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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Elena Hamciuc^a; Ilie Diaconu^a; Maria Brum^a

^a "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

To cite this Article Hamciuc, Elena , Diaconu, Ilie and Brum, Maria(1991) 'Polybenzimidazole-Ester-Imides', Journal of Macromolecular Science, Part A, 28: 7, 633 – 640

To link to this Article: DOI: 10.1080/00222339108052114

URL: <http://dx.doi.org/10.1080/00222339108052114>

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POLYBENZIMIDAZOLE-ESTER-IMIDES

ELENA HAMCIUC, ILIE DIACONU, and MARIA BRUMĂ

“P. Poni” Institute of Macromolecular Chemistry
R-6600 Jassy, Romania

ABSTRACT

Thermostable heterocyclic polymers containing benzimidazole and imide rings, as well as flexible ester groups, have been synthesized by solution polycondensation of diaminobenzimidazoles with dianhydrides incorporating preformed ester linkages. The thermal stability and the electrical insulating properties of these products are discussed and compared with related heterocyclic polymers.

INTRODUCTION

Fully aromatic and heteroaromatic polymers are well known for their high thermal stability, but they rarely can be processed due to their complete insolubility and infusibility. Among thermostable polymers widely studied in the last decades, special attention has been paid to polyimides and polybenzimidazoles, some presently in production. Polyimides are made by a two-stage process: in the first step a soluble linear prepolymer, named “polyamic acid,” is obtained which can be processed into films, fibers, or thin-layer coatings and then, in the second step, these materials undergo a special treatment that leads to the final heterocyclic structure [1]. But the polyamic acids present the disadvantage of being very unstable to hydrolysis; in addition, they give low-molecular volatile products during polyheterocyclization which strongly affect the mechanical properties of the final articles. It has been reported that polybenzimidazole-type polymers also show a remarkable stability at

high temperature along with good mechanical properties, but at the same time they are very difficult to process due to their poor solubility [2]. A combination of imide and benzimidazole structures into one macromolecular chain by introducing flexible ester groups between aromatic and heteroaromatic rings was expected to provide high-performance physical and thermal characteristics as well as readily processable polymers.

Thus, polybenzimidazole-ester-imides have been synthesized by the polycondensation reaction of monomers which incorporate preformed benzimidazole and ester units, respectively, creating imide rings during the reaction at high temperature.

EXPERIMENTAL

Synthesis of the Monomers

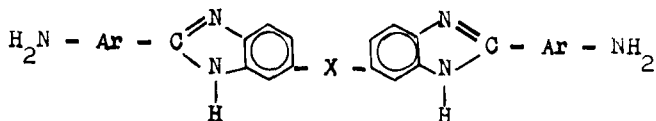
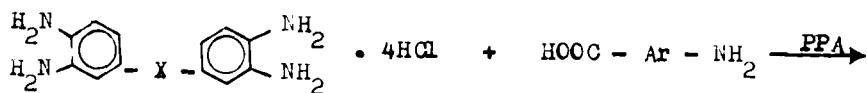
Diaminobenzimidazoles (I) used in the synthesis of polybenzimidazole-ester-imides were prepared by the reaction of aromatic tetraamines, such as diaminobenzidine, 3,3',4,4'-tetraaminodiphenylmethane, or 3,3',4,4'-tetraaminodiphenylether, with *p*- or *m*-aminobenzoic acid, using polyphosphoric acid (PPA) as solvent and dehydrating reagent [3], following Scheme 1.

The same heterocyclic diamines were prepared by a different method by starting from aromatic tetraamines and *p*- or *m*-nitrobenzoyl chloride in dioxane and pyridine, followed by cyclization in PPA and then reduction with hydrazine hydrate [4], according to Scheme 2.

This latter way is a little longer but it gives a more pure product. The diaminobenzimidazoles were purified by dissolving them in methanol, treating them with charcoal, and precipitating them in water. Melting points: Ia, 320–322°C; Ib, 202–204°C; Ic, 206–208°C; Id, 321–323°C.

Diesteranhydrides (II) were prepared by two methods. The first method consisted of the acidolysis reaction of trimellitic anhydride with aromatic diacetoxy compounds which have been synthesized from diphenols, such as 2,2-bis(*p*-hydroxyphenyl)propane or hydroquinone, and excess acetic anhydride [5]. The reaction of 2 mol trimellitic anhydride with 1 mol diacetoxy compound proceeds smoothly in the melt or by the use of a high-boiling solvent, such as polyalkylbenzene, with the elimination of acetic acid, as shown in Scheme 3.

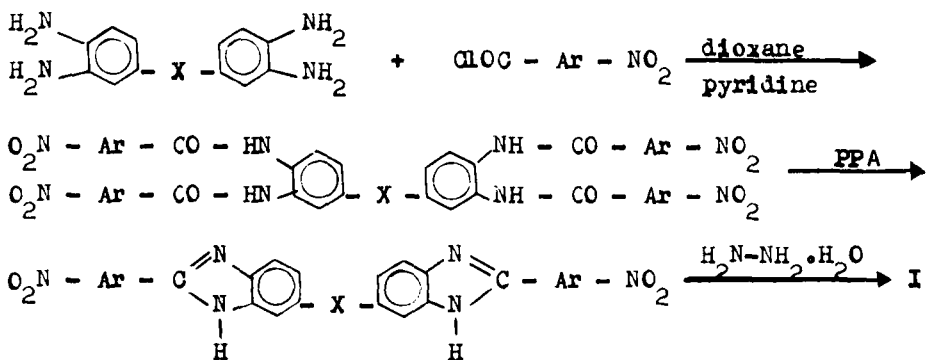
The diesteranhydrides were purified by recrystallization from acetic anhydride. Melting points: IIa, 193–195°C; IIb, 272–274°C.



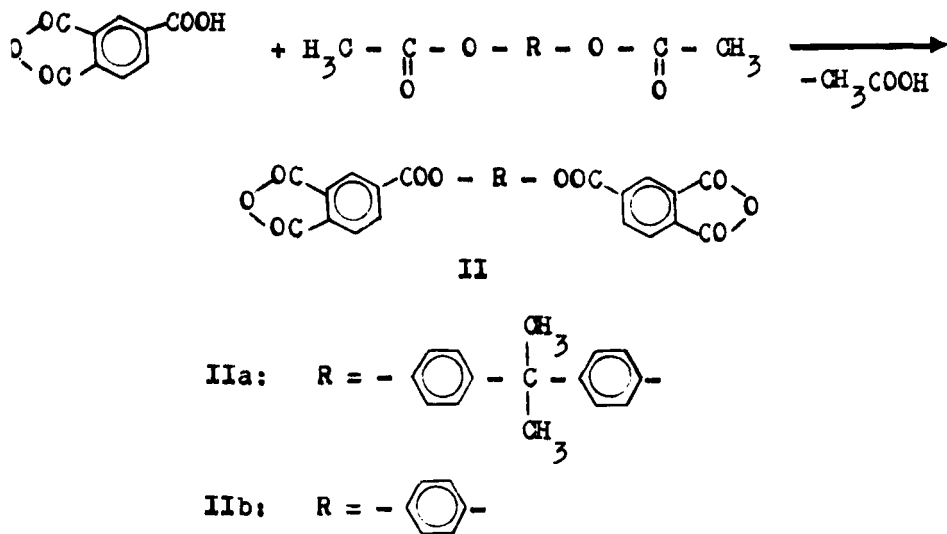
I

- a) Ar = p-C₆H₄ ; X = -
 b) Ar = m-C₆H₄ ; X = O
 c) Ar = m-C₆H₄ ; X = CH₂
 d) Ar = p-C₆H₄ ; X = CH₂

SCHEME 1.



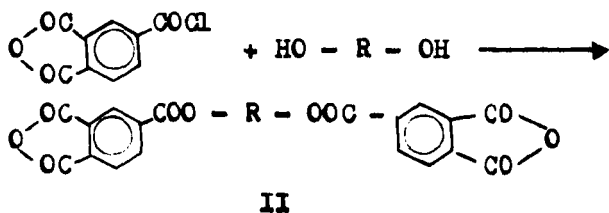
SCHEME 2.



SCHEME 3.

The second method used to prepare the diesteranhydrides was the reaction of the monoacid chloride of trimellitic anhydride (2 mol) with an aromatic dihydroxy compound, such as 2,2-bis(*p*-hydroxyphenyl)propane or hydroquinone (1 mol), using benzene as solvent and pyridine as acid acceptor [6], following Scheme 4.

The crude product was first washed with water in order to eliminate the pyridine chlorohydrate and then it was recrystallized from acetic anhydride. The melting points of these compounds were identical to those obtained according to the first method. Because this method re-



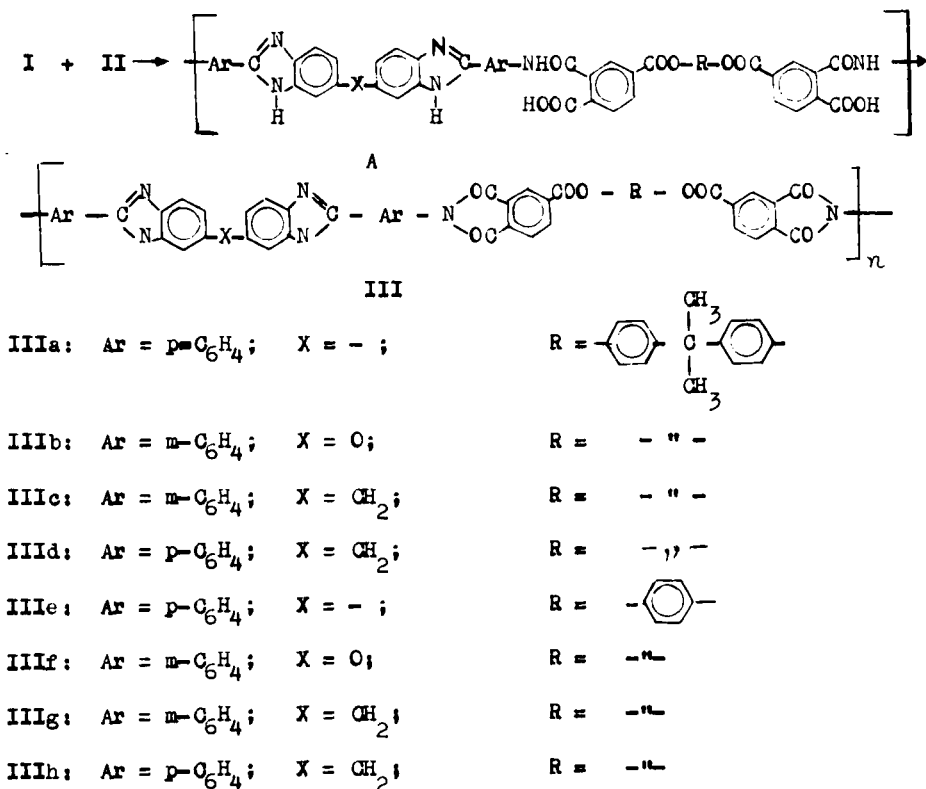
SCHEME 4.

quires only a moderate temperature (80°C), we found it more convenient for the synthesis of diesteranhydrides.

Synthesis of the Polymers

Polybenzimidazole-ester-imides (III) were synthesized by solution polycondensation of equimolar amounts of diaminobenzimidazoles (I) and diesteranhydrides (II) in *N*-methylpyrrolidone at a concentration of 15–18%, according to Scheme 5.

The polycondensations were run either by adding the anhydride to the amine solution or by adding the amine to the anhydride-solvent slurry, followed by stirring for 2 h at room temperature and 1 h at reflux



SCHEME 5.

under a nitrogen atmosphere. The reaction proceeds first to the polyamic acid (A) which, when heated, is converted to the cyclic imide (III) with the elimination of water. The order of mixing the reagents seemed to have no visible influence; in all cases the inherent viscosities were approximately the same. A small part of the resulting yellow polymer solution was used for film casting. It was poured onto glass plates and dried by gradually raising the temperature to 220°C over 1 h and then it was kept at 220°C for 30 min. The resulting clear films had excellent adhesion to glass and metal substrates. The rest of the polymer solution was precipitated by pouring it into water. The resulting product was washed and dried, and then it was used for further investigation.

RESULTS AND DISCUSSION

The structures of polybenzimidazole-ester-imides were identified by IR spectra and elemental analyses. The strong bands appearing at 1780, 1720, and 720 cm^{-1} were assigned to the imide ring. Also, all spectra showed absorptions at 1620, 1400, and 965 cm^{-1} due to the benzimidazole unit. Elemental analysis data for C, H, and N were in good agreement with calculated values.

All these polymers are easily soluble in polar aprotic solvents, such as *N*-methylpyrrolidone and dimethylacetamide. Inherent viscosities are 0.2–0.4 dL/g, measured in *N*-methylpyrrolidone at a concentration of 0.5 g/dL at 20°C (Table 1). All these products gave transparent films having good adhesion to substrates by casting 15–18% polymer solutions on glass or metal plates.

The thermal stability of these polymers was evaluated by thermogravimetric analysis (TGA) performed in air at a heating rate of 12°C/min by using a Derivatograph MOM, Budapest. The TGA curves showed no weight loss up to 300°C. Polymers IIIa–d begin to decompose above 340°C, while the others decompose above 360°C. This difference is due to the presence of 2,2-diphenylpropane units in Polymers IIIa–d. By comparing the thermal stability of the present polybenzimidazole-ester-imides with related polymers, such as polybenzimidazole-imides [4] and polyester-imides [7], the following order was found: polybenzimidazole-imides > polyester-imides \approx polybenzimidazole-ester-imides. This means that the introduction of ester linkages into the macromolecular chain of polybenzimidazole-imides gives a little lower thermostability, but the solubility of these polymers is much improved. While polybenzimidazole-

TABLE 1. Properties of Polybenzimidazole-Ester-Imides

Polymer	η_{inh} , dL/g	TGA		Insulating properties	
		Initial decomposition temperature, °C	Weight loss at 400°C, %	Resistivity, $\Omega \cdot \text{cm}$	Activation energy, eV
IIIa	0.3	340	14	2.22×10^{14}	1.41
IIIb	0.3	340	13	1.58×10^{14}	1.22
IIIc	0.2	345	11	1.10×10^{14}	1.04
IIId	0.3	340	13	1.25×10^{13}	1.10
IIIe	0.3	380	15	1.11×10^{13}	1.16
IIIf	0.2	380	14	1.06×10^{13}	1.10
IIIg	0.2	360	15	1.40×10^{13}	1.05
IIIh	0.4	360	15	4.0×10^{13}	1.15

zole-imides are soluble only in concentrated H_2SO_4 , the present polybenzimidazole-ester-imides are easily soluble in polar aprotic solvents, and this is very important for practical applications. Also, this increased solubility makes it possible to perform the imidization process in solution so that the final polymer is obtained as a completely imidized product, which is more convenient than the polyamidic acid. So the present polymers can be stored for a long time before use, while polyamidic acid precursors of related polybenzimidazole-imides can only be stored for short time periods under special conditions.

The electrical insulating properties of these polybenzimidazole-ester-imides are appreciated because of their electrical parameters, i.e., activation energy of conduction (E_a) and resistivity at 20°C (ρ), determined from dc conductivity measurements carried out at 0–200°C. Conductivity measurements were performed in dry nitrogen on disk-shaped samples ($\phi = 16$ mm) prepared by compressing the polymers in a mold under a pressure of 10^5 N/cm². Pellets were provided with vacuum-evaporated silver electrodes of circular form ($\phi = 14$ mm) centrally placed on both sides. The resistivity and activation energy values (Table 1) show that the polymers, particularly Products IIIa–c, have good electrical insulating properties. This fact makes them promising for insulating coatings on metal surfaces.

CONCLUSIONS

Polybenzimidazole-ester-imides of various structures have been synthesized by solution polycondensation of aromatic diamines containing preformed benzimidazole units with dianhydrides incorporating preformed ester linkages. These polymers show high thermal stability, with the decomposition temperature being over 340°C. Comparison of these compounds with related benzimidazole-imide polymers leads to the conclusion that the decomposition of the former ones takes place at a somewhat lower temperature, but there is a compensation: they are easily soluble in polar aprotic solvents, which makes them suitable for technical processing. These polymers also show good electrical insulating properties and good adhesion to different substrates, which recommends them for coatings on metal surfaces.

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