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I. Sideridou-karayannidou^a; G. P. Karayannidis^a

^a Laboratory of Organic Chemical Technology, Aristotelian University of Thessaloniki, Thessaloniki, Greece

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SYNTHESIS AND CHARACTERIZATION OF *o*-NITROSUBSTITUTED POLYIMIDES

I. SIDERIDOU-KARAYANNIDOU and G. P. KARAYANNIDIS

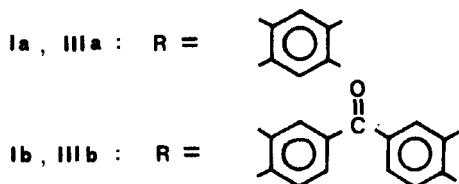
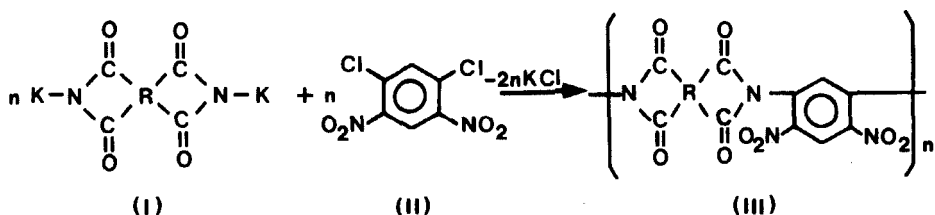
Laboratory of Organic Chemical Technology
Aristotelian University of Thessaloniki
GR-540 06 Thessaloniki, Greece

ABSTRACT

Poly(*o*-nitro)imides have been synthesized by one-stage polycondensation in DMAc at 130°C of 1,3-dichloro-4,6-dinitrobenzene with the dipotassium salt of pyromellitic or 3,3',4,4'-benzophenonetetracarboxylic acid diimide. The structure was confirmed by elemental analysis, IR, and UV-Vis spectroscopy, and the influence of the *o*-nitrosubstituents on the solubility and the thermal stability of the prepared polymers was studied. These polymers could be used as pyrrole precursors. The model compound for these polymers has been also prepared by condensation of 1,3-dichloro-4,6-dinitrobenzene with potassium phthalimide.

INTRODUCTION

It is known that the most widely used method of synthesis of aromatic polyimides [1, 2] is the two-stage process involving the preparation of a soluble poly(amic acid) precursor, by solution polycondensation of an aromatic diamine with a dianhydride, which is then converted to the corresponding, usually insoluble, polyimide, by thermal or chemical intramolecular cyclodehydration. Such a method, however, has certain disadvantages connected with the reaction of the dianhydride with the solvent [3]; the dependence of stability of the poly(amic acid) solutions on the temperature, concentra-



SCHEME 1.

tion, and moisture [4, 5]; and mainly with the incomplete cyclization of the poly(amic acid) to polyimide [6, 7].

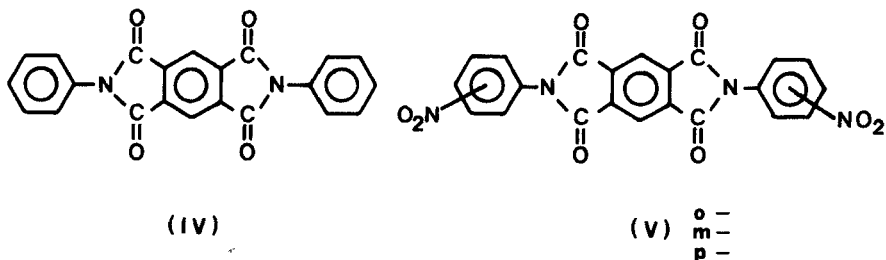
This paper describes an attempt to prepare fully cyclized aromatic polyimides by one-stage solution polycondensation of 1,3-dichloro-4,6-dinitrobenzene with the dipotassium salt of pyromellitic or 3,3',4,4'-benzophenone-tetracarboxylic acid diimide according to Scheme 1.

The dipotassium salt of pyromellitic acid diimide (Ia) has already been used [8, 9] for the preparation of a polyimide in a solution polycondensation with 4,4'-bis(chloromethyl)diphenyl ether. However, attempts [8] to prepare polyimides by solution polycondensation of pyromellitic acid diimide with 1,3- or 1,4-dichlorobenzene in the presence of an acid acceptor were unsuccessful.

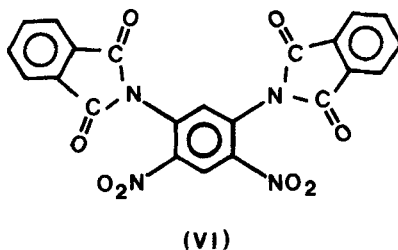
The presence of the *o*-nitrosubstituents, which are known as strong electron-withdrawing groups, in the structure of Monomer II was considered necessary in order to permit the nucleophilic substitution of the aromatic chlorine atoms. However, the presence of these groups in the structure of Polymer III was expected to increase the solubility of the polymer; first, because of the ($-\text{R}$) resonance effect of the nitro groups, which reduce the intramolecular and intermolecular charge transfer between the aromatic rings of the same or adjacent macromolecules correspondingly; second, because

of the steric effect of the *o*-substituents, which causes the disruption of the planarity and polarization of the macromolecules, resulting in the reduction of the close packing and of intra- and intermolecular interaction.

Such effects of the *o*-nitrosubstituents are reported in the literature [10] and are based on the study of the properties of the aromatic imides IV and V:



In this paper the preparation and study of some properties of the new Model Compound VI are also described:



The presence of the *o*-nitrosubstituents in Polymers IIIa and IIIb could permit the use of these polymers as precursors for the preparation of the corresponding pyrones by the reductive polyheterocyclization method [11]. Such a preparation will be the subject of a future publication.

EXPERIMENTAL

Starting Materials

Potassium phthalimide (Fluka, purum >98%) was used after stirring with boiling absolute ethanol for 10 min, filtering, and drying at 100°C/0.1 torr for 10 h.

Dipotassium salt of pyromellitic acid diimide (Ia) was prepared from pyro-

mellitic acid diimide obtained according to the literature [12]. The latter, after repeated recrystallizations from DMF, was stirred with a solution of potassium hydroxide in absolute ethanol at room temperature for 12 h. After filtration, washing with absolute ethanol, and drying at 100°C/0.1 torr for 10 h, Ia was obtained (yield 98%) as a white powder. IR (KBr): 1780, 1740, 1715, 1690 (Imide I), 1610, 1600 cm^{-1} .

Analysis. Calculated for $\text{C}_{10}\text{H}_2\text{N}_2\text{O}_4\text{K}_2$: C, 41.08; H, 0.69; N, 9.59%. Found: C, 40.97; H, 0.72; N, 9.65.

Dipotassium salt of 3,3',4,4'-benzophenonetetracarboxylic acid (Ib) was prepared (yield 96.5%) analogously to the above salt from 3,3',4,4'-benzophenonetetracarboxylic acid diimide (obtained as described in the literature [13]) and a solution of potassium hydroxide in absolute ethanol. IR (KBr): 1780, 1700 (Imide I), 1660 (linking $-\text{CO}-$ group), 1610, 1590 cm^{-1} .

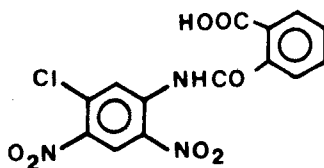
Analysis. Calculated for $\text{C}_{17}\text{H}_6\text{N}_2\text{O}_5\text{K}_2$: C, 51.50; H, 1.52; N, 7.07%. Found: C, 51.66; H, 1.54; N, 7.12%.

1,3-Dichloro-4,6-dinitrobenzene (II) was prepared and purified as in Ref. 14. Acetonitrile (Merck, purum) was stirred with calcium hydride for 3 days and fractionally distilled at 81.6°C. *N,N*-Dimethylacetamide (DMAc) (Merck, purum) was stirred with fresh barium oxide for 3 days and fractionally distilled at 55-58°C/11 torr.

Model Compound

1,3-Bisphthalimido-4,6-dinitrobenzene (VI). 4.74 g (0.02 mol) of II and 8.14 g (0.044 mol) of potassium phthalimide were added to 65 mL of acetonitrile. The orange reaction mixture turned red after heating at reflux for about 30 min. The heating was continued at reflux for another 6 h. Then the contents were cooled and filtered.

When ethanol and a small amount of water were added to the red filtrate for the quantitative isolation of the reaction products, a crystalline red precipitate was formed, which after remaining in the refrigerator for about 2 h turned yellow. This yellow precipitate after two recrystallizations from DMAc-methanol (1:1) showed a mp at 170°C and elemental analysis C, 46.07; H, 2.18; N, 10.80%. These values are consistent with the calculated values (C, 45.98; H, 2.20; N, 10.78%) for Structure VII. Also, the IR of this compound showed the characteristic absorption bands at 3340 (N-H) and 1710-1700 ($-\text{COOH}$) while the absorption bands of the imide groups were absent. The thermogravimetric analysis (TGA) of VII showed a beginning weight loss at 180°C (heating rate, 20°C/min) which is attributed to decomposition which occurred with a maximum rate at 337°C.



(VII)

The precipitate on the filter was repeatedly treated with boiling water and ethanol and dried at 100°C/0.1 torr for 10 h. Thus 6.59 g (yield 72%) of VI were obtained, which were insoluble in methanol, ethanol, acetone, and soluble in hot DMAc, DMF, and NMP. After two recrystallizations from DMAc-methanol (1:1), the pale yellow crystalline Compound VI showed a mp at 308-309°C. IR (KBr): 1780, 1750, 1730 (Imide I), 1530 (asymmetric stretching of $-\text{NO}_2$), 1370, 1350 (attributable to Imide II and $-\text{NO}_2$) 1070 (Imide III), and 720 (Imide IV) cm^{-1} . UV-Vis (DMF): λ_{max} 305 nm (shoulder), 420 nm (shoulder).

Analysis. Calculated for $\text{C}_{22}\text{H}_{10}\text{N}_4\text{O}_8$: C, 57.65; H, 2.19; N, 12.22%. Found: C, 57.81; H, 2.21; N, 12.33%.

The above reaction of II with potassium phthalimide, when carried out at 50°C, also for 5 h, gave VI in lower yield (34%). When DMAc instead of acetonitrile was used as solvent, some problems arose because of the higher solubility in this solvent and the consequent difficulty of isolation.

Polymers

Poly[pyromellitimido(4,6-dinitro-1,3-phenylene)] (IIIa). Ia (2.92 g, 0.01 mol) and II (2.37 g, 0.01 mol) were added to 53 mL of DMAc and heated at 130°C for 10 h. The orange-red reaction mixture, after cooling, was poured into 500 mL of distilled water. The yellow polymer precipitated and was removed by suction filtration. The polymer was extracted with ethanol for 24 h and dried at 100°C/0.1 torr for 10 h. 3.26 g (yield 88%) of IIIa was obtained. IR (KBr): 1780, 1770, 1730 (Imide I), 1530 ($-\text{NO}_2$), 1350 (br, attributable to Imide II and $-\text{NO}_2$), 1080 (Imide II), and 720 (Imide IV) cm^{-1} . UV-Vis (DMF): λ_{max} 330 (shoulder), 430, 530 nm (shoulder).

Analysis. Calculated for $(\text{C}_{14}\text{H}_4\text{O}_8\text{N}_4)_n$: C, 50.53; H, 1.06; N, 14.74%. Found: C, 49.24; H, 1.06; N, 14.38%.

Poly[1,4-phthalimidediylcarbonyl-1,4-phthalimidediyl (4,6-dinitro-1,3-phenylene)] (IIIb). Equimolar quantities of Ib and II gave, analogously to the above procedure, Polymer IIIb as a yellow powder (yield 92%). IR

(KBr): 1780, 1730 (Imide I), 1670 (the linking $-\text{CO}-$ group of the diimide), 1530 ($-\text{NO}_2$), 1350 (br, attributable to Imide II and $-\text{NO}_2$), 1090 (Imide III), and 720 (Imide IV) cm^{-1} . UV-Vis (DMF): λ_{max} 323 (shoulder), 430, and 530 nm.

Analysis. Calculated for $(\text{C}_{23}\text{H}_8\text{N}_4\text{O}_9)_n$: C, 57.03; H, 1.66; N, 11.57%. Found: C, 55.62; H, 1.56; N, 11.22%.

Measurements

Infrared spectra were recorded on a Perkin-Elmer 281-B spectrophotometer and the UV-Vis spectra on a Pye-Unicam SP 8000 spectrophotometer. Elemental analyses were performed with a Perkin-Elmer Model No. 240 analyzer. The solubility measurement of the Model Compound VI in hot DMF was carried out as reported in the literature [10]. The melting point of VI was determined in a capillary tube in a Buchi (Dr Tottoli) apparatus and is uncorrected. The inherent viscosity of the polymers was measured with an Ubbelohde viscometer. The thermal behavior of the prepared model compound and polymers was studied on a Perkin-Elmer DSC-2 assisted by a computer baseline and on a Perkin-Elmer TGS-2.

RESULTS AND DISCUSSION

In our attempt to prepare fully cyclized aromatic polyimides, we first examined if phthalimide can be used as a nucleophile for the nucleophilic substitution of aromatic chlorines activated by the presence of *o*-nitro groups. The reaction of 1,3-dichloro-4,6-dinitrobenzene with excess (10%) phthalimide in acetonitrile and with triethylamine as acid acceptor, after heating at reflux for 5 h and cooling gave a quantitative yield of white needles of unreacted phthalimide. After the removal of phthalimide, Compound VI was isolated in very poor yield (3%) by the addition of diethyl ether to the reaction mixture. Compound VI could be prepared, however, in good yield from 1,3-dichloro-4,6-dinitrobenzene and potassium phthalimide. This had a melting point (Table 1) lower than that of its Isomer V (*o*-) which was not accompanied by decomposition although the TG curve of VI (Fig. 1) showed a 1% weight loss at the temperature (311°C) at which the DSC curve showed the melting of VI. This low weight loss may have been caused by the removal of residual solvent. The decomposition of VI was shown by TGA and DTG to occur in nitrogen in one step, with the maximum rate at 430°C . However, the DSC curve showed, after the sharp peak of melting, two broad peaks

TABLE 1. Some Properties of Compounds IV-VI

Compound	Solubility parameter (p) ^a	Solubility ^b in DMF ($p = 12.1$)	Melting point, °C	IR ^c
IV	12.65	0.01 ^d	444-446 ^d	0.11 ^d
V (<i>o</i> -)	13.08	0.84 ^d	354-356 (dec) ^d 353-354 ^e	0.52 ^d
VI	13.08	8.33	308-309	0.81

^aCalculated by Fedors' method [15] and expressed in $(\text{cal}/\text{cm}^3)^{1/2}$.

^bSolubility: g in 10 g of refluxing DMF.

^cRatio of relative peak height of the absorption band at 1780 cm^{-1} to the corresponding one at 1730 cm^{-1} .

^dReference 10.

^eReference 16.

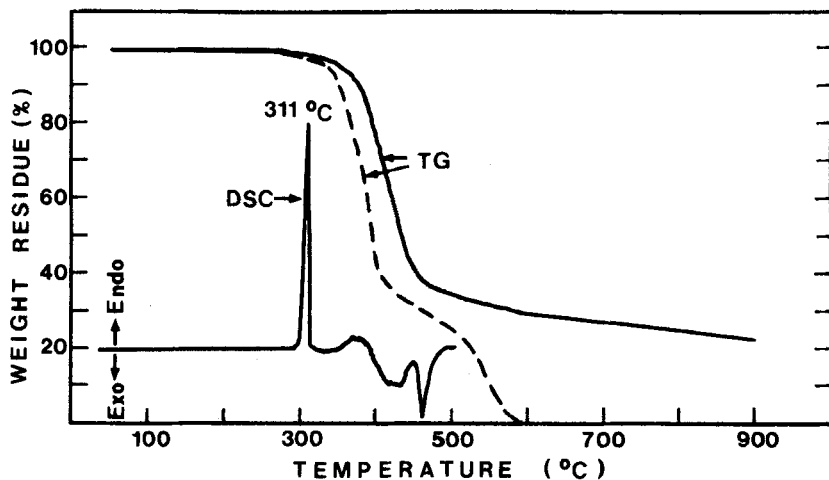


FIG. 1. (—) DSC and TG curves of the Model Compound VI in nitrogen (heating rate, $20^\circ\text{C}/\text{min}$). (---) TG curve of the Model Compound VI in air (heating rate, $5^\circ\text{C}/\text{min}$).

at about 370 and 430°C, characteristic of decomposition, and a sharp peak at 460°C. In air, a two-step degradation of VI was observed with maximum rates at 400 and 560°C. An analogous two-step degradation in air was reported [16] for V (*p*-).

The solubility parameters of IV and V, shown in Table 1, were calculated by Fedors' method [15]. A representative example of application of this method to heat-resistant polymers was reported previously [17]. Although the presence of the nitro groups in Compounds V and VI caused an increase of the solubility parameter, their solubility in DMF was increased. The much higher solubility of VI in DMF compared to V, in spite of the same solubility parameter, must be due to the lower planarity and polarization of the former. This view is also confirmed by the lower mp of VI. Moreover, the higher ratio of relative peak heights of the absorption bands of carbonyl imide at 1780 and 1730 cm^{-1} is in agreement with the observation reported in the literature [10] that imides with lower melting point and higher solubility show an increase of the absorption band at 1780 cm^{-1} (in-phase vibration of carbonyl imide) with respect to the absorption at 1730 cm^{-1} (out-of-phase).

Polyimides IIIa and IIIb were obtained in one stage in good yields, but with relatively low inherent viscosity (Table 2), in spite of the long reaction time, probably because of the dipotassium salts used could not be prepared in very high purity.

Their elemental analysis was close to that of the expected chemical structure, except for the low carbon value. Such an exception was also reported by Dine-Hart and Wright [18]. The IR spectra of the polymers showed the characteristic absorption bands of the imide ring and the nitro groups analogous to model Compound VI. The two absorption bands of the yellow solutions of the polymers in DMF at 430 and 530 nm, in comparison with the single absorption band of the model compound at 430 nm (shoulder), must be due to the higher intra- and intermolecular interaction [19] in the former.

Polymers IIIa and IIIb were soluble in polar solvents, such as DMF, DMAc, and NMP, and in strong acids, such as formic and sulfuric. Yellow brittle films were obtained from solutions of the polymers in DMF. It is interesting to note that the unsubstituted polyimide derived from pyromellitic dianhydride and *m*-phenylenediamine is soluble only in strong acids. The higher solubility of the *o*-nitrosubstituted polyimide IIIa cannot be attributed exclusively to the lower solubility parameter, close packing, or intra- and intermolecular interaction because of the different preparative conditions for the two polymers and, mainly, the much lower inherent viscosity of the substituted polymer (Table 2).

The thermal behavior of the polymers was studied by DSC, TG, and DTG

TABLE 2. Some Properties of Polymers IIIa and IIIb

Polymer	η_{inh} , dL/g	Solubility parameter (p) ^a	Maximum decomposition temperature rate, °C		
			In nitrogen	In air	In air
IIIa	0.16 ^b	14.97	330 ^c	364 ^d	340 ^c
			430 ^c	465 ^d	440 ^c
			586 ^c	610 ^d	548 ^c
IIIb	0.21 ^b	14.25	420 ^c	455 ^d	430 ^c
			618 ^c	650 ^d	563 ^c
Unsubstituted polyimide ^e	>0.3	15.66			

^aCalculated by Fedors' method.

^bIn DMF ($c = 0.5\%$) at 25°C.

^c5°C/min heating rate.

^d20°C/min heating rate.

^ePrepared [20] by cyclodehydration of the corresponding polyamic acid, obtained from pyromellitic dianhydride and *m*-phenylenediamine. η_{inh} in 0.5% H₂SO₄.

analysis. The initial weight loss (Fig. 2) can be attributed to the removal of residual solvent or to degradation of end groups. This weight loss, not clearly detected by DSC, occurred at a maximum rate at 330°C for Polymer IIIa, whereas an analogous maximum was observed neither for Polymer IIIb nor for the model Compound VI. On the contrary, both polymers, on heating at higher temperatures, showed two maximum rates of decomposition at about the same temperatures (Table 2). The decomposition of the polymers with a maximum rate at about 420-460°C, which is analogous of that of the Compound VI, was observed by DSC to occur exothermically (Fig. 3).

The thermal stability of Polymer IIIa under isothermal conditions is illustrated in Fig. 4.

Polymer IIIb, based on 3,3',4,4'-benzophenonetetracarboxylic diimide, showed, both in nitrogen and air, slightly superior stability than IIIa based on pyromellitic diimide. Such an observation has also been reported previously [18, 21].

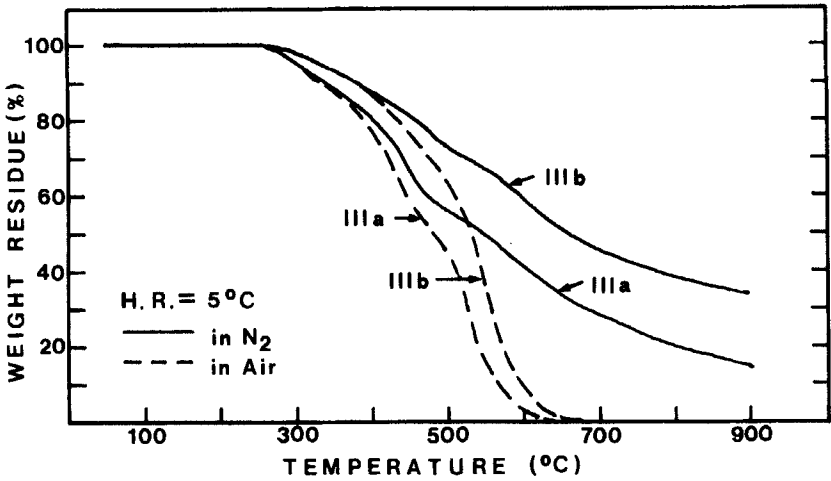


FIG. 2. TG curves of Polymers IIIa and IIIb.

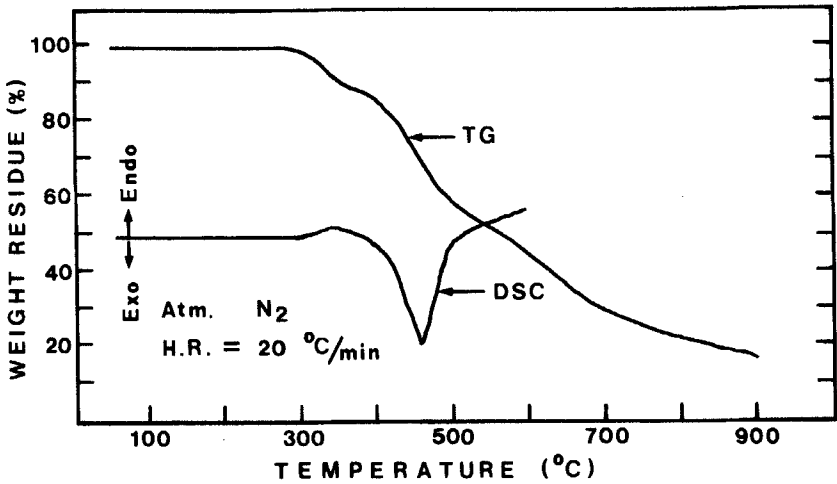


FIG. 3. TG and DSC curves of Polymer IIIa.

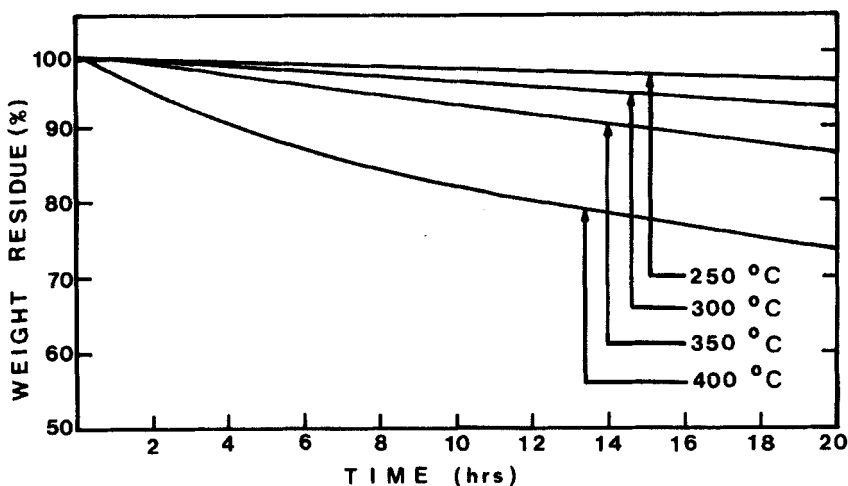


FIG. 4. Isothermal weight loss of Polymer IIIa.

The *o*-nitro substituted Polyimide IIIa showed lower thermal and thermo-oxidative stability than the corresponding unsubstituted one [20], both under gradient and isothermal conditions, mainly because of the presence of the nitro substituents and also because of other factors (molecular weight, intra-, and intermolecular interactions).

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