Synthesis of 4,4′-bis(4-aminophenoxy)benzophenone and polyimides based on this compound

A. L. Rusanov, G. S. Matvelashvili, G. V. Kazakova, M. L. Keshtov, and A. K. Mikitaev*

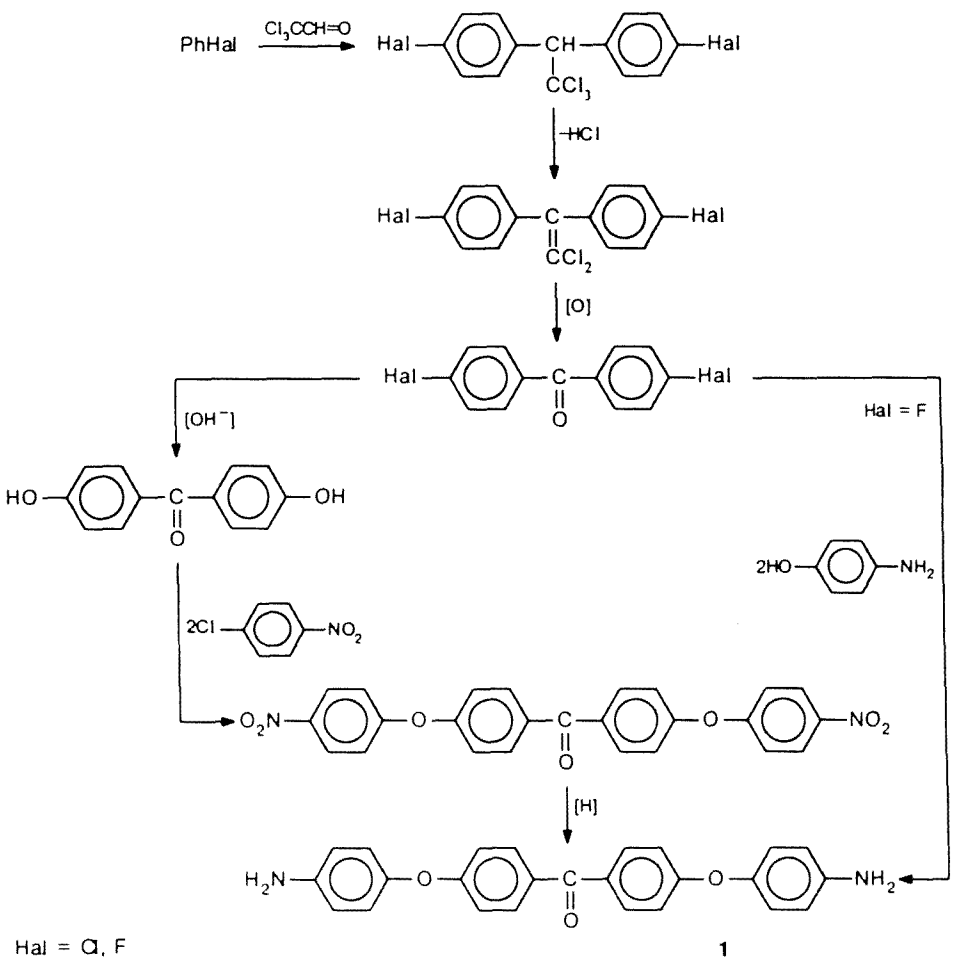
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: dir@neosoft.ineos.free.msk.su, dir@ineos.msk.su

Synthesis of 4,4′-bis(4-aminophenoxy)benzophenone was performed starting from chloral. Various polyimides were obtained by reactions of 4,4′-bis(4-aminophenoxy)benzophenone with aromatic tetracarboxylic acid dianhydrides. Some of the polyimides obtained are crystalline compounds.

Key words: chloral, 4,4′-bis(4-aminophenoxy)benzophenone, etheretherketone fragments, polyimides.

Condensation monomers containing aromatic etheretherketone fragments are of considerable interest because these compounds make it possible to obtain crystalline polyetheretherketones under milder conditions

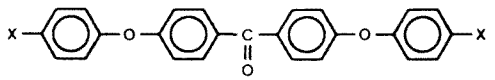
Scheme 1



1

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 673—676, March, 1996.

Table 1. Characteristics of compounds of the general formula



X	M.p. °C	Yield (%)	Found / Calculated (%)			Empirical formula
			C	H	N	
NO_2	146—148.5	79.4	65.70 65.79	3.60 3.53	6.05 6.14	$C_{25}H_{16}N_2O_7$
NH_2	151—152	11.0	75.71 75.74	5.19 5.08	7.78 7.06	$C_{25}H_{20}N_2O_3$

compared to those used in conventional synthesis.[1,2] Of particular interest are diamines containing etheretherketone fragments; important condensation polymers, like polyamides, and, particularly polyimides, can be obtained starting from these diamines.

In this work, 4,4′-bis(4-aminophenoxy)benzophenone (**1**)[3–5] was synthesized by two methods starting from halobenzenes and chloral (Scheme 1).

Selected characteristics of compound **1** and of the intermediate product (4,4′-bis(4-nitrophenoxy)benzophenone) are given in Table 1. Potentiometric titration demonstrated that diamine **1** has a sufficiently high basicity (pK_{a_1} = 5.22; pK_{a_2} = 4.03) for obtaining high-molecular condensation polymers, in particular polyimides, from this diamine.

Aromatic polyimides containing etheretherketone fragments were synthesized by reactions of **1** with dianhydrides of pyromellitic, benzophenone-3,3′,4,4′-tetracarboxylic, and diphenyl ether-3,3′,4,4′-tetracarboxylic acids as well as with 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (Scheme 2).

The two-stage polycyclocondensation used involves the low-temperature reaction of the initial compounds in the *N*-methyl-2-pyrrolidone medium followed by catalytic cyclization of poly(*o*-carboxy)amides formed with the use of orthophosphoric acid as a catalyst.[6]

The first stage of this reaction proceeds homogeneously, whereas imidization processes, depending on the nature of dianhydride, are either attended by precipitation of polymers from the reaction solutions (pyromellitic dianhydride and benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride), *i.e.*, proceed under conditions of so-

Scheme 2

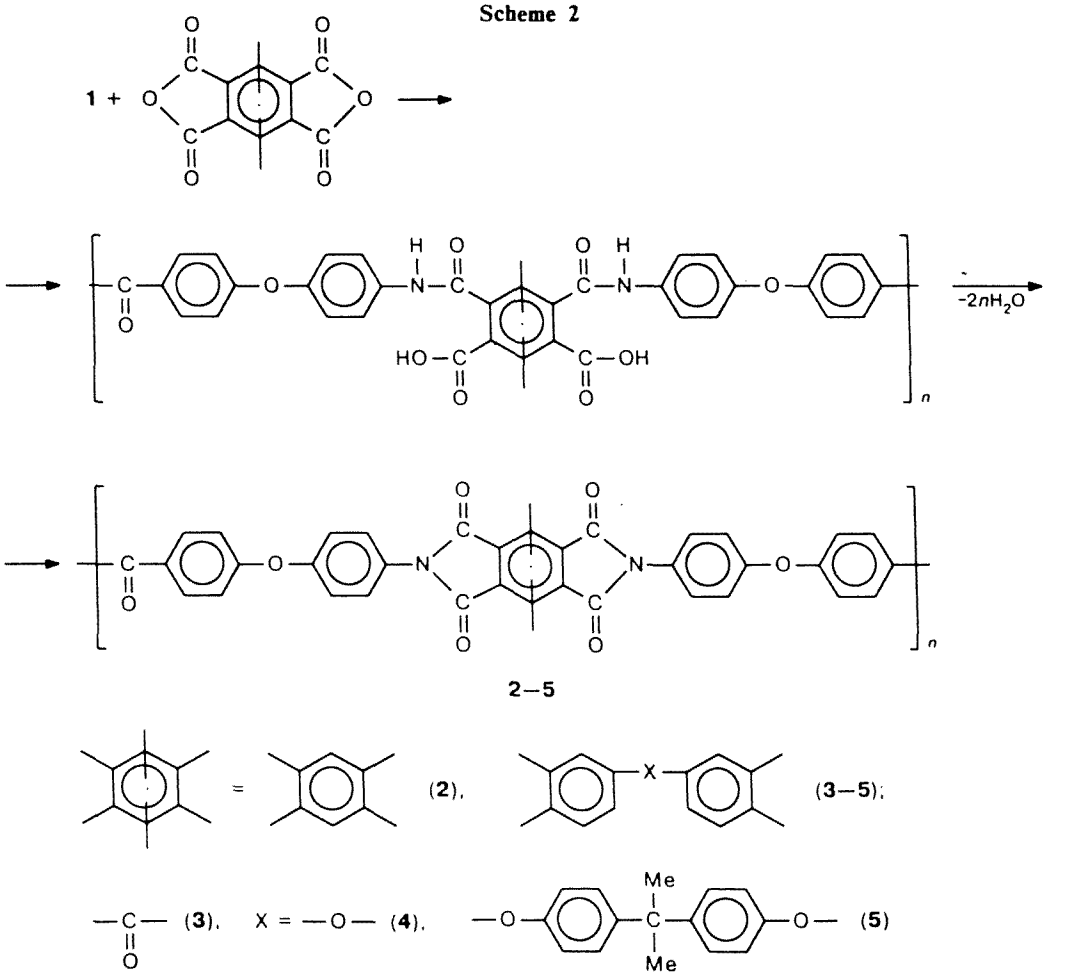
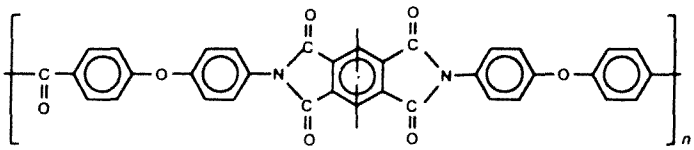
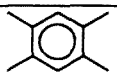
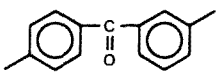
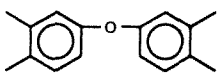
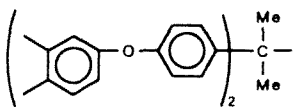


Table 2. Characteristics of polyimides of the general formula



Compound		η_{lim}/dL g^{-1}, (25 °C, H_2SO_4)	T_{soft}[a] °C	T_{decomp}[b] °C	OI[c]
2		0.42	—	490	33
3		0.40	—	485	32
4		1.75[d]	240	460	30
5		2.16[d]	220	450	30

[a] Softening temperatures were determined from the thermomechanical curves.
[b] Decomposition temperatures were determined from the points on the DTGA curves (air, ΔT = 4.5 K/min) corresponding to 10 % weight loss.
[c] Oxygen indices of polymers were determined by B. B. Serkov (Higher Technical School for Fire Engineering, Moscow).
[d] Viscosity was measured in a tetrachloroethane : phenol (3 : 1) mixture.

called precipitative polyheterocyclization,[7,8] or occur homogeneously (diphenyl ether-3,3′,4,4′-tetracarboxylic acid dianhydride and 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane dianhydride.

Structures of the polymers synthesized were confirmed by the IR spectra according to which polyimides are virtually free of noncyclized units. Selected characteristics of the polymers are given in Table 2.

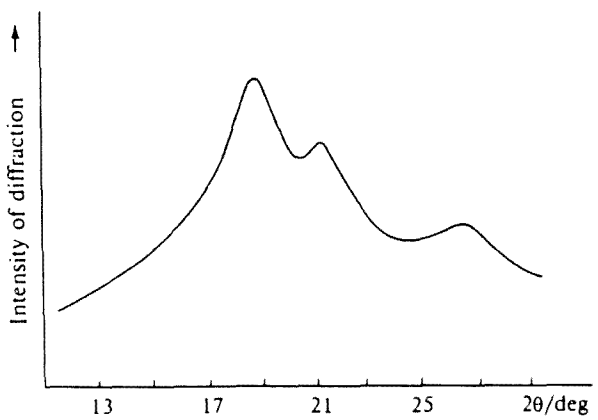


Fig. 1. Diffraction pattern of polyimide **1**.

Based on the results of X-ray structural study, the polymers based on pyromellitic dianhydride and benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride are crystalline compounds similar to a number of polyimides with ether and ketone groups.[9–13] This fact is illustrated by the diffraction pattern of polypyromellitimide (Fig. 1).

Polyimides based on diphenyl ether-3,3′,4,4′-tetracarboxylic acid dianhydride and 2,2-bis[(dicarboxyphenoxy)phenyl]propane dianhydride are amorphous.

Unlike amorphous polyimides containing etheretherketone fragments (**3** and **4**, Table 2), which are soluble in a tetrachloroethane : phenol mixture, crystalline polyimides are insoluble in organic solvents and are soluble only in concentrated H_2SO_4. Crystallinity of these polymers determines the absence of large deformations (Fig. 2) up to temperatures corresponding to the onset of intense thermal destruction (Fig. 3).

Experimental

Initial and intermediate compounds (Scheme 1) were obtained by the known procedures; their melting points correspond to the data in the literature for 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane,[14] 1,1-di(4-chlorophenyl)ethyl-

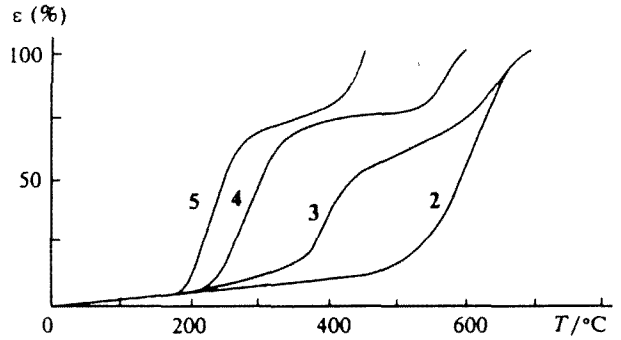


Fig. 2. Thermomechanical curves of polyimides based on 4,4′-bis(4-aminophenoxy)benzophenone (**2**—**5**).

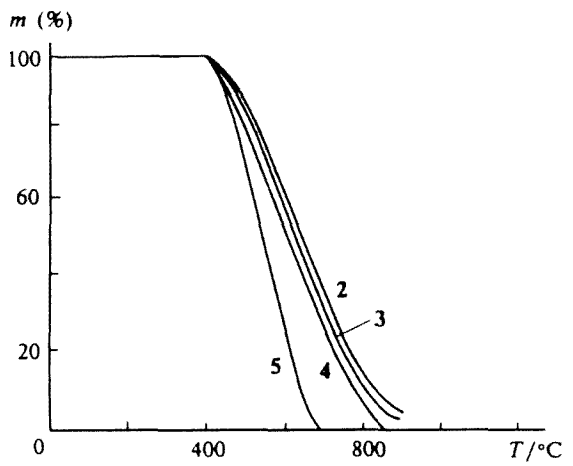


Fig. 3. Dynamic TG curves of polyimides based on 4,4′-bis(4-aminophenoxy)benzophenone (**2**—**5**) (air, ΔT = 4.5 K/min).

ene,[15] 4,4′-dichlorobenzophenone,[16] 4,4′-dihydroxybenzophenone,[17] 4,4′-bis(4-nitrophenoxy)benzophenone,[18] 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane,[19] 1,1-dichloro-2,2-di(4-fluorophenyl)ethylene,[20] and 4,4′-difluorobenzophenone.[16,20]

4,4′-Bis(4-aminophenoxy)benzophenone (1). a) The reduction of 4,4′-bis(4-nitrophenoxy)benzophenone by the known procedure.[18] The yield of ketone **1** was 11 %, m. p. 151—152 °C (*cf.* Ref. 18).

b) The reaction of 4,4′-difluorobenzophenone with *p*-aminophenol. *p*-Aminophenol (0.05 mol), DMAA (50 mL), and toluene (50 mL) were placed in a three-neck flask supplied with a Dean-Stark trap. Powdered K_2CO_3 (0.10 mol) was added to the mixture, and water was removed by azeotropic distillation with toluene upon boiling and stirring under a stream of nitrogen. After the removal of water (3 h), the remaining toluene was distilled upon heating to 160 °C. Then 4,4′-difluorobenzophenone (0.025 mol) was added portionwise to the reaction mixture cooled to 100 °C, and the mixture was stirred under an inert atmosphere at 140—150 °C for 5 h. The mixture was cooled and poured into 500 mL of water. The precipitate formed was filtered off, dried, and recrystallized from a toluene : ethanol mixture (1 : 1). The yield of product **1** was 55 %, m.p 151—153 °C.

The synthesis of polyimides was carried out by the procedure described in Ref. 6, with the difference that polycondensation was performed directly in the reaction solutions of poly(*o*-carboxy)amides.

References

1. L. K. English, *Mater. Eng.*, 1989, **106**, 43.
2. A. A. Berlin and L. K. Pakhomova, *Vysokomol. Soedin., Ser. A*, 1990, **32**, 1347 [*Polym. Sci. USSR*, 1990, **A32** (Engl. Transl.)].
3. V. V. Korshak, A. L. Rusanov, S. Kh. Fidler, D. S. Tugushi, R. G. Kakauridze, Yu. N. Margalitadze, and S. N. Zinov'ev, *Plastmassy*, 1984, 32 (in Russian).
4. E. R. Kekharsaeva, G. B. Shustov, A. K. Mikitaev, and V. T. Dorofeev, *Plastmassy*, 1985, 9 (in Russian).
5. V. V. Korshak and A. L. Rusanov, *Usp. Khim.*, 1989, **58**, 1006 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].
6. G. V. Kazakova, A. Ya. Chernikhov, E. A. Seliverstova, and V. V. Isaeva, *Vysokomol. Soedin., Ser. A*, 1985, **27**, 2594 [*Polym. Sci. USSR*, 1985, **A27** (Engl. Transl.)].
7. V. V. Korshak, A. L. Rusanov, A. Ya. Chernikhov, G. V. Kazakova, A. M. Berlin, S. Kh. Fidler, and T. V. Lekae, *Dokl. Akad. Nauk SSSR*, 1985, **282**, 375 [*Dokl. Chem.*, 1985, **282** (Engl. Transl.)].
8. V. V. Korshak, A. L. Rusanov, A. Ya. Chernikhov, G. V. Kazakova, A. M. Berlin, S. Kh. Fidler, M. O. Shalikiani, T. V. Lekae, and Z. B. Shifrina, *Abstracts of papers, X International Microsymposium on Polycondensation*, Varna, 1985, 47.
9. P. M. Hergenrother and S. J. Havens, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25**, 1093.
10. P. M. Hergenrother and S. J. Havens, *J. Polym. Sci., Polym. Chem. Ed.*, 1989, **27**, 1161.
11. P. M. Hergenrother and S. J. Havens, *J. Polym. Sci., Polym. Chem. Ed.*, 1992, **30**, 1209.
12. P. M. Hergenrother, *Polym. J.*, 1987, **19**, 73.
13. P. M. Hergenrother, *Angew. Makromol. Chem.*, 1986, **145/146**, 323.
14. O. Zeidler, *Ber.*, 1874, **7**, 1180.
15. M. Troj and J. Hubacek, *Chem. Listy*, 1957, **51**, 752.
16. H. Haller, P. Bartlett, and N. Drake, *J. Am. Chem. Soc.*, 1945, **67**, 1591.
17. G. S. Mironov, I. V. Budnii, K. A. Chernyakhovskaya, and M. I. Farberov, *Zh. Org. Khim.*, 1972, **8**, 597 [*J. Org. Chem. USSR*, 1972, **8** (Engl. Transl.)].
18. V. V. Korshak, A. L. Rusanov, Yu. N. Margalitadze, and N. Z. Makharashvili, *Vysokomol. Soedin., Ser. B*, 1988, **30**, 188 [*Polym. Sci. USSR*, 1988, **B30** (Engl. Transl.)].
19. H. L. Bradlow and C. A. Werf, *J. Am. Chem. Soc.*, 1947, **69**, 662.
20. F. A. Gunther and R. C. Blinn, *J. Chem. Educ.*, 1950, **27**, 654.

Received July 24, 1995;
in revised form November 1, 1995