l^{-1})	Yield (%)	η_{inh}[b] (dl g^{-1})
1	**3a**	0.11	102	0.54
2		0.33	103	1.04
3	**3b**	0.11	102	0.34
4		0.33	104	0.56
5	**3c**	0.11	99	0.77
6		0.33	103	1.90
7	**3d**	0.11	101	0.73
8		0.24	102	0.87
9		0.33	103	0.88
10		0.42	101	0.84
11	**3e**	0.11	99	0.42
12		0.33	102	1.32
13	**3f**	0.33	101	0.58[c]

[a] Polycondensation conditions: **1**, 2 mmol; **2**, 2 mmol; LiCl, 0.4 g; $CaCl_2$, 1.2 g; triphenylphosphite, 4 mmol; 115°C, 5 h; solvent: NMP

[b] Measured at a concentration 0.5% in conc. H_2SO_4 at 30°C

[c] Measured at a concentration 0.5% in DMAc at 30°C

at 170°C (calculated weight loss for **1**·NMP: 20.5%). Elemental analysis and t.g.a. together indicated that the crystalline product was a 1:1 adduct of **1** and NMP. The adduct was heated at 170°C for 2 h under reduced pressure. NMP-free **1** was obtained as a light yellow powder.

Prior to polymerization, a model reaction was performed as follows:

$$\mathrm{I} + H_2N{-}C_6H_5 \xrightarrow[\text{LiCl, CaCl}_2]{(C_6H_5O)\,P/Py,\ NMP} 6$$

The product (**6**) was obtained in a quantitative yield, and its structure was confirmed by spectroscopic data as well as by elemental analysis.

Poly(iminoaryleneiminocarbonyl - 1,4 - phenylene - 2-phenylimidazole-4,5-diyl-1,4-phenylenecarbonyl)s (**3a**–**3f**) were prepared from 2-phenyl-4,5-imidazoledibenzoic acid **1** and aromatic diamines, e.g. *p*-phenylenediamine, *m*-phenylenediamine, benzidine, 4,4′-oxydianiline, 4,4′-methylenedianiline and 2,2-bis(4-aminophenyl-4,1-phenoxy)propane (BAPP), by direct polycondensation[6], under conditions similar to those employed for the model reaction. Results of polycondensation are summarized in *Table 1*. Polymers **3** are slightly hygroscopic. Higher monomer concentrations generally gave polyamides with higher inherent viscosities.

Flexible and tough films were formed with polymers whose inherent viscosities were greater than 0.4 dl g^{-1} by casting from dimethylacetamide (DMAc) or NMP. In d.s.c., all of the first runs showed small changes at T_g. The second runs using samples heated to 20°C above T_g and quenched to room temperature showed much clearer changes in d.s.c. curves. Therefore, the temperatures obtained in the second runs were adopted as T_g values. In d.m.a., T_g values of **3a** and **3c** were not measured because of instrumental limitations, the maximum measurable temperature being 370°C. However, the dynamic modulus of **3a** began to decrease around 360°C, indicating that T_g exists slightly above 370°C. The transition at 358°C of **3c** detected by d.s.c. may be a secondary transition point, other than a glass transition, not observable by d.m.a. The data for other polymers are summarized in *Table 2*. The T_g values of all polymers are higher than that of commercially available Aramid (Nomex: 280°C)[7] and those of the polyamides[3,4] containing 2,3-quinoxalinediyl units or 5,6-(1,2,4-triazine)diyl units in the main chain. Polymer decomposition temperatures are above 440°C, and the weight residues at 600°C are ~80%. These results indicate that the polyamides containing 2-phenyl-4,5-imidazolediyl units in the main chain have high T_g and high thermostability.

The mechanical properties of the polymer films are summarized in *Table 3*. The tensile strengths of the polymers are 83–124.3 MPa, elongations at break 9.8–12.8% and tensile moduli 1.09–1.63 GPa.

The solubilities of the polymers are summarized in *Table 4*. All of the polymers are soluble in polar solvents such as dimethylformamide (DMF), NMP, DMAc and *m*-cresol. Polymers other than **3e** are also soluble in pyridine. Furthermore, high-concentration DMAc or NMP solutions (up to 15 wt% of polymer) can be prepared easily without addition of a salt such as LiCl or $CaCl_2$.

In conclusion, polyamides having 2-phenyl-4,5-imidazolediyl unit prepared from **1** and aromatic diamines show high thermal stability and high solubility in polar solvents. Apparently, the rigidity of the imidazole ring contributes to the high thermal stability, and the asymmetric structure of the main chain, the affinity of imidazole rings to solvents and the pendant phenyl substituent contribute to the high solubility of the polymer.

Table 2 Thermal properties of polyamides from 4,4′-(2-phenyl-4,5-imidazole)dibenzoic acid and aromatic diamines

Polymer	T_g[a] (°C)		T_d[b] (°C)	Weight residue at 600°C (%)
	D.s.c.	D.m.a.		
3a	361	>370	487	80.3
3b	343	(>295)[c]	483	84.3
3c	(358)[d]	>370	487	80.7
3d	329	313	486	82.4
3e	326	328	461	78.1
3f	292	292	444	77.0

[a] D.s.c., heating rate 10°C min^{-1} in nitrogen atmosphere; d.m.a., heating rate 3°C min^{-1} in air

[b] Temperature at which a 5% weight loss was recorded by t.g.a.; heating rate 10°C min^{-1} in nitrogen atmosphere

[c] Test piece was severed at 295°C

[d] See text

Table 3 Mechanical properties[a] of polyamides from 4,4′-(2-phenyl-4,5-imidazole)dibenzoic acid and aromatic diamines

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
3a	124.3	11.0	1.63
3b	83.0	9.8	1.20
3c	90.0	10.5	1.58
3d	100.6	12.3	1.09
3e	102.2	11.1	1.32
3f	87.5	12.8	1.33

[a] Measured by autograph (Shimadzu AG-10TB)

Table 4 Solubility of polymer from 4,4′-(2-phenyl-4,5-imidazole)dibenzoic acid and aromatic diamines[a]

Polymer	HMPT	CHO	DMAc	Py	*m*-Cre	NMP	DMF	DMSO	HCOOH
3a	±[b]	±	+	+	+	+	+	+	+
3b	±	±	+	+	+	+	+	+	+
3c	±	±	+	+	+	+	+	±	+
3d	±	±	+	+	+	+	+	+	+
3e	±	±	+	±	+	+	+	+	+
3f	+	±	+	+	+	+	+	+	+

[a] HMPT, hexamethylphosphoric triamide; CHO, cyclohexanone; DMAc, dimethylacetamide; Py, pyridine; *m*-Cre, *m*-cresol; NMP, 1-methyl-2-pyrrolidone; DMF, dimethylformamide; DMSO, dimethylsulphoxide

[b] +, soluble; ±, partially soluble; −, insoluble

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