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Abstract

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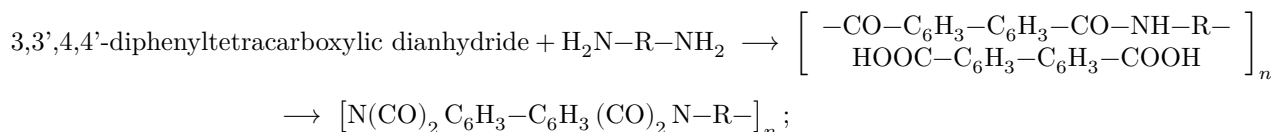
CHEMISTRY

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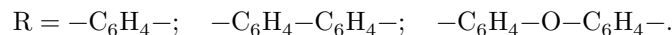
SYNTHESIS OF NEW AROMATIC POLY- IMIDES BASED ON 3,3':4,4'-DIPHENYLTETRACARBOXYLIC DIANHYDRIDE

Among all currently known heat-resistant polymers containing carbo- and heterocyclic units in the main chain, cyclic polyimides are of the greatest interest, combining high thermal stability with a remarkable set of physicomechanical properties. The literature contains data on polyimides obtained on the basis of pyromellitic dianhydride and aromatic diamines (¹).

In the case of preparing polymers containing benzimidazole units in the main chain, a grouping consisting of two benzene rings linked to each other in the meta position has been used successfully (^{2,3}). It was of interest to use this grouping also for introduction into the chain of aromatic polyimides. For this purpose, a series of aromatic polyimides was obtained by us through the reaction of 3,3',4,4'-diphenyltetracarboxylic dianhydride with aromatic diamines. The reaction may be represented by the following equation:



where



The reaction of polyimide formation proceeds in two stages. The polyamidic acids formed in the first stage are soluble in dimethylformamide and have characteristic viscosities $[\eta] = 0.5-0.7$ (1% solution in dimethylformamide, 20°). Formation of the polyimides takes place upon heating the polyamidic acids.

The structure of the polymers at both stages was confirmed by IR spectra (Fig. 1). In the IR spectrum of the polyamidic acid, the characteristic absorption

bands are in the regions 1720 cm^{-1} (the $-\text{CO}$ group), 1650 cm^{-1} ($-\text{CO}$ at NH), 3600 cm^{-1} (hydroxyl groups), and 3300 cm^{-1} (NH groups). After carrying out the imidization reaction, the IR spectra of the polymers change sharply. In the spectrum of the polyimide there are two absorption bands in the region of 1730 and 1783 cm^{-1} , characteristic of a five-membered imide ring.

Owing to the presence of a bond in the meta position between two benzene rings, the chain of polymers obtained on the basis of 3,3',4,4'-diphenyltetracarboxylic dianhydride possesses greater flexibility than the chain of polymers obtained on the basis of pyromellitic dianhydride.

This makes it possible to use available aromatic diamines, for example *p*-phenylenediamine and benzidine, to obtain infusible polymers. All the polymers obtained are stable when heated in air to $450\text{--}500^\circ$ and are capable of forming strong films.

Experimental part

m-Ditolyldicyanide ⁽⁴⁾ was obtained by the action of cuprous cyanide on diazotized *o*-tolidine. After recrystallization from alcohol, *m*-ditolyldicyanide had a melting point of $188\text{--}190^\circ$ (lit. 190°).

m-Ditolyldicarboxylic acid ⁽⁴⁾ was obtained by saponification of *m*-ditolyldicyanide by boiling it with dilute H_2SO_4 . The *m*-ditolyldicarboxylic acid purified by reprecipitation from alkaline solution with HCl had m.p. 320° (lit. m.p. above 300°).

Fig. 1. IR spectra of polymers obtained by polycondensation of the dianhydride of 3,3',4,4'-diphenyltetracarboxylic acid and 4,4'-diaminodiphenyl ether. 1 – polyamidic acid, 2 – polyimide.

3,3',4,4'-Diphenyltetracarboxylic acid ⁽⁴⁾ was obtained by oxidation of *m*-ditolyldicarboxylic acid with an alkaline solution of potassium permanganate. 3,3',4,4'-Diphenyltetracarboxylic acid, recrystallized from water, had m.p. 286° (lit.: no melting up to 250°). The purity of the acid, determined by titration, was 99.5–99.8%.

The **dianhydride of 3,3',4,4'-diphenyltetracarboxylic acid** was obtained by heating the corresponding acid at 230° in vacuum for 1.5 h. The dianhydride of 3,3',4,4'-diphenyltetracarboxylic acid, recrystallized from acetic anhydride, had a melting point of 286° .

Found, %: C 65.83, 65.73; H 2.28, 2.19
 $\text{C}_{16}\text{H}_6\text{O}_6$. Calculated, %: C 65.30; H 2.04

The IR spectra of 3,3',4,4'-diphenyltetracarboxylic acid and its dianhydride contain all absorption bands characteristic of these compounds.

General method for preparing polymers. The reacting substances were taken into the reaction in strictly equimolecular ratios. To a solution of the

diamine in dry dimethylformamide at 10–15°, with stirring, the dianhydride of 3,3',4,4'-diphenyltetracarboxylic acid was added in small portions. The solution of polyamidic acid may be used to obtain films, or the polymer may be precipitated from the solution with a suitable solvent (dry ether, dry benzene).

Imidization was carried out by heating the polyamidic acid with a stepwise increase in temperature from 80 to 350° over two hours.

On the basis of the dianhydride of 3,3',4,4'-diphenyltetracarboxylic acid and aromatic diamines, a series of new aromatic polyimides was obtained that are capable of forming thermostable strong films.

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