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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To cite this Article Brumă, M. , Neamţu, G. and Sava, I.(1985) 'Heterocyclic Polyimides', Journal of Macromolecular Science, Part A, 22: 5, 833 — 847

To link to this Article: DOI: 10.1080/00222338508056639

URL: http://dx.doi.org/10.1080/00222338508056639

J. MACROMOL. SCI.–CHEM., A22(5-7), pp. 833-847 (1985)

Heterocyclic Polyimides

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ABSTRACT

This paper presents the synthesis of certain polyimides which contain one of the following heterocycles: oxadiazole, benzoxazinone, benzthiazole. Their properties, particularly thermal stability and hydrolytic stability, are compared to fully aromatic polyimides. Poly-1,3,4-oxadiazole-imides have been synthesized either by the reaction of ditetrazole monomers which contain preformed imide cycles with diacid chlorides, or by the reaction of an aromatic diamine containing a preformed oxadiazole ring with diacid chlorides containing preformed imide rings. Polybenzoxazinone-imides have been synthesized by polycondensation of a bis(amino acid), 4,4'-diaminodiphenylmethane-3,3'-dicarboxylic acid, with diacid chlorides containing preformed imide rings. Polybenzthiazole-imides have been obtained by polycondensation of aromatic diamines containing a preformed benzthiazole ring with diacid chlorides containing preformed imide rings. Thermal stabilities of these heterocyclic polyimides are similar and in certain cases are higher than those of fully aromatic polyimides. It was also found that the hydrolytic stability of heterocyclic polyimides is definitely superior to that of aromatic polyimides.

0022-233X/85/2205-0833$3.50/0

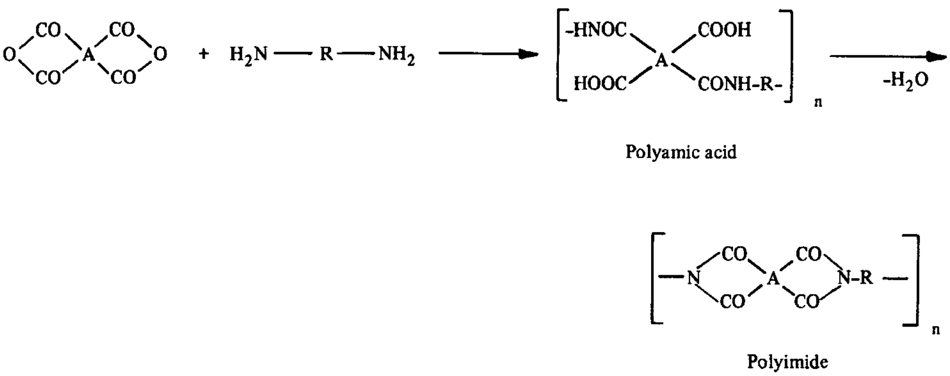
GENERAL BACKGROUND

The impetus for the development of the chemistry of thermostable polymers during the last two decades is due to research regarding the introduction of heterocyclic units into the macromolecular chain. Among heterocyclic thermostable polymers, polyimides are the best studied ones. They have been given special attention due to their outstanding properties (thermooxidative stability, electrical insulation, flexibility at low temperature, chemical resistance, etc.) and due to the advantageous method of synthesizing them in two steps.

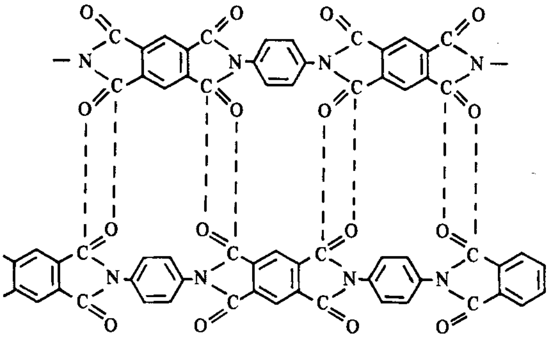
The general method to obtain aromatic polyimides is the polycondensation in two steps of aromatic diamines with aromatic dianhydrides in polar aprotic solvents [1]. In the first step a soluble linear polymer results which is a polyamidic or polyamic acid. In the second step, cyclodehydration takes place, leading to an insoluble, infusible polyimide, according to Scheme 1.

A viscous solution of polyamic acid can be processed into films, fibers, coatings, etc., and then the final product undergoes thermal or chemical cyclodehydration. A polyamic acid solution presents the inconvenience of being unstable when kept for a long time. Also, the cyclization process is never complete, the best yields being 70-80%. This fact made it desirable to study new ways to obtain polyimides; for example, by utilizing monomers containing preformed imide cycles because it is known that the cyclization reaction of imides with monofunctional compounds takes place with very good yield.

Aromatic polyimides are characterized by outstanding thermal stability due to several factors [2, 3]: the existence of conjugation along the macromolecular chain as proved by ESR spectra and quantum-mechanical calculations; the existence of interactions between chains, leading to the formation of π-complexes as a consequence of



SCHEME 1.



SCHEME 2.

the inductive and resonance effects produced in the imide cycle; the existence of a molecular superstructure with strong packing of chains which leads to insolubility and particularly high melting points. Scheme 2 shows the formation of π-complexes between two polyimide chains.

Of all the structures of aromatic polyimides which have been studied, the one obtained from pyromellitic dianhydride and 4,4'-diaminodiphenylether shows the best thermostability, correlated with excellent physicomechanical and electrical properties. This type of polyimide has been commercialized in the United States in different forms: H or Kapton film, enamel, impregnated glass fabric, adhesives, etc. [4].

Aromatic polyimides have unsatisfactory resistance to alkaline media. This fact has led to numerous studies based mainly on the use of monomers containing preformed imide cycles or on the introduction into the macromolecular chain of new heterocycles.

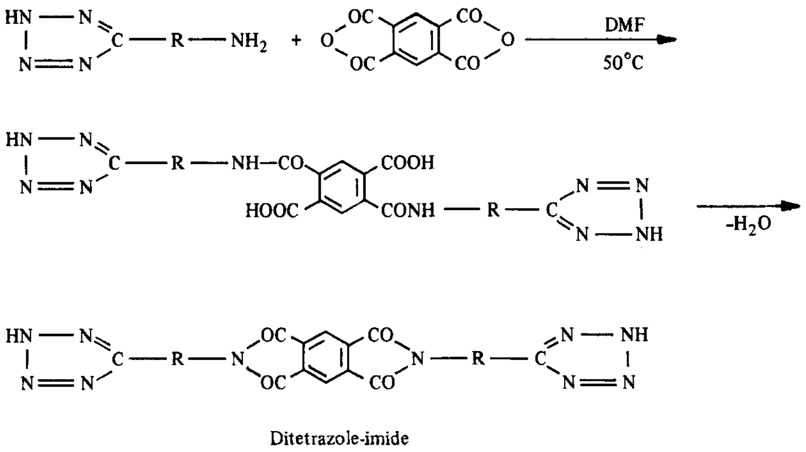
This paper presents our research on obtaining certain polyimides which contain one of the following heterocycles: oxadiazole, benzoxazinone, benzthiazole.

POLY-1,3,4-OXADIAZOLE-IMIDES

The 1,3,4-oxadiazole ring has special interest due to its superior thermal stability in an oxidative atmosphere [5]. This property is determined by the following factors:

The oxadiazolic ring doesn't contain any H atoms. From the spectral and electronical points of view, it is similar to a p-phenylene structure, which is known to be thermoresistant.

It lacks tension, it doesn't have any possibilities of rearrangement, it has structural symmetry, and it is thermally unreactive.



Ditetrazole-imide

SCHEME 3.

We have synthesized poly-1,3,4-oxadiazole-imides by two methods [6]. The first consists of the reaction of ditetrazole monomers which contain preformed imide cycles with diacid chlorides. In this method the oxadiazole ring is formed during the polycondensation reaction.

The second method consists of the reaction of an aromatic diamine containing a preformed oxadiazole ring with diacid chlorides containing preformed imide rings.

Ditetrazole-imide monomers have been synthesized according to the first method by the condensation of 5-aminotetrazole with pyromellitic dianhydride as shown in Scheme 3.

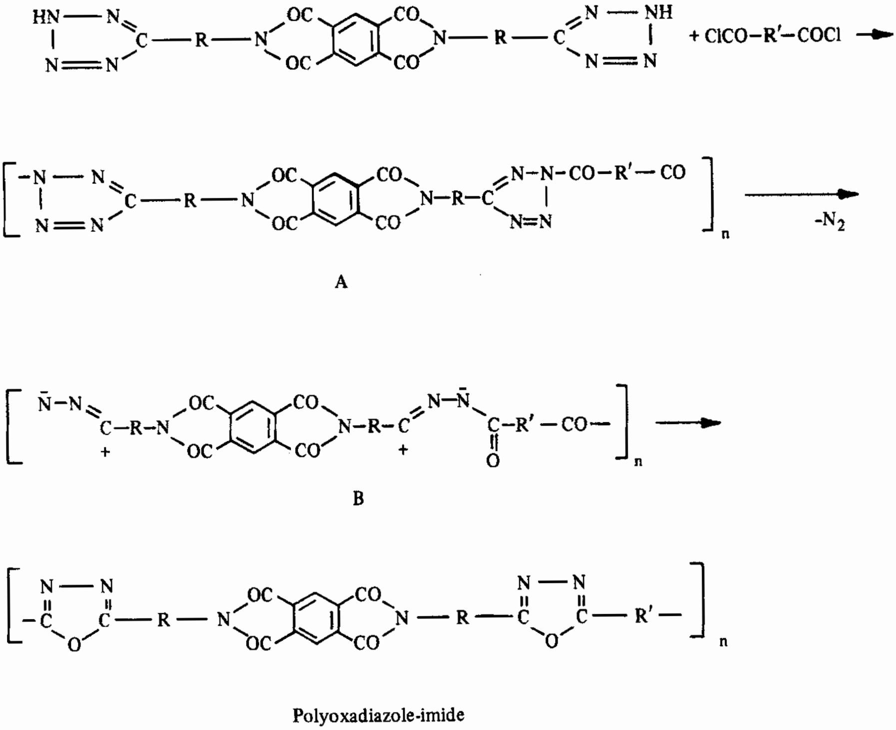
In the first step of this reaction a tetrazole-amidic acid results which leads to the corresponding ditetrazole-imide by thermal cyclodehydration.

The polycondensation of ditetrazole-imides with dichlorides of aromatic or aliphatic dicarboxylic acids gives poly-1,3,4-oxadiazole-imides, according to Scheme 4.

The reaction of tetrazoles with electrophylic reagents, studied by Huisgen for monofunctional compounds [7], was applied by us to the synthesis of polyoxadiazoles. In the first step N-acyl tetrazole (A) is formed, which by subsequent heating eliminates nitrogen to give the hypothetical intermediate (B) which by cyclization gives polyoxadiazole-imides.

The polyoxadiazole-imides thus obtained are soluble in dipolar amidic solvents but insoluble in common solvents. Thermogravimetric analysis shows that the polymers containing only aromatic and heterocyclic units don't decompose up to 400°C in air, while the polymers containing aliphatic units $-(CH_2)_4-$ begin to decompose at 340°C.

The second method of obtaining poly-1,3,4-oxadiazole-imides uses



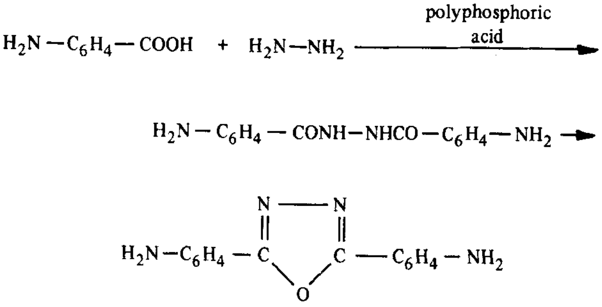
$R = -; p\text{-}C_6H_4; R' = p\text{-}C_6H_4; -(CH_2)_4$

SCHEME 4.

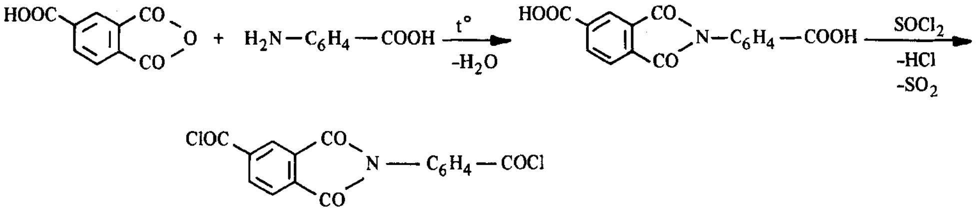
monomers containing both preformed imide and oxadiazole rings, so that growth of the chain consists of the formation of amidic linkages between aromatic and heteroaromatic units [8]. The monomer containing the oxadiazole ring is 2,5-bis-p-(aminophenyl)-1,3,4-oxadiazole which has been obtained from p-aminobenzoic acid and hydrazine by cyclization of the corresponding dihydrazide [9], according to Scheme 5.

Monomers containing preformed imide rings are dichlorides of dicarboxylic imidic acids. Nonsymmetric diacid chlorides have been synthesized by treating the dicarboxylic imidic acids obtained from trimellitic anhydride and p-aminobenzoic or m-aminobenzoic acid with thionyl chloride, according to Scheme 6.

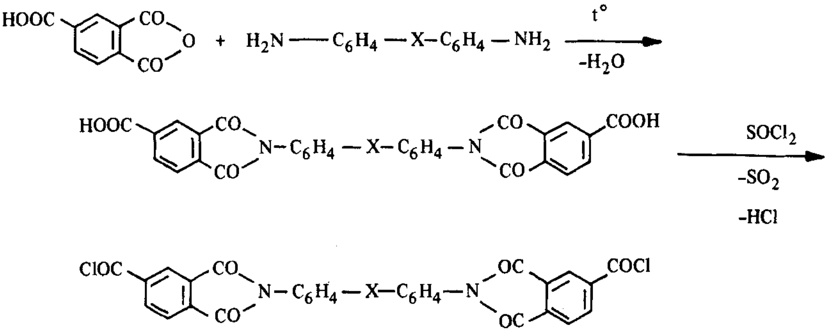
Symmetric diacid chlorides have been synthesized by treating the dicarboxylic imidic acids obtained from trimellitic anhydride and such aromatic diamines as 4,4'-diaminodiphenylmethane, 4,4'-diamino-



SCHEME 5.



SCHEME 6.

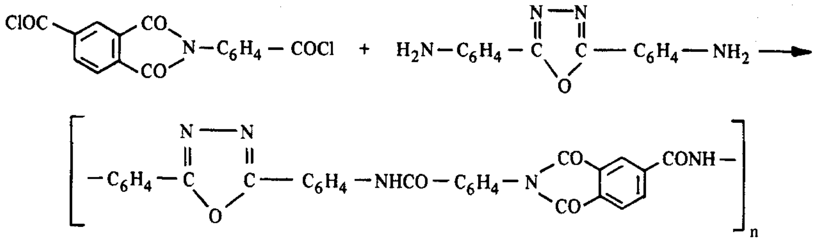


X = $-CH_2-$; $-O-$; $-SO_2-$

SCHEME 7.

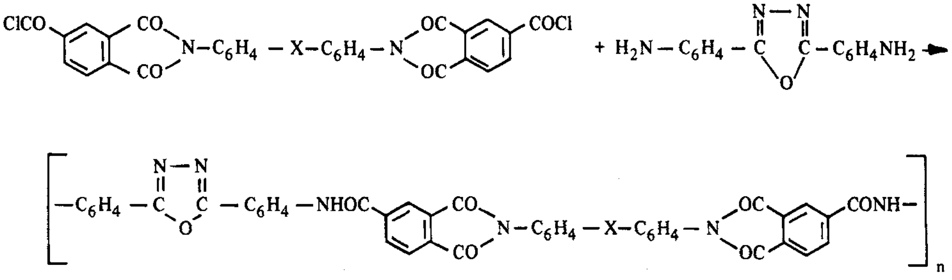
diphenylether, and 4,4'-diaminodiphenylsulfone with thionyl chloride according to Scheme 7.

Polycondensation of 2,5-bis(p-aminophenyl)-1,3,4-oxadiazole with diacid chlorides containing preformed imide rings gave partially or-



X = —CH$_2$— ; —O—; — SO$_2$—

SCHEME 8.



X = —CH$_2$— ; —O—; —SO$_2$—

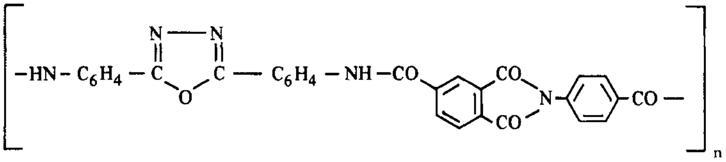
SCHEME 9.

dered poly-1,3,4-oxadiazole-amide-imides, according to Scheme 8, and ordered poly-1,3,4-oxadiazole-amide-imides, according to Scheme 9.

Polyoxadiazole-amide-imides thus obtained are soluble in dipolar amidic solvents containing lithium chloride. Thermogravimetric analysis shows that polymers containing only aromatic and heterocyclic units don't decompose up to 440°C while those containing $-CH_2-$ groups decompose at about 400°C.

By comparing the thermal stability of ordered polyoxadiazole-amide-imides with that of polyoxadiazole-amides (that is, related polymers which don't contain imide rings [10]), it can be seen that the former decompose over 440°C while the latter decompose at about 360°C. The superior thermal stability of polyoxadiazole-amide-imides is due to their ordered structure and to the fact that in the reaction monomers containing already formed heterocycles were used.

TABLE 1. Mechanical and Electrical Properties[a] of Polyoxadiazole-amide-imide with the Formula



Property	Polyoxadiazole-amide-imide	Kapton film
Tensile strength (kg_f/cm^2)	11.7	12.1
Dielectric loss (tg δ)	0.0023	0.003
Dielectric constant	3.0	3.5
Volume resistivity (ohm·cm)	5.3×10^{15}	9×10^{16}

[a] All data were obtained on films of 30 μm. Dielectric properties were measured at 1 kHz at room temperature.

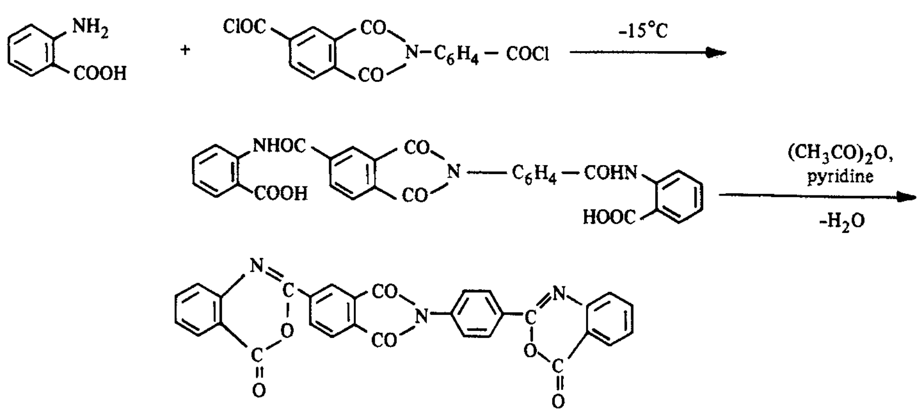
Polyoxadiazole-amide-imides have mechanical and electrical properties comparable to those of Kapton film, as it can be seen in Table 1.

POLYBENZOXAZINONE-IMIDES

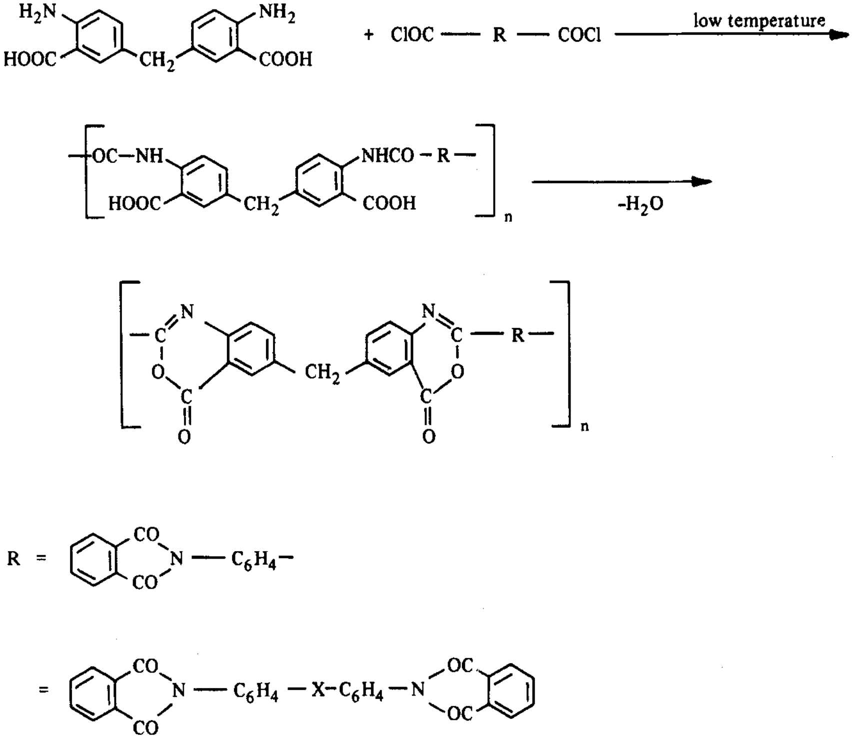
Another heterocycle introduced into a macromolecular chain along with the imide cycle is the benzoxazinone condensed system [11, 12]. Polybenzoxazinone-imides have been synthesized by polycondensation of a bis(amino acid) (that is, 4,4'-diaminodiphenylmethane-3,3'-dicarboxylic acid) with diacid chlorides containing preformed imide rings. The diacid chlorides are those described in the synthesis of poly-oxadiazole-amide-imides. The reaction was first studied on models to find the conditions for the formation of benzoxazinone units according to Scheme 10.

The polycondensation of 4,4'-diaminodiphenylmethane-3,3'-dicarboxylic acid with diacid chlorides first led to the formation of a soluble linear polymer having a polyamidic acid structure, which by further thermal treatment gave polybenzoxazinone-imides according to Scheme 11.

The linear prepolymer is slightly soluble in dipolar amidic solvents, giving solutions stable to hydrolysis. These solutions can be processed



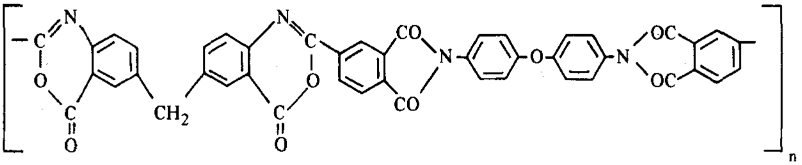
SCHEME 10.



$X = —O—; —CH_2—; —SO_2—$

SCHEME 11.

TABLE 2. Physical and Mechanical Properties[a] of Polybenzoxazinone-imide with the Formula



Properties	Polybenzoxazinone-imide	Kapton film
Tensile strength (kg_f/cm^2)	11.1	12.1
Elongation, %	5	6
Dielectric loss (tg δ)	0.004	0.003
Dielectric constant	3.9	3.5

[a] All data were obtained on films of 30 μm. Dielectric properties were measured at 1 kHz at room temperature.

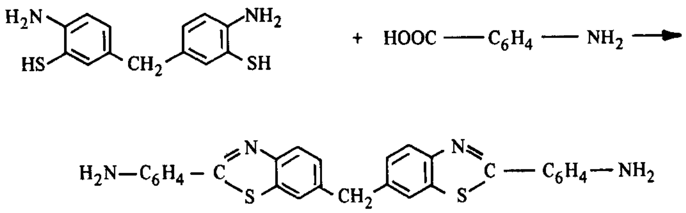
into films or coating following their cyclization to polybenzoxazinone-imides by heating at 200-300°C. Thermogravimetric analysis shows that polybenzoxazinone-imides don't decompose up to 400°C. Films obtained from these polymers have good mechanical and electrical properties, comparable to Kapton film, as shown in Table 2.

The hydrolytic stability of polybenzoxazinone-imide film is almost double that of Kapton film: kept for 5 days at room temperature in 10% NaOH solution, polybenzoxazinone-imide film showed no change, while Kapton film became a gel.

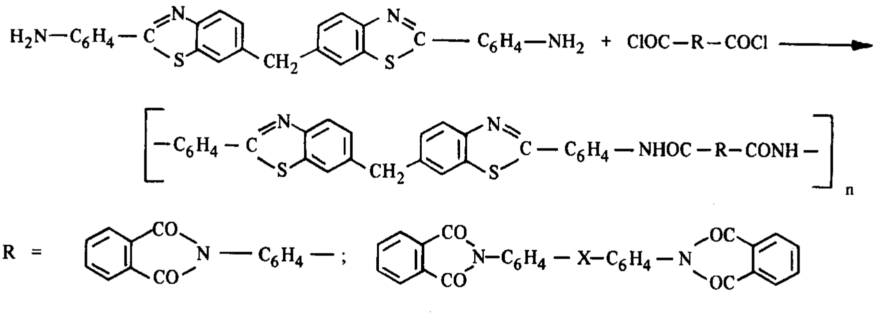
POLYBENZTHIAZOLE-AMIDE-IMIDES

Because of the high thermal stability of benzthiazole condensed systems, we considered it interesting to synthesize polymers containing this heterocycle along with the imide ring, alternating with amidic linkages [13].

Polybenzthiazole-amide-imides have been synthesized by the polycondensation of aromatic diamines containing preformed benzthiazole ring with diacid chlorides containing preformed imide rings. Diamino benzthiazoles have been obtained from aromatic o-dimercaptodiamines and p- or m-aminobenzoic acid, according to Scheme 12.



SCHEME 12.



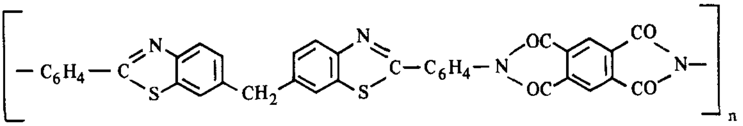
$X = -CH_2-;\ -O-;\ -SO_2-$

SCHEME 13.

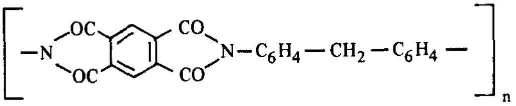
The polycondensation reaction at low temperature (-15°C) of these heterocyclic diamines with diacid chlorides containing preformed imide rings, previously described in dipolar amidic solvents has led to the formation of ordered polybenzthiazole-amide-imides, according to Scheme 13.

The polymers obtained are soluble in dipolar amidic solvents whose solutions on evaporation give transparent, flexible films. Thermogravimetric analysis shows that these polymers are stable up to 400°C. By comparing their thermostabilities with related polymers such as polybenzthiazole-imides and polyimides whose structures are showed in Scheme 14, the order shown there was found: polybenzthiazole-imide > polybenzthiazole-amide-imide > polyimide.

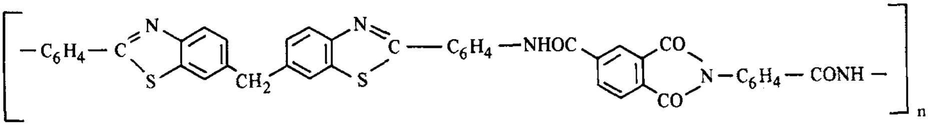
The hydrolytic stability of polybenzthiazole-amide-imides is superior to that of Kapton polyimidic film. After 7 days, films of polybenzthiazole-amide-imides kept in 10% NaOH solution at room temperature were unchanged while Kapton film became a gel. Even after 21 days under this treatment, polybenzthiazole-amide-imide was still a film, but breakable. Mechanical and electrical properties of these polymers are comparable to those of Kapton film, as shown in Table 3.



Polybenzthiazole-imide



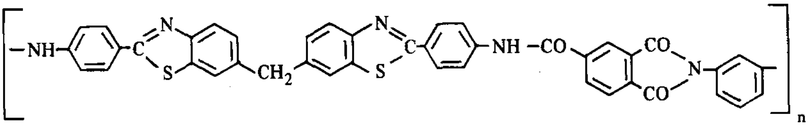
Polyimide



Polybenzthiazole-amide-imide

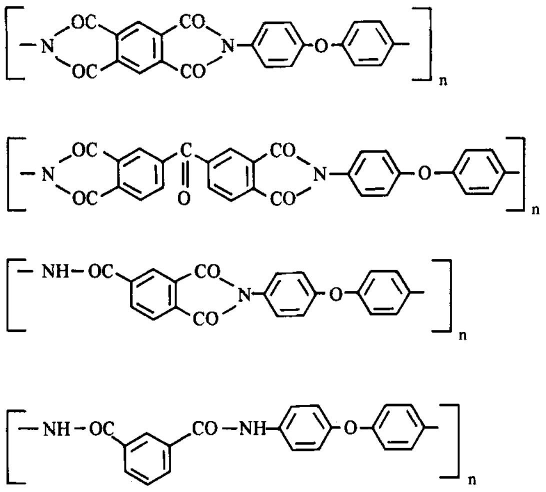
SCHEME 14.

TABLE 3. Insulating Properties[a] of Polybenzthiazole-amide-imide with the Formula



Properties	Polybenzthiazole-amide-imide	Kapton film
Dielectric loss (tg δ)	0.00067	0.003
Dielectric constant	3.1	3.5
Volume resistivity (ohm·cm)	6.5×10^{15}	9×10^{16}
Dielectric strength (kV/mm)	130	275

[a] All data were obtained on films of 30 μm. Dielectric properties were measured at 1 kHz at room temperature.

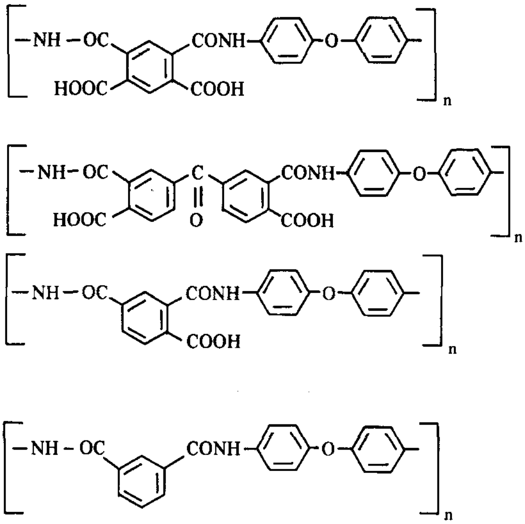


SCHEME 15.

A comparative study of the hydrolytic stability of certain polymers having related structures (polyamides, polyamide-imide, and polyimides) has been carried out. It has been shown that polyimides have the lowest hydrolytic stability due to the catalytic effect of carboxylic groups in the ortho-position toward the amidic group of polyamidic acids which results in the first step of hydrolysis [14]. The structures of the polymers whose behavior toward alkaline hydrolysis was studied are shown in Scheme 15.

Alkaline hydrolysis of polyimides begins with a nucleophilic attack of the –OH ion on the imidic cycle, leading to the formation of polyamidic acids. Polyamidic acids can be considered to be polyamides having carboxylic substituents in the ortho-position, as shown in Scheme 16.

Then the hydrolysis of amidic linkages takes place. It is known that substituents which decrease the electronic density to the carbon atom of the amidic group produce an increase of the hydrolysis rate [15]. The presence of COOH groups in the ortho-position toward the amidic group leads to an increase of the hydrolysis rate in the case of polyamide-imides. In the case of polyimides obtained from pyromellitic dianhydride during alkaline hydrolysis, two COOH groups appear on the same ring, which makes the hydrolysis rate even higher. In the case of polyimides obtained from benzophenontetracarboxylic dianhydride, during hydrolysis only one COOH group appears on the ring, which makes this polymer more stable to hydrolysis than those obtained from pyromellitic dianhydride.



SCHEME 16.

CONCLUSIONS

The thermal stabilities of heterocyclic polyimides such as polyoxadiazole-imides, polybenzthiazole-imides, and polybenzoxazinone-imides are similar, and in certain cases they are higher than those of aromatic polyimides. Disturbance of interchain packing, which is responsible for the excellent thermal stability of aromatic polyimides, is compensated for in the case of the heterocyclic polyimides described in the present paper by the superior thermal stability of the heterocycle introduced in the chain. Also, it was found that the hydrolytic stability of heterocyclic polyimides is definitely superior to that of aromatic polyimides. This property is explained by the fact that a part of the imide cycles is replaced with heterocycles more stable to hydrolysis.

Thus, to improve the alkaline stability of polyimides and preserve their thermal stability at the same time, it is necessary either to reduce the number of imidic cycles by replacing them with another heterocycle whose hydrolytic stability is superior, or to synthesize polyimides from monomers containing preformed imidic cycles, thus avoiding the existence of noncyclized amidic acid units which are vulnerable to hydrolysis.

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