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Poly(aroylene-bisbenzimidazoles) and Polyimides Based on Aromatized Adducts of Bisfurans with Maleic Anhydride

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ABSTRACT

A synthesis procedure has been developed for dianhydrides of the aromatic tetracarboxylic acids which are the starting compounds for producing poly(aroylene-bisbenzimidazoles) (PAB) and polyimides (PI). The procedure involves Diels-Alder reaction between maleic anhydride and bisfurans—Schiff bases of furfurol or 5-phenylfurfurol with aromatic diamines, bis(α-furyl)arylenes, cyclic acetals of furfurol and pentaerythritol, or other tetramethylol derivatives and bisfurfuryl esters of the aromatic dicarboxylic acids. The diene synthesis results in bisadducts; two water molecules are split out under the action of acidic reactants, resulting in dianhydrides of aromatic tetracids. The latter are used for synthesis of PAB and PI, either with isolation of the prepolymer or in one step in polyphosphoric acid. All the polymers produced are soluble in concentrated acids, and the PAB based on the dianhydrides with phenyl substituents are soluble

also in organic solvents. The polymers possess high thermoxidation and ablation resistance.

INTRODUCTION

Among the organic polymers which possess high thermal and thermoxidative stability, of great practical interest are polyimides (PI) and poly(aroylene-bisbenzimidazoles) (PAB) [1, 2]. These polymers are produced by polycondensation of dianhydrides of tetracarboxylic acids with aromatic di- and tetramines, respectively, in a double-stage process. At the first stage prepolymers which are soluble in organic solvents namely, polyamido acids (PAA) or polyaminoamido acids (PAAA) are produced; thermal intramolecular cyclization of these results in the PI or PAB structures [3, 4]. The second stage occurs, as a rule in an article molded from the prepolymer. A one-stage process can be used for the polymers which are soluble following cyclization, namely, polycondensation in polyphosphoric acid (PPA) at high temperatures [5, 6].

At the time this study was started, only a few dianhydrides, generally produced by oxidation of aromatic compounds, were available for producing PAB and PI [7]. However, selection of the starting compounds of appropriate structure makes it possible to control the structure of the PI and PAB macrochains and hence their physicochemical and mechanical properties, so that some outstanding problems in this field of the polymer chemistry such as combination of the imide or imidazopyrrolone structures with other organic groups, development of the thermoreactive properties in PI and PAB, and simplification of processing of these polymers for manufacturing articles, may be solved.

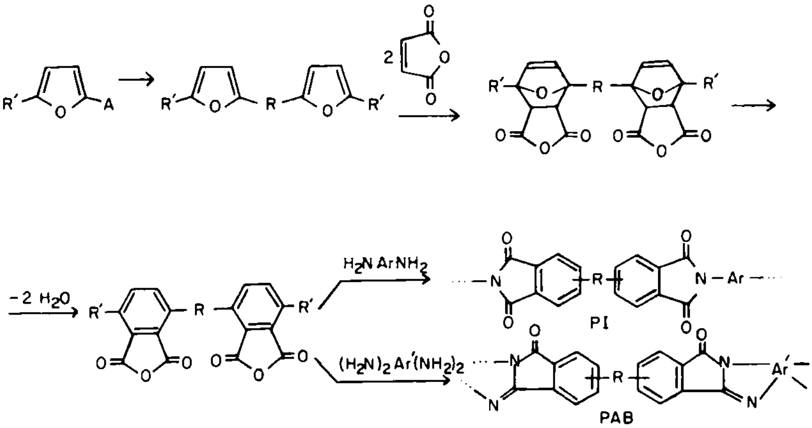
This paper deals with development of a new process for producing dianhydrides of the aromatic tetracarboxylic acids and the synthesis and studies of the thermostable PI and PAB based on them. The method of dianhydride synthesis involves Diels-Alder reaction between maleic anhydride and bisfurans, followed by aromatization of the adducts.

RESULTS AND DISCUSSION

A study of the available processes for producing tetracarboxylic acids [7] shows that the Diels-Alder reaction can be highly useful for producing the starting compounds for PI and PAB, since adducts of some types convert into aromatic structures in the process of production or as a result of the subsequent reactions, even though no attempts have been made until recently to synthesize dianhydrides with this procedure.

We have synthesized dianhydrides using the reactions between the bisfuran compounds and maleic anhydride [8]. The reasons for using bisfurans as bisdienes include the following: bisfurans may be readily synthesized from either the furan itself or from easily available and cheap functional derivatives, namely, furfurol, furfuryl alcohol, and 2-furancarboxylic acid; the furan ring is a sufficiently active diene in the reaction with maleic anhydride and gives rise to rather stable adducts in 90-95% yields [9]; arylation of furan and its functional derivatives gives rise to compounds with the aryl substituents at the 5 position of the furan ring [10, 11]; and, most important, the adducts of furan and maleic anhydride are capable of dehydration, giving rise to derivatives of phthalic anhydride [12].

Our process for producing dianhydrides of the aromatic tetracarboxylic acids and the polymers based on them is described by the scheme (1).



(1)

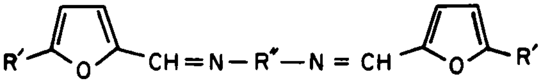
The stage at which the bisfuran compound is synthesized determines the structure of the radical R and, subsequently, the structure of the polymer macrochain. Since we can synthesize a large number of bisfurans with various groups between the furan rings, we can vary the structure of the PI and PAB macromolecules over a wide range and thus produce polymers with a combination of properties required for a given useful application.

Bisfurans

The following products have been produced and used as the starting bisfurans:

N,N'-Bis(5-R'-furfurylidene)diaminoarylenes (Ia-i, IIa-c)

Compounds I and II were produced by condensation of furfurol or 5-phenylfurfurol with various aromatic diamines when the components were directly mixed or in benzene solution with azeotropic distillation of water. The reaction is complicated by formation of resinous compounds, and the pure products were separated by chromatography of boiling solutions in the alumina columns. The azomethyne system I and II is resistant to concentrated sulfuric acid, glacial acetic acid, and 0.1 N hydrochloric acid. 5-Phenylfurfurol was produced by the Meerwein arylation reaction [13] and by formylation of α-phenylfuran [11].



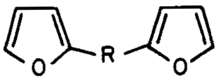
I, II

Ia, b: R' = H, R" = m-, p-phenylene
Ic: R' = H, R" = 4,4' diphenylene
Id: R' = H, R" = 3,3'-dimethyl-4,4'-diphenylene
Ie: R' = H, R" = 1,4-naphthylene
If: R' = H, R" = 4,4'-C_6H_4–O–C_6H_4–
Ig: R' = H, R" = –SO_2–
Ih: R' = H, R" = –CH_2–
Ii: R' = H, R" = –CH_2CH_2–

IIa: R' = C_6H_5, R" = p-phenylene
IIb: R' = C_6H_5, R" = 4,4'-diphenylene
IIc: R' = H, R" = 4,4'-diphenylene oxide.

Bis(α-furyl)arylenes (III a-c)

Several methods for producing III have been tested and the following have been found to be suitable: a modified Homberg arylation reaction with decomposition of solid acetates of bisdiazonium salts of aromatic diamines in furan in the presence of sodium acetate

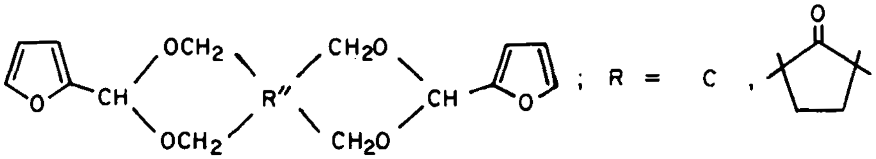


III

IIIa: R = p-phenylene
IIIb: R = 4,4'-diphenylene
IIIc: R = 4,4'-diphenylene oxide

(10-15% yield) and the thermal decomposition of N,N'-bisnitroso-N,N'-diacetyldiaminoarylenes in the furan excess (40-60% yield).

Cyclic Acetals of Furfurol with Polyatomic Alcohols (IVa, b)



IV

Compounds IV were produced in high yields by condensation of furfurol with pentaerythritol or 2,2,5,5-tetramethylolcyclopentanone in the presence of anhydrous zinc chloride [14].

Bisfurfurylterephthalates and Isophthalates (Va, b)

Compounds V were produced by re-esterification of the dimethyl or diethyl esters of terephthalic and isophthalic acids with sodium furfurylate with azeotropic distillation of the lower alcohols [15]. The yield of V was 60-70%.

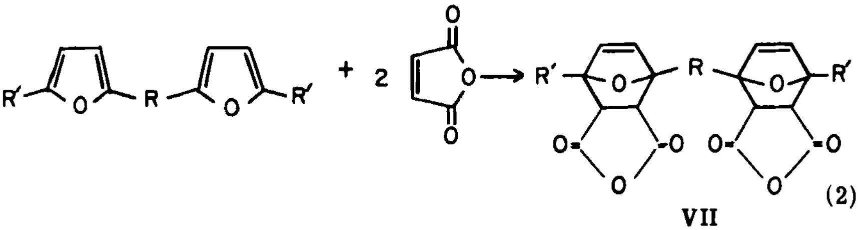
N,N'-Bisfurfuryldiaminoarylenes (VIa, b)

Compounds VI are produced by reducing compounds Ib and Ic, respectively, under the action of lithium aluminum hydride in tetrahydrofuran (THF).

Diene Synthesis

Diene synthesis involving bisfurans has not been described in the literature, even though addition of maleic anhydride to furans in general has been studied to a considerable extent [9].

Addition of maleic anhydride to compounds I-VI gives rise to a mixture of endo- and exo- isomers of bistetrahydro-endoxo-tetrahydrophthalic acids (VII):



VII (2)

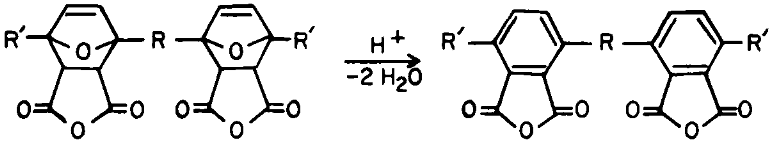
In our case the equilibrium is shifted towards formation of the adduct by selecting a solvent which must dissolve the starting components and, to a certain extent, the bis-adduct in order to avoid the precipitation of the mono-adduct from solution. Of many solvents studied, THF has proved to be the most suitable one in most cases. For instance, the Schiff bases produce 30% solutions in THF, and 0.1-0.5% of the VII compounds dissolve in it (UV spectra). In this case the diene synthesis reaction proceeds to the end, that is, with a 85-85% yield of VII even at 25° C, while at 60° C the reaction is completed in 1-2 hr. No large excesses of dienophil are needed for full consumption of the Schiff base. The maximum product yield is obtained even at a diene: dienophil ratio of 1:2.1. The reaction is monitored spectrophotometrically by the variation of the bisdiene concentration or accumulation and consumption of the charge transfer complex between the Schiff base and maleic anhydride (λ = 360 and 550 nm, respectively). The furylarylenes III have the lowest diene activity compared to other bisfurans studied: only under rigorous conditions (THF, ampoule, 100-120° C) did we manage to produce bis-adducts in low yields (up to 40%).

The majority of the compounds VII are resistant to acids and they dissolve in alkalies without decomposition. When heated in vacuo they decompose at about 110° C, giving rise to maleic anhydride. However, the bis-adducts based on the acetals IV and the esters V are stable only in solution at room temperature; in the solid state they form waxy resins.

The endo-oxygen bridge in the furan adducts is thermodynamically stable and is not detached at elevated temperatures [16]; therefore protonic or Lewis acids should be used as catalysts for aromatization of the VII adducts.

Aromatization

The best method for aromatization of the adducts based on compounds I-III and VI is dehydration [17] in concentrated sulfuric acid in the temperature range from -30 to 0° C [Eq. (3)]. The yield of aromatic dianhydrides VIII is 68-80%. Aromatization proceeds especially easily for the adducts based on compounds II.



(3)

The adducts which contain acetal and ester groups can be aromatized only in glacial acetic acid solution on bubbling gaseous hydrogen bromide or hydrogen chloride through the solution [12].

All the adducts are readily dehydrated in PPA at 20-50° C, the yield of the aromatic dianhydrides VIII being 60-90%. This fact makes it possible to use the VII bis-adducts which are aromatized in the process of polymer synthesis in the direct one-stage synthesis of PI and PAB.

Characterization of Adducts

The structures of all the above products have been verified by their UV, IR, and NMR spectra as well as by chemical methods.

A sufficiently reliable identification of the structure of bisfurans can be made by comparing their absorption spectra with the capability for addition of two maleic anhydride molecules. Identification of the structure of the VII adducts is much more difficult, but a comparison of the spectra of bisfurans and their bis-adducts makes it possible to identify the structure of the latter products. We have obtained a large number of bisfurans of various structures, thus making it possible to determine the characteristic absorption bands of the furan ring in the IR spectra: δ of the ring is about 750-760 cm^{-1}, γ of CH is at 885 and about 920 cm^{-1}, the ring is at about 1020 cm^{-1}, δ of CH is about 1080 and 1145-1153 cm^{-1} (cf. the data of Katrizky and Lagowsky [18], along with other bands typical of R, for instance, azine, diaryl ether, acetal and other such groups. The addition of maleic anhydride to bisfurans results in a disappearance of the absorption bands of the furan rings and the emergence of the intense absorption ν for C=O at ca. 1880 and ~1790 cm^{-1} and ν for C–O–C at ca. 1230 cm^{-1} owing to the anhydride groups [19], while the R characteristic bands are retained. The IR spectra of the aromatized adducts of VIII are similar to the spectra of the well-known aromatic five-membered anhydrides [20].

The IR and visible absorption spectra have proved to be very useful for the studies of the Schiff bases. Compounds I and II have the azomethyne structure and their spectra exhibit two characteristic bands: $\lambda_1 \simeq 290$ nm [$\epsilon = (2.1\text{-}3.7) \times 10^4$] and $\lambda_2 \simeq 333\text{-}400$ nm [$\epsilon = (2.6\text{-}5.85) \times 10^4$] in THF [21]. The azomethyne system is disrupted in the bis-adduct and the spectrum exhibits one band, λ 310-330 nm [$\epsilon = (2.85\text{-}4.7) \times 10^4$]. Aromatization results in restoration of the azomethyne system and the spectrum of the VIII dianhydrides has two bands: $\lambda_1 \simeq 280$ nm and $\lambda_2 \simeq 350\text{-}420$ nm.

The NMR spectra also confirm the structure of the products; the ratio between the signals of the aliphatic protons at 3.31 and 1.47-1.6 ppm in the spectra of the VII bis-adducts indicates that either pure endo- isomer or a mixture of stereoisomers is produced, depending on the conditions of synthesis.

Polymers from VII and VIII

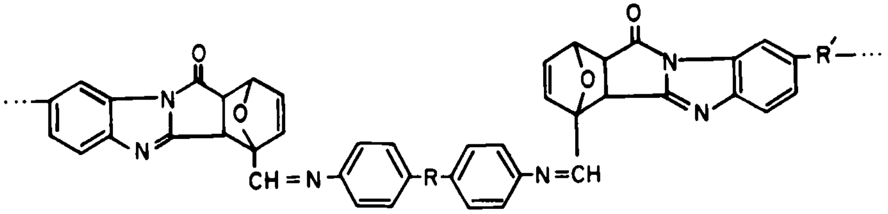
Our process for synthesizing PI and PAB makes it possible to produce polymers possessing new valuable properties. This allows us to synthesize regular block copolymers in which the imide or imidazopyrrolone groups and other given structures alternate. Moreover, the two-stage synthesis process can be used for producing the copolymers which, in fact, solves the problem of processing.

This may be exemplified by the polymers produced on the basis of the VIII dianhydrides which contain groups of the Schiff bases and are copolymers of imides or imidazopyrrolones with the Schiff bases. In this case the polymers have a fully conjugated structure and are capable of forming three-dimensional networks at the expense of the reactions at the C=N bonds.

Despite all the advantages of the two-stage synthesis method for PI and PAB, it has one essential shortcoming, namely, that since intramolecular cyclization occurs in the article, its microstructure is necessarily disrupted by the water vapor, and the remaining amide solvent is liberated. This factor, which is especially important for PAB, results in lower mechanical strength and thermostability of the article. Furthermore, purely thermal dehydration does not provide for a sufficient degree of cyclization [20], since very high temperatures are needed for this process go to completion in rigid macromolecules. Our method allows us to make PI and PAB soluble in the organic solvents by selecting a dianhydride of a given structure.

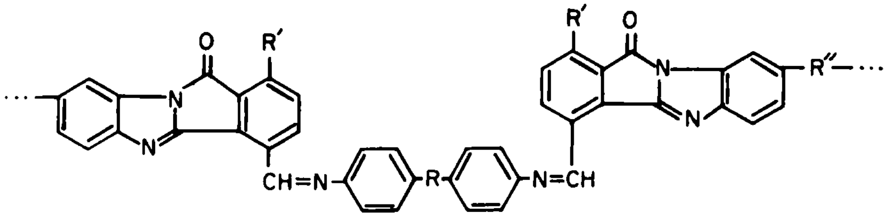
Introduction of bulk side substituents into the polymer macromolecules is known to hinder close packing of the macromolecules and, hence, to increase the polymer solubility [23, 24]. In our case the aryl substituents can be rather easily introduced into the polymer macrochains by using a 5-aryl-substituted bisfuran, for instance, compound II.

In the course of this study, which aimed primarily at synthesizing thermostable polymers, we have produced and studied PAB and PI based on dianhydrides containing azomethyne groups (IX-XIII).



IX

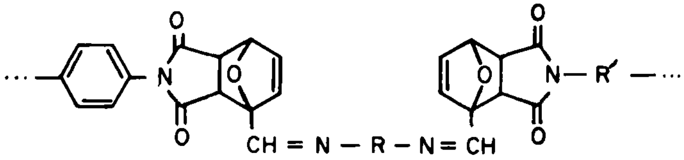
IXa: R, R' absent;
IXb: R absent, R' = –O–
IXc: R = –O–, R' absent



X, XI

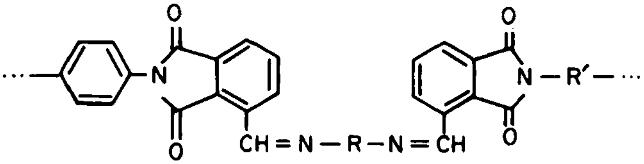
Xa: R' = H, R" absent, R = p-phenylene
Xb: R' = H, R" absent, R = 4,4'-diphenylene
Xc: R' = H, R" absent, R = 4,4'-diphenylene oxide
Xd: R' = H, R" absent, R = 4,4'-diphenylenemethane
Xe: R' = H, R" = $-CH_2-$, R = 4,4' diphenylene
Xf: R' = H, R" = $-CH_2-$, R = 3,3'-dimethyl-4,4'-diphenylene
Xg: R' = H, R" = $-CH_2-$, R = 4,4'-diphenylene oxide

XIa: R' = C_6H_5, R" absent, R = p-phenylene
XIb: R' = C_6H_5, R" absent, R = 4,4'-diphenylene
XIc: R' = C_6H_5, R" absent, R = 4,4'-diphenylene oxide



XII

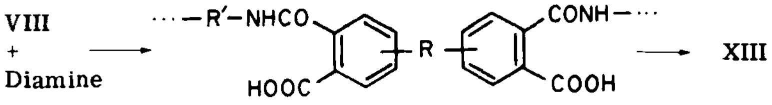
XIIa: R' absent, R = p-phenylene
XIIb: R' absent, R = 4,4'-diphenylene
XIIc: R' = –O–, R = 4,4'-diphenylene oxide



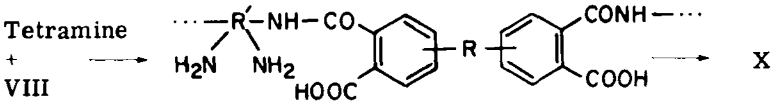
XIII

XIIIa: R = R' = p-phenylene
XIIIb: R = R' = 4,4'-diphenylene oxide
XIIIc: R = R' = 4,4'-diphenylene ethane
XIIId: R = 1,4-naphthylene, R' = 4,4'-diphenylene oxide

We have studied the conditions for formation of the compounds IX-XIII both in the one-stage process and by way of production of a prepolymer PAA or PAAA:



PAA



PAAA

As in many other cases [5, 25], dry dimethyl sulfoxide proved to be the best solvent at the first polycondensation stage. The viscosity of prepolymers in DMSO is 15-20% higher than in dimethylacetamide and 20-30% higher than in dimethylformamide. Prepolymers of the highest molecular weight are produced with a 2-3% excess of dianhydrides VIII and a 4-6% excess of adducts VII (Fig. 1). The order of addition of the components does not significantly affect the molecular weight of PAA or PAAA, as found earlier [3, 5]. The prepolymer production is not accompanied by gelation, even when condensation is carried out at high total concentration of the monomers (up to 25%) and high reaction temperature (up to 80°C).

Shown in Fig. 2 is the viscosity of PAAA as a function of the temperature and the time of the reaction. Noticeable are the low formation rate for PAAA based on the aromatic anhydrides VIII and the low degrees of conversion of monomers at 25° C, while formation of PAAA based on the adducts VII occurs at a considerable rate, even at 20-25°C. Thus, in contrast to other five-membered dianhydrides, for instance pyromellitic dianhydride (PMDA), the dianhydrides VIII have lower reactivities in reactions with amines and the reaction solutions do not tend to gel.

The electrophilic activity of a dianhydride is a decisive factor for the successful synthesis of PAAA and formation of the aroylene-benzimidazole structures. The fact is that the PAB synthesis process provides for use of starting compounds whose functionality is more than two, thus making possible branching and gelation at the prepolymer synthesis stage and incomplete intramolecular cyclization at the second stage. The tendency to branch depends on the ratio between the reactivities of the same functional groups in monomer, in the macrochain, and at the ends of macromolecules. When the reactivities of these three groups differ considerably, branching of the macromolecule may be prevented up to high degrees of

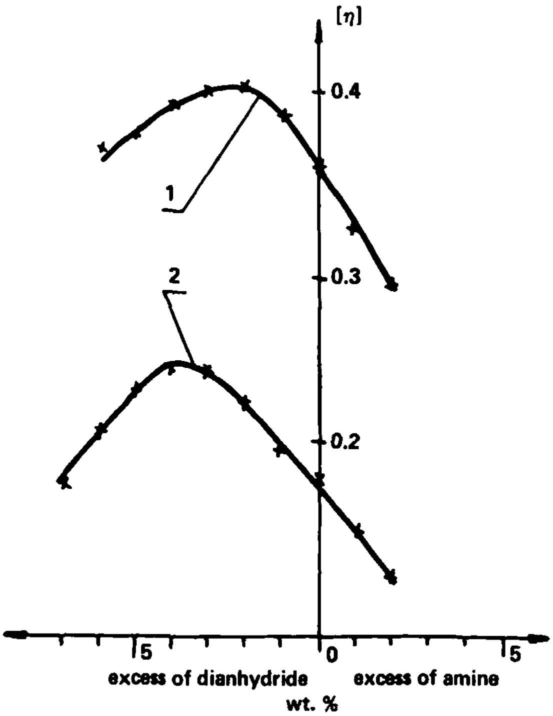


FIG. 1. Effect of the component ratios on the viscosity of the PAB prepolymers: (1) the prepolymer of Xb; (2) prepolymer of IXa.

conversion if the selectivity of the second reactant is sufficiently high.

In the 3,3',4,4'-tetraminodiphenyls which are usually used for synthesizing PAB, the 4,4'-amino groups are somewhat more basic than the 3,3'-amino groups (owing to a mutual donor effect of the 4,4'-groups) and considerably larger than the amino groups in the prepolymer macrochains (owing to the electron-accepting effect of the carboxyl and amide groups). The lower the electrophilic activity of a dianhydride, the higher its selectivity in the reactions with amino groups of various basicity and the lower the probability of branching of macromolecules.

Condensation of PMDA with tetramines is known [26] to give

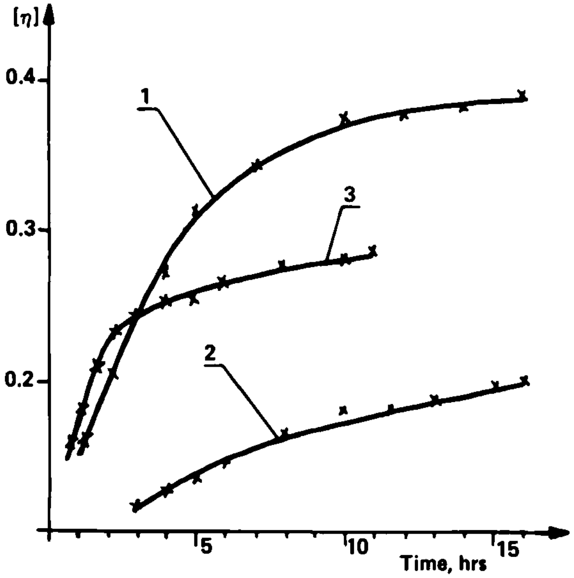


FIG. 2. Viscosity of the PAB prepolymers as a function of the reaction time: (1) prepolymer of Xb at 65°C; (2) prepolymer of Xb at 25°C; (3) prepolymer of IXa at 25°C.

rise to highly branched structures and gelation even at the early reaction stages at 0-20°C; that is, PMDA attacks all the three types of amino groups with practically the same probability. This fact is, to a great extent, responsible for the low degree of cyclization of the polymer and for occurrence of processes not related to formation of PAB when the reaction is carried out in PPA [27]. Another extreme case is that of the dianhydride of 3,4,9,10-perylenetetracarboxylic acid, which reacts with tetramines only under very rigorous conditions (140-170°C) [28], since the electrophilicity of the dianhydride is greatly reduced owing to the electron-donating effect of the perylene ring.

However, when PAB is synthesized from the dianhydride of 1,4,5,8-naphthalenetetracarboxylic acid (DANTA) the reaction occurs with a noticeable rate at temperatures greater than 60°C, and branching of macrochains of the prepolymer takes place only with rather high degrees of conversion [5, 29]. In PPA there are formed PAB whose degrees of cyclization are practically 100% [30].

The above considerations are confirmed by the data on the synthesis of PAAA based on the dianhydrides VIII and the adducts VII. Compounds VIII have a developed conjugation system, and the azomethyne system exhibits electron-donating properties with the respect to the anhydride groups, so that their reactions with amines occur at the normal rate at only 60-80° C, and mainly linear macromolecules are formed. The azomethyne system in the bis-adducts is isolated from the anhydride groups, and condensation occurs with a high rate even at 25° C.

An analysis of the above data shows that for synthesizing PAB it is expedient to use dianhydrides of moderate electrophilicity whose reactivity is close to those of DANTA or VIII.

When selecting the conditions of the one-stage polymer synthesis from the dianhydrides VIII, we used the results obtained in the studies of the mechanism of formation of poly(naphthoylenebisbenzimidazoles) [5]. The character of the relationship between the PAB viscosity and the temperature and time of the reaction (Fig. 3) is similar to the results obtained for condensation of DANTA,

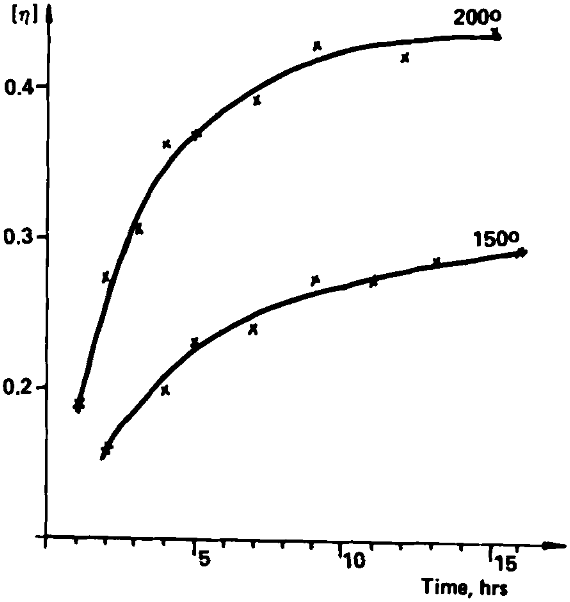


FIG. 3. Viscosity of the Xb polymer as a function of the reaction time in polyphosphoric acid.

showing once again that DANTA and VIII have similar electrophilicities. The IR spectra, however, show that the Xc polymer has a considerably lower degree of cyclization (about 70%) than the DANTA polymers, which seems to reflect the difference in the ease with which five- and six-membered heterocyclics are formed.

It was shown above that PPA is an excellent reactant for aromatization of the bis-adducts. Therefore, we carried out one-stage polymer synthesis based on the bis-adducts VII. The concentration of monomers was reduced to 1.5-3% and the reaction mixture was kept for 4 hr at 50° C, after which condensation was carried out in the same way as with the VIII dianhydrides. The polymers produced from the compounds VII are fully identical in their properties and structure to the polymers produced from the respective compounds VIII. The synthesis of PAB and PI from the VII bis-adducts in PPA makes it possible to carry out the process without aromatization of the bis-adducts as a separate step and without purification of the aromatic tetracid, which is especially important.

Properties of Polymers

All the PAB and PI produced in the one-stage process in PPA and in the two-stage process from the VIII dianhydrides are soluble in the concentrated acids. PAB made from PPA continue to be soluble even after additional heating in vacuo at 250-300° C and form insoluble structures only at 350-380° C. The thermal cyclization products of the prepolymers cease to be soluble even at 250-280° C after one hour. This fact shows the advantages of cyclization in PPA compared to the purely thermal cyclization.

The phenyl-substituted polymers XI produced in PPA have a highly valuable practical property. After completion of the intramolecular cyclization they are soluble in organic solvents, namely, m-cresol, m-chlorophenol, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide; in the last three solvents, the concentration of solutions may be about 10%, which is quite sufficient for manufacture of molded articles by means of conventional techniques.

Our polymers are highly resistant to degradation by thermooxidation (Fig. 4, Table 1). The fully aromatic PAB are stable in the air up to 560-580° C; the DTA peaks at 350-400° C for the polymers X correspond to the temperatures at which the solubility ceases and may reflect formation of new bonds involving the C=N groups (change in the IR spectra in the 1640-1600 cm^{-1} range). The thermooxidative degradation of the polymers XI proceeds via the same mechanism as for the unsubstituted analogs, though the polymers XI are somewhat less thermostable: the degradation begins at 480-500° C. However,

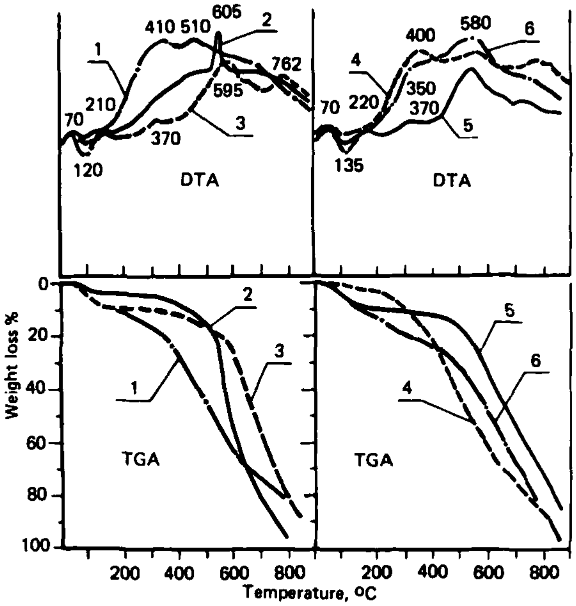


FIG. 4. DTA and TGA of some PAB in air: (1) IX, two-stage process; (2) Xa; (3) Xe; (4) Xg; (5) Xb; (6) IXa, two-stage process.

the polymers produced from the adducts VII in the two-stage process lose 15-20% of the weight during cyclization and then undergo intense degradation at 390-410°C. Our PI are stable in the air up to 400-470°C, depending on the structure.

Given in Table 1 are the data on the ablation resistance of our PAB [25] *which is determined by the following three factors:* mechanical strength, thermostability, and the structurization ability. The kinetics of the ablative degradation of all the polymers studied are similar in character (see Fig. 5). The maximum rate of weight loss A_V in a stream of heated gas flow is reached in the first few seconds of the test owing to the thermooxidative degradation of the surface layers of the sample. The process is especially intense for the polymers with a low degree of cyclization. Concurrently, additional intramolecular cyclization and structurization occur in the bulk of the sample and therefore the ablation rate drops sharply with time.

TABLE 1. Some Properties of Poly(aroylene-bisbenzimidazoles)

Polymer	$[\eta]$[a] (dl/g)	Heat treatment Temp (°C)	Heat treatment Time (hr)	σ_{compr} (kg/cm^2)	Decomposition temp (°C)	$A_V \times 10^{-4}$ (kg/m^2-sec)[b]	Note
Xa	0.29	200	2	212	560	17.1	c
	–	250	2	400	–	3.2	
	–	300	2	400	–	4.5	
	0.32	350	2	–	590	18.2	c,d
Xb	0.36	200	2	184	560	15.6	c
	–	300	2	354	–	5.4	e
	–	400	2	–	–	5.5	f
Xe	0.28	200	2	682	420	7.0	
	–	400	2	–	–	5.7	f
Xf	0.24	200	2	354	452	10.6	
	–	400	1	–	–	7.2	f
Xb	0.30	200	2	246	410	10.1	g
	–	400	2	–	–	6.7	g
Xg	0.17	200	4	–	385	8.3	g

[a] Intrinsic viscosity in sulfuric acid at 25° C.

[b] After 30 sec testing.

[c] The sample disintegrated under the effect of the temperature gradient and the shock wave.

[d] Heat treatment of the sample at 350° C prior to molding.

[e] Composition of 90% polymer and 10% m-phenylene-bis-maleimide.

[f] Heat treatment in argon.

[g] Polymer was produced with the two-stage process.

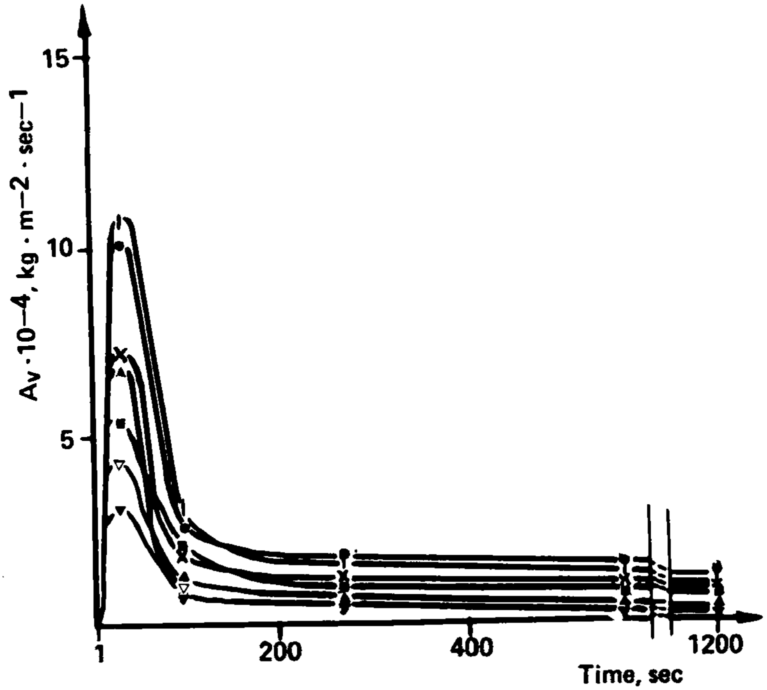


FIG. 5. Rate of aerodynamic disintegration of polymers with the flow of heated air at 425° C: (▼) Xa; (▽) Xa, heat treatment at 300° C; (■) composition of 90% Xb and 10% m-phenylene bismaleimide; (△) Xb; (X) Xf (●) IXa, two-step process. (|) IXc, two-step process.

The polymers which contain continuous conjugated chains, e.g., Xa, c, have the highest thermooxidative stability, but this factor also ordains a higher rigidity of the macrochains [33]. For instance, the samples molded from Xa, c at 200° C are rather brittle; they disintegrate in a stream of heated gas owing to the effects of the temperature gradient and the shock wave. However, strong ablation-resistant plastics may be produced by increasing the molding temperature and by heat treatment of the sample at 400° C in vacuo as well as by introduction of about 10% of m-phenylene bismaleimide as "temporary" plasticizer [32]. The best samples exhibit a practically intact surface after 20 min under a gas flow.

In the polymers with a "hinge" group (–O–, $-CH_2-$), for instance, Xc-g, the macromolecules are rather flexible; this leads to high mechanical strength but also a lower thermooxidation resistance of the polymer [33]. The result is that such polymers have an ablation resistance 1.5-2 times lower than that of the Xa, c polymers; however, heat treatment in an inert atmosphere improves the polymer properties.

Materials of a good mechanical strength and ablation resistance have been produced by selecting the polymer structure and the conditions of sample preparation.

EXPERIMENTAL

Characterization

The IR spectra were recorded with an UR-20 instrument on KBr disks. The UV spectra were recorded with a Spekord-UV-Vis in THF or DMFA solutions, and the NMR spectra were recorded with a Varian-HA-100 in DMSO-d_6, hexachloroacetone, or deuteroacetic acid. The acid numbers of the VII and VIII dianhydrides were determined by titration in a Radiometer instrument with automatic recording of the titration curve. Thermooxidation degradation was studied with a MOM derivatograph, on 50-100 mg samples at a heating rate of 3° C/min in air. The ablation resistance was studied by using the standard procedure [32]; the samples (disks 3.5 mm × 5 mm in diameter) were molded (200° C, 560 MN/m^2, 2 hr); the total mean pressure of the gas flow was $15 \times 10^4 N/m^2$, the temperature was 425° C.

General Synthesis Procedures for the Bis-Adducts VII

Bisfuran (0.05 mole) was dissolved in 1 liter of deoxygenated THF and 0.15 mole of maleic anhydride was added. The crimson color of the solution disappeared in 4-5 hr and the crystals of VII began to appear. In 12-16 hr the sediment was filtered off under argon and dried in vacuo at 40-50° C. The data on the bis-adducts produced are given in Table 2.

Alternatively, 0.1 mole of I, II, or III was dissolved in 0.7 liter of boiling THF under argon flow and 0.25 mole of maleic anhydride added. After 20-30 min of boiling, VII began to precipitate, and after 2-3 hr the reaction mixture was cooled and VII filtered off.

TABLE 2. Adducts of Bisfurans with Maleic Anhydride

Diene	Yield of VII (%)	Acid number[a]		Formula	Analysis found (calcd)[a]		
		Found	Calcd		C (%)	H (%)	N (%)
Ia	92	453	452	$C_{24}H_{20}N_2O_{10}$	57.8 (58.1)	4.24 (4.06)	5.64 (5.64)
Ib	82	450	452	$C_{24}H_{20}N_2O_{10}$	57.6 (58.1)	4.12 (4.06)	5.81 (5.64)
Ic	88	375	374	$C_{30}H_{24}N_2O_{10}$	62.6 (62.9)	4.45 (4.23)	5.30 (4.99)
Id	92	370	368	$C_{32}H_{28}N_2O_{10}$	63.8 (64.0)	4.87 (4.70)	5.31 (5.66)
Ie	84	408	410	$C_{28}H_{22}N_2O_{10}$	62.0 (61.6)	4.65 (4.43)	5.02 (5.13)
If	94	381	381	$C_{30}H_{24}N_2O_{11}$	65.5 (65.2)	3.48 (3.65)	5.32 (5.07)
Ig	67	346	350	$C_{30}H_{24}N_2O_{12}S$	56.5 (56.6)	3.78 (3.80)	4.11 (4.40)
Ih	90	362	365	$C_{31}H_{26}N_2O_{10}$	63.5 (63.8)	4.68 (4.47)	4.42 (4.78)
Ii	94	356	357	$C_{32}H_{28}N_2O_{10}$	63.8 (64.2)	4.55 (4.69)	4.80 (4.67)
IIa	84	346	346	$C_{36}H_{38}N_2O_{10}$	66.1 (66.8)	4.56 (4.35)	4.52 (4.38)
IIb	88	313	310	$C_{42}H_{32}N_2O_{10}$	70.4 (69.7)	4.61 (4.46)	3.72 (3.87)
IIc	89	300	303	$C_{42}H_{32}N_2O_{11}$	68.2 (68.4)	4.71 (4.33)	3.60 (3.78)
IIIb	16	410	414	$C_{28}H_{22}O_{10}$	65.4 (64.9)	4.01 (4.25)	– –
IVa	68	430	428	$C_{23}H_{24}O_{14}$	52.6 (52.8)	4.44 (4.61)	– –
IVb	74	380	384	$C_{27}H_{28}O_{15}$	54.7 (54.8)	4.92 (4.76)	– –

Va	67	402	402	$C_{28}H_{22}O_{14}$	56.1 (56.0)	3.72 (3.96)	– –
Vb	63	402	402	$C_{28}H_{22}O_{14}$	56.3 (56.0)	4.17 (3.96)	– –
VIa	76	451	451	$C_{24}H_{22}N_2O_{10}$	58.1 (58.0)	4.36 (4.12)	5.75 (5.62)
VIb	88	392	391	$C_{30}H_{22}N_2O_{10}$	67.3 (67.1)	4.28 (3.82)	5.53 (5.12)

[a] For tetraacids.

General Synthesis Procedures for the Dianhydrides VIII

Aromatization in Sulfuric Acid

VII (10 mmole) was added in parts to 150 ml of vigorously stirred concentrated sulfuric acid cooled to -20°C. Cooling was then discontinued, and when the temperature reached 0°C (1 hr), the solution was poured on ice, the sediment filtered off, washed with water, dried, and recrystallized from acetic acid. Heat treatment at 140-150°C gave rise to the aromatic dianhydride VIII. The data on the dianhydrides produced are given in Table 3.

Aromatization of Adducts Based on IV and V

A 20-mmole portion of the adduct was dissolved in 0.7 liter of glacial acetic acid saturated with hydrogen bromide and slowly heated to 80-100°C under a continuous stream of HBr for 6 hr. Acetic acid was distilled off in vacuo, and VIII was separated from the residue. The data on dianhydrides are given in Table 3.

Aromatization in Polyphosphoric Acid

A 13-mmole portion of the adduct was dissolved in 100 ml of 116% PPA (phosphoric anhydride content 74.7%) and the mixture stirred and heated to 40-50°C. After 10-12 hr reaction the product was poured into 2 liters of water with ice, the sediment was filtered off, carefully washed with water, reprecipitated with hydrochloric acid from sodium hydrate solution and recrystallized from acetic acid. Heating at 140-150°C for 4-5 hr yielded VIII.

Two-Step Process for Polymer Syntheses

Dianhydride (10 mmole) and 9.4 mmole of di- or tetramine were dissolved in dry dimethyl sulfoxide (concentration of 12-15%) in a flask equipped with a stirrer, calcium chloride tube, and a capillary for argon feed. The solution was heated to 65-75°C and kept at this temperature for 16-18 hr. The product was poured into methanol and the precipitate dried at 60-70°C in vacuo. The intramolecular cyclization was carried out at 250-300°C under 10^{-2} Torr. The data on the prepolymer are given in Table 4.

TABLE 3. Aromatic Dianhydrides VIII

Bisfuran	Yield of VIII (%)	Acid number		Melting point (°C)	Formula	Analysis found (calcd)		
		Found	Calcd			C (%)	H (%)	N (%)
Ib	82	530	528	>360	$C_{24}H_{12}N_2O_6$	67.8 (67.8)	2.99 (2.83)	6.73 (6.60)
Ic	73	448	448	>360	$C_{30}H_{16}N_2O_6$	71.8 (72.0)	3.24 (3.20)	5.71 (5.60)
Id	89	427	424	>360	$C_{32}H_{20}N_2O_6$	72.4 (72.7)	3.83 (3.79)	5.18 (5.28)
Ie	64	469	473	>360	$C_{28}H_{14}N_2O_6$	70.7 (70.9)	3.20 (2.91)	– –
If	85	428	434	337.5-338.5	$C_{30}H_{16}N_2O_7$	70.1 (69.9)	3.27 (3.10)	5.26 (5.42)
Ii	88	425	424	327-328	$C_{32}H_{20}N_2O_6$	73.0 (72.6)	3.74 (3.85)	5.15 (5.30)
IIa	93	388	388	247.5-249.5	$C_{36}H_{20}N_2O_6$	74.6 (75.0)	3.52 (3.48)	5.03 (4.86)
IIb	90	348	344	300 (decomp.)	$C_{42}H_{24}N_2O_6$	77.7 (77.4)	3.24 (3.69)	4.12 (4.30)
IIc	74	332	335	258-260	$C_{42}H_{24}N_2O_7$	76.0 (75.5)	3.42 (3.61)	3.98 (4.18)
IIIb	79	605	605	230 (subl.)	$C_{22}H_{10}O_6$	71.6 (71.4)	3.03 (2.71)	– –
IVa	51	490	495	284 (decomp.)	$C_{23}H_{16}O_{10}$	61.3 (61.0)	3.51 (3.40)	– –
IVb	64	443	443	242 (decomp.)	$C_{27}H_{20}O_{11}$	64.0 (64.1)	4.40 (4.35)	– –
Va	56	457	469	316-317	$C_{26}H_{14}O_{10}$	64.2 (64.1)	3.18 (2.98)	– –
Vb	59	458	460	288-289	$C_{26}H_{14}O_{10}$	64.6 (64.1)	2.74 (2.98)	– –

TABLE 4. Prepolymers of Poly(aroylene-bisbenzimidazoles) and Polyimides

Polymer	Yield (%)	[η] (dl/g)[a]	Formula	Analysis found (calcd)		
				C (%)	H (%)	N (%)
IXa	92	0.18	$C_{42}H_{34}N_6O_8$	65.8 (67.2)	5.05 (4.56)	11.0 (11.2)
IXb	83	0.25	$C_{42}H_{34}N_6O_9$	64.8 (65.8)	4.33 (4.47)	10.5 (11.0)
Xb	85	0.40	$C_{42}H_{30}N_6O_6$	69.4 (70.6)	4.81 (4.23)	11.5 (11.8)
Xc	87	0.32	$C_{42}H_{30}N_6O_7$	68.4 (69.0)	4.25 (4.14)	11.7 (11.5)
Xg	78	0.17	$C_{42}H_{22}N_6O_8$	66.8 (67.6)	4.55 (4.05)	11.2 (11.8)
XIIa	92	0.14	$C_{36}H_{23}N_4O_8$	62.5 (63.4)	4.72 (4.25)	9.79 (9.86)
XIIb	89	0.23	$C_{42}H_{32}N_4O_8$	69.7 (70.0)	4.30 (4.48)	7.50 (7.77)
XIIc	73	0.30	$C_{42}H_{32}N_4O_{10}$	67.2 (67.0)	3.87 (4.29)	7.35 (7.44)
XIIIa	95	0.32	$C_{30}H_{20}N_4O_6$	66.6 (67.6)	4.11 (3.79)	9.47 (10.5)

[a] Intrinsic viscosity in DMFA, 25° C.

TABLE 5. Poly(aroylene-bisbenzimidazoles) and Polyimides

Polymer	Yield (%)	[η] (dl/g)[a]	Formula	Analysis found (calcd)		
				C (%)	H (%)	N (%)
IXa	95	–	$C_{42}H_{26}N_6O_4$	72.4 (74.3)	4.23 (3.86)	11.8 (12.4)
I Xb	89	–	$C_{42}H_{26}N_6O_5$	71.8 (72.6)	4.03 (3.77)	12.5 (12.1)
IXc	84	0.42	$C_{42}H_{26}N_6O_5$	71.5 (72.6)	4.12 (3.77)	11.8 (12.1)
Xa	90	0.25	$C_{36}H_{18}N_6O_2$	75.8 (76.3)	3.30 (3.20)	14.5 (14.8)
Xb	85	0.36	$C_{42}H_{22}N_6O_2$	78.3 (78.5)	4.05 (3.45)	12.5 (13.1)
Xc	82	0.51	$C_{42}H_{22}N_6O_3$	76.5 (76.6)	3.58 (3.37)	12.5 (12.8)
Xd	93	0.25	$C_{44}H_{26}N_6O_2$	78.5 (78.8)	4.51 (3.91)	11.9 (12.5)
Xe	85	0.27	$C_{43}H_{24}N_6O_2$	78.5 (79.1)	3.22 (3.52)	13.0 (12.8)
Xf	73	0.31	$C_{44}H_{26}N_6O_2$	78.2 (78.8)	4.40 (3.91)	12.4 (12.5)
Xg	96	0.38	$C_{42}H_{22}N_6O_4$	74.5 (74.8)	3.67 (3.29)	12.2 (12.5)
XIa	90	0.30	$C_{48}H_{26}N_6O_2$	80.0 (80.4)	3.82 (3.62)	11.8 (11.7)
XIb	88	0.46	$C_{54}H_{30}N_6O_2$	79.8 (81.6)	4.02 (3.78)	10.3 (10.6)
XIc	85	0.27	$C_{54}H_{30}N_6O_3$	79.0 (80.1)	4.13 (3.53)	10.2 (10.0)
XIIa	76	–	$C_{36}H_{24}N_4O_6$	65.2 (67.7)	4.37 (3.79)	10.8 (10.5)
XIIb	82	–	$C_{42}H_{28}N_4O_6$	71.6 (73.7)	4.72 (4.12)	8.05 (8.18)
XIIc	87	–	$C_{42}H_{28}N_4O_8$	69.3 (70.4)	4.44 (3.93)	7.93 (7.82)

(continued)

TABLE 5 (continued)

Polymer	Yield (%)	[η] (dl/g)[a]	Formula	Analysis found (calcd) C (%)	H (%)	N (%)
XIIIa	87	0.12	$C_{30}H_{16}N_4O_4$	70.9 (72.6)	4.00 (3.25)	11.4 (11.3)
XIIIb	90	0.25	$C_{42}H_{24}N_4O_6$	73.5 (74.1)	3.67 (3.55)	8.50 (8.23)
XIIIc	84	0.42	$C_{46}H_{32}N_4O_4$	78.0 (78.5)	4.83 (4.53)	7.82 (7.92)
XIIId	79	0.12	$C_{40}H_{22}N_4O_5$	73.7 (75.5)	3.84 (3.45)	8.60 (8.78)

[a] Intrinsic viscosity, in sulfuric acid, 25° C.

One-step Process for Polymer Synthesis

A 9.4-mmole portion of hydrochloride of di- or tetramine are heated in the PPA solution at 130-140° C until hydrogen chloride was no longer liberated. The solution was cooled to 50-60° C, 10 mmole of dianhydride (monomer concentration is 5-7%) was added to the solution, the mixture was slowly heated to 180-200° C and kept in a stream of argon for 16-24 hr. The polymer was poured into water with ice, and the precipitate washed with water, ammonium carbonate, and again water. Additional cyclization was carried out at 250-300° C in vacuo. The data on the polymers are given in Table 5.

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