MODERN TRENDS IN AROMATIC POLYIMIDES CHEMISTRY

A. L. Rusanov

A. N. Nesmeyanov Inst. of Organoelement Compounds
Russian Academy of Sciences
28 Vavilov St.
Moscow, 117813, Russia

ABSTRACT

The most important modern trends in aromatic polyimides chemistry are analyzed. In the last decade a large family of flexible-chain aromatic polyimides was developed. The most important representatives of these polymers are polyetherimides based on aromatic tetracarboxylic acids dianhydrides containing ether groups ("Ultem" and related systems) and/or diamines containing ether groups and other flexibilizing fragments, e.g., *m*-phenylene rings, isopropylidene or hexafluoroisopropylidene groups, phenoxy substituents, etc. Flexible-chain polyimides are soluble in organic solvents and may be processed by injection molding processes.

A large variety of rigid-rod polyimides was developed and used for the preparation of polymeric films combining good thermal and mechanical (high-strength, high-modulus) properties. Of the greatest interest are rigid-rod polyimides soluble in organic solvents. These polymers may be obtained on the basis of "rigid" aromatic tetracarboxylic acids (pyromellitic, 3,3',4,4'-diphenyltetracarboxylic) dianhydrides and/or diamines (*p*-phenylenediamine, benzidine) containing solubilizing substituents - phenyl, phenoxy, trifluoromethyl groups. Processable rigid-rod polynaphthylimides were obtained on the basis of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride and unsymmetrical diamine - 5(6)-amino-2-(*p*-aminophenyl)-benzimidazole.

INTRODUCTION

The development of aromatic polyimides (API) chemistry (1-5) led to the preparation of a large variety of these polyheteroarylenes demonstrating very different properties. One of the most important factors influencing API properties is their macromolecules rigidity; as a result, the two most important groups of the new API are flexible-chain and rigid-rod polyimides.

Development of flexible-chain polyimides was stimulated by the need of highly processable polyimides soluble in common organic solvents and demonstrating large "windows" between their softening (melting) and degradation temperatures (6-8). Development of rigid-rod polyimides was stimulated by the need of new high-strength and high-modulus polymeric materials (9,10).

The molecular design of flexible and rigid-chain polyimides is very different. Flexible-chain API must contain in the main chain such structural elements as unsymmetrical phenylene rings (m-phenylene), flexibilizing groups (ether, thioether, isopropylidene, hexafluoroisopropylidene, etc.) and/or side groups (phenyl, phenoxy, trifluoromethyl etc.) (6-8). In rigid-rod API the backbone molecules must possess a high level of alignment and preferably contain symmetrical *p*-phenylene and heterocyclic rings without any flexibilizing units (11).

FLEXIBLE-CHAIN API

The most important flexible-chain API are polyimides containing in their macromolecules ether bonds - the so-called polyetherimides (PEIs). A large variety of PEIs was obtained by the interaction of various aromatic diamines containing ether groups with aromatic tetracarboxylic acids dianhydrides containing the same groups (1).

A large group of bis(phthalic anhydride)s containing no less than 2 ether groups - bis(ether phthalic anhydride)s (BEPA) - was developed (6-8, 12, 13) using aromatic nucleophilic nitrodisplacement reactions (14,15) of bisphenolates and nitrosubstituted phthalimides or phthalonitriles.

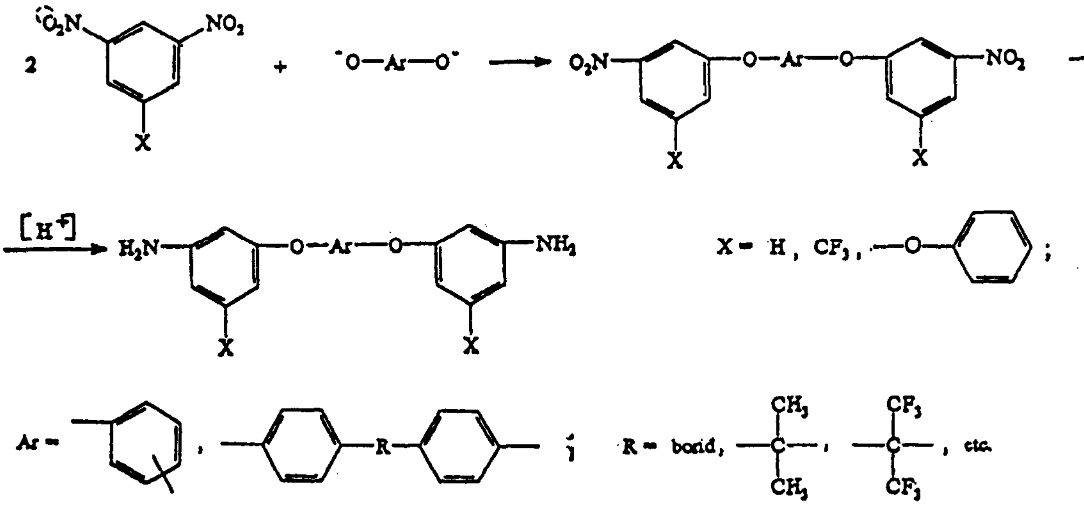
Interaction reactions of BEPAs with common aromatic diamines - *m*-phenylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl methane, etc. - were carried out in melt (16), using high-temperature solution polycondensation in amide solvents (17) non-polar organic solvents (18). and phenolic solvents (19, 20).

Among the various PEIs synthesized the main emphasis was given to polymer based on cheap and available *m*-phenylenediamine and "dianhydride A" - BEPA on the basis of bis-phenol A. This polymer contains *m*-phenylene rings, ether and isopropylidene groups in the main chain and is extremely flexible - the value of its Kuhn segment is 19 Å. This polymer was chosen as a starting product for the preparation of the high-performance engineering plastic "Ultem" manufactured by General Electric Company (6).

The polymer is characterized by high strength, high rigidity and good ductility in combination with high heat distortion temperature, excellent flame resistance and non-smoking property (6).

An alternative approach to flexible-chain, highly processable PEIs is based on the utilization of a relatively new family of aromatic diamines containing in their molecules no less than 2 ether groups and no less than 2 *m*-phenylene rings.

Large variety of such diamines was obtained by the reaction of various bis-phenolates and two-fold molar amounts of unsubstituted and substituted *m*-dinitrobenzenes (21~26) using aromatic nucleophilic nitrodisplacement reactions (Scheme 1).



(1),

In general aromatic nucleophilic nitrodisplacement reactions proceed smoothly when the activating groups are located at the ortho- and para-positions to the nitro group. Because of their high reactivity however, even meta-substituted dinitro compounds undergo the displacement reaction in some instances (4,6,7).

The main attention in this field was paid, naturally, to the preparation of the diamines using unsubstituted m-dinitrobenzene as starting dinitrocompound (21-26), Among these diamines products containing isopropylidene and hexafluoroisopropylidene groups are of great interest.

The synthesis of PEIs using such diamines as monomers was carried out in N-MP. (23~26). The first steps of the reactions were carried out at ambient temperatures; poly-(*o*-carboxy)-amides obtained were imidized in reaction solutions using

- pyridine:acetic anhydride (1:1) complex as catalyst;
- *o*-phosphoric acid as catalyst;
- no catalyst, but adding azeotrope-forming compounds.

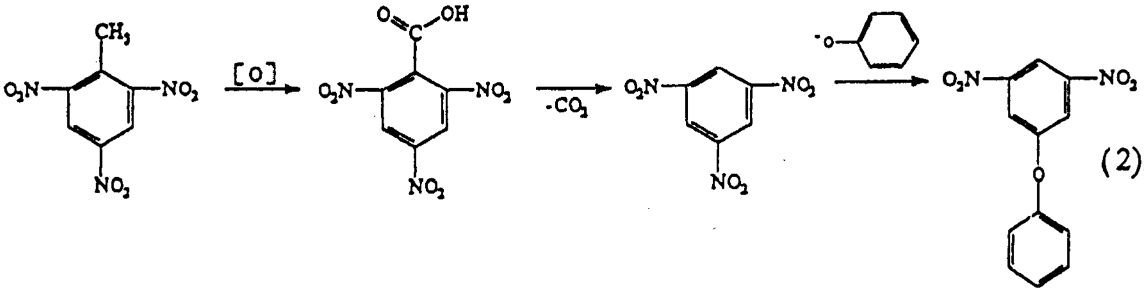
All reactions proceeded homogeneously and led to the formation of high molecular weight polyimides with high cyclization degrees.

All polyimides have relatively low glass transition temperatures (180÷225°C) and high degradation temperatures. The melt viscosities of these polymers are low enough polyimides to be processed using injection molding.

The polyimides obtained are very soluble in organic solvents - N-MP, *m*-cresol, methylenechloride, chloroform etc.; the good solubility is due to their structure and method for their preparation - it is known that polyimides obtained under mild conditions are more soluble than the same polymers obtained at high temperatures (27).

Even better solubility is typical for polyimides based on diamines containing trifluoromethyl side groups (28, 29). The diamines were obtained in accordance with scheme 1 using 3,5-dinitrobenzotrifluoride as starting compound (28,29). Synthesis of the polyimides based on such diamines and dianhydrides of the simplest binuclear tetra carboxylic aromatic acids was carried out using polycyclocondensation in N-MP without any catalyst (29). The polyimides obtained combine rather low glass transition temperatures (180-210°C) with high degradation temperatures and complete solubility not only in amide, phenolic and chlorinated solvents but in cyclohexanone and butyrolactone, too.

For the preparation of new diamines not only *m*-dinitrobenzene and 3,5-dinitrobenzotrifluoride were used but 3,5-dinitrodiphenyl ether, too (30-34). This product was prepared on the basis of a very cheap and readily available explosive - 2,4,6-trinitrotoluene (TNT) - in accordance with a scheme 2 :



(2).

Interaction of these products with various different bis-phenolates led to the preparation of bis(ethernitro)compounds containing phenoxy side groups. Reduction of the bis(ethernitro)compounds led to the formation of bis(etheramines) containing phenoxy side groups.

Polyimides were prepared using a two-stage procedure including room-temperature synthesis of poly-(*o*-carboxy)-amides in N-MP followed by catalytic polyimidization using a pyridine:acetic anhydride (1:1) complex as catalyst. All reactions proceeded heterogeneously and led to the formation of high-molecular weight polyimides with high cyclization degrees.

All polyimides obtained demonstrate relatively low glass transition temperatures and high degradation temperatures in combination with good solubility on organic solvents. Almost all polymers were soluble not only in amide, phenolic and chlorinated solvents, but also in cyclohexanone, acetone and butyrolactone.

RIGID-ROD APIs

As it was mentioned above the rigid-rod APIs backbone molecules must posses a high level of alignment and preferably contain symmetrical *p*-phenylene and heterocyclic rings without any flexibilizing units.

The simplest aromatic polyimides with the required rod-like *p*-ordered geometry can be prepared from pyromellitic or biphenyl-3,3',4,4'-tetracarboxylic acid dianhydrides and carbocyclic - *p*-phenylenediamines, benzidine, 4',4"-diaminoterphenvl, etc. - or heterocyclic - 2,5-bis-(*p*-aminophenyl)-pyrimidine, etc. - diamines (35-39).

The Kuhn segment value for polypyromellitimide based on 4,4'-diaminoterphenyl is 625Å and for polypyromellitimide based on 2,5-bis-(*p*-aminophenyl)-pyrimidine 1750Å indicating extremely high stiffness of the macromolecules (37).

High molecular weight poly-(*o*-carboxy)-amides have been prepared in amide solvents (DMAc, etc.) with these monomers, however, thermal or chemical cyclodehydration reactions lead to insoluble, infusible materials.

Fabrication of these materials is normally carried out via the DMAc soluble poly-(*o*-carboxy)amides which produce two moles of water per repeat unit during the high temperature thermal cyclodehydration to the imide structure. The volatiles produced by the process limit the utility of these materials in the fabrication of thick components (35).

The approach various research groups have taken to circumvent the evolution of the imidization water has been to synthesize rigid-rod polyimides soluble in organic solvents. Usually improvement in polymers solubility requires introduction of large bulky side groups in the macromolecule.

The best results were obtained when diamines or/and dianhydrides containing trifluoromethyl side groups were used as starting monomers (40 -43). Preparation of polyimides was carried out using 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl and the dianhydrides of pyromellitic, diphenyl-3,3'4,4'-tetracarboxylic, 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic and 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic acids.

The best polymer was obtained on the basis of 2,2'-bis(trifluoromethyl)-4,4'-diaminodiphenyl and 3,3',4,4'-biphenyltetracarboxylic acid dianhydride using high-temperature polycondensation in *m*-cresol (42,43). This polyimide is soluble in hot *m*-cresol, allowing fibers to be spun from an isotropic solution using a dry-jet wet spinning method.. The as-spun fibers have low tenacities and low moduli, but they can be drawn at high temperatures (>380°C) under tension to large draw ratios (up to 10 times), which produces a remarkable increase in strength and modulus. Drawn fibers display a tensile strength of about 25 g·den^{-1} (3.2 GPa) and an initial modulus higher than 1000 g·den^{-1} (130 GPa). The fibers show excellent thermal stability and retain relatively high strength and modulus at elevated temperatures.

Rigid-rod polyimides soluble in phenolic solvents were obtained also by the reaction of 3,3',4,4'-bisphenyltetracarboxylic acid dianhydride with phenylated *p*-phenylenediamine and 1,1'-binaphthyl-4,4'-diamine (44). Reactions were carried out in *m*-cresol or *p*-chlorophenol at 200°C using isoquinoline or tertiary amines as catalysts.

The polyimides obtained are soluble in *m*-cresol and *p*-chlorophenol and combine high solution viscosities with high glass transition and degradation temperatures.

The same diamines were reacted with the dianhydrides of 3-phenylpyromellitic and 3,5-diphenylpyromellitic acids using high-temperature (200°C) polycondensation reactions in *m*-cresol with isoquinoline as catalyst (45).

The obtained polyimides are soluble in *m*-cresol and *p*-chlorophenol and combine high solution viscosities with high glass transition and degradation temperatures.

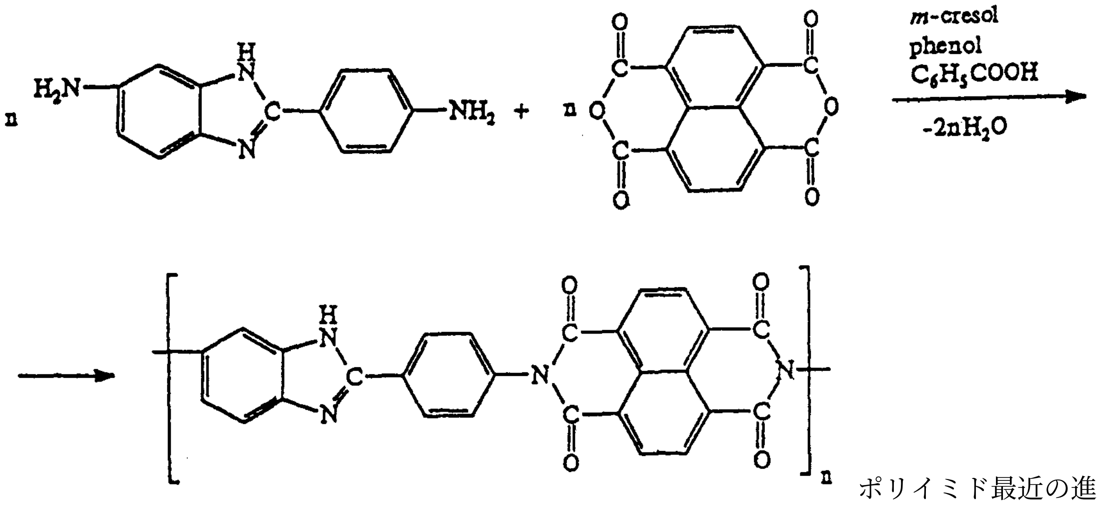
Rigid-rod polypyromellitimide was obtained also on the basis of 1,7-diphenyl-2,6-di-(*p*-aminophenyl)benzo[1,2-d;4,5-d']diimidazole (46) using high-temperature solution polycondensation in phenolic solvents. The reaction proceeded by precipitative polyheterocyclization and led to the formation of a polyimide insoluble in organic solvents.

In contrast a polymer soluble in trifluoroacetic acid and TCE : phenol mixture was obtained by the reaction of the same diamine and naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (46) using high-temperature (200°C) solution polycondensation in *m*-cresol with benzoic acid as catalyst. This polymer combines high solution viscosity with extremely high glass transition and degradation temperatures (540°C).

It seems to be quite possible that improved solubility of polynaphtylimides when compared with polypyromellitimides is typical not only for the above-mentioned systems.

In general polynaphthylimides have some considerable advantages over polyphthalimides: they are more stable towards hydrolysis and thermolysis (47). This is why the main attention in our investigation was paid to the preparation of soluble polynaphthylimides.

The most important, remarkable and unexpected result was obtained when we carried out the reaction of naphthalene-1,4,5,8-tetracarboxylic dianhydride with the unsymmetrical monomer-2-(p-aminophenyl)-5(6)-aminobenzimidazole-(commercialized in Russia) in accordance with scheme 3. (48):



(3)

The reaction was carried out under conditions of high temperature solution polycondensation in phenolic solvents using benzoic acid as catalyst. Despite the absence of any substituents in the diamine and dianhydride, the reaction proceeded homogeneously and resulted in high-molecular weight [$M = 120000$ (49)] polymer soluble (before isolation from reaction solution) in phenolic solvents. The obtained polyimide is moderately rigid, its Kuhn segment is equal to 320Å (49).

From the reaction solutions of the polyimide strong and flexible films were cast. After the heat treatment at 140°C for 12 hrs followed by treatment at 250°C for 3 hrs in vacuo the film properties became even better and after drawing the tensile strength was equal to 930±10 MPa and the modulus - to 20±1 GPa.

CONCLUSION.

As may be seen from the above-mentioned data large variety of flexible and rigid-chain polyimides was developed. Some of these systems are of great practical interest because of improved tractability or outstanding mechanical properties of the material therefrom. Unlimited possibilities of organic and macromolecular synthetic chemistry promise new successes of these field of polymer science.

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