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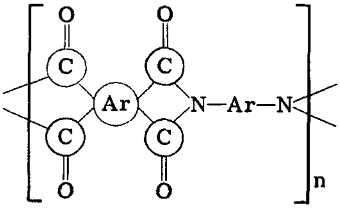
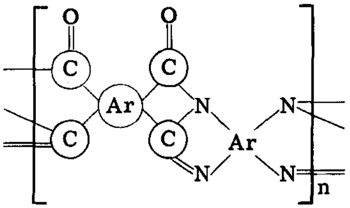
LETTER TO THE EDITOR

Polymers Containing Imidazopyrrolone-Imide or -Imidazole Structures

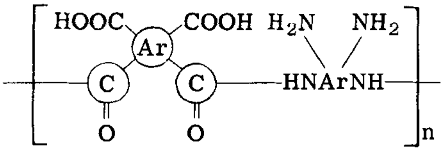
A recent communication [1] on imide-imidazopyrrolone copolymers prompts us to report on similar and related polymers which have been under syntheses and study for some time as part of a major investigation in our laboratories. The polyimides (I) are step-ladder polymers derived from aromatic dianhydrides and aromatic diamines; they show high thermal stabilities [2]. The polyimidazopyrrolones, (II), are ladder polymers derived from aromatic tetraamines and aromatic dianhydrides; they also exhibit outstanding thermal stabilities [3, 4] which are somewhat higher than those of the polyimides (I), but the expected much higher stability is not realized in (II). This may be the result of some incompleted ring closures shown in (III) and (IV) due to the rigid chain structure, thereby introducing step-ladder segments in a ladder structure.



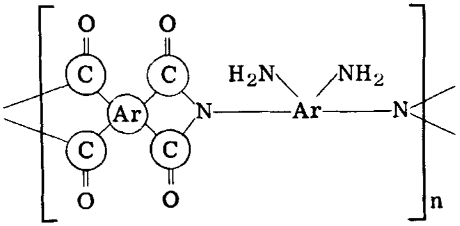
(I)



(II)



(III)



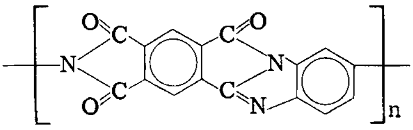
(IV)

Part of our investigation is concerned with polymers which alternate the imidazopyrrolone structure with either an imide or an imidazole structure, with the expectancy of reducing chain rigidity and thereby attaining more extensive ring closures.

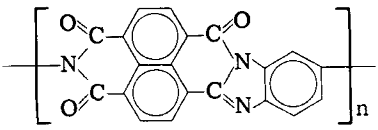
We have also condensed in dimethylacetamide (DMAC) stoichiometric quantities of 1, 2, 4-triaminobenzene (TAB) with pyromellitic anhydride (PMA) and 3, 3′, 4, 4′-benzophenonetetracarboxylic anhydride, respectively, confirming the reported results [1] by obtaining prepolymers as viscous solutions which could be converted by cyclodehyration to heat-resistant poly—(imide-imidazopyrrolones). However, we were unsuccessful in isolating the condensation in DMAC of 1, 4, 5, 8-naphthalenetetracarboxylic acid anhydride with 1, 2, 4-triaminobenzene as a prepolymer completely soluble in DMAC. The condensation product precipitated from the reaction mixture as a solid of relatively low intrinsic viscosity, 0.10 dl/g in 97% H_2SO_4. Since our interest was concerned with cyclized polymers of sufficient molecular weight that they could be converted to thermally stable fibers, we performed the condensations also in polyphosphoric acid (PPA).

The polymers were prepared by condensing stoichiometric quantities of 1, 2, 4-triaminobenzene or its dihydrochloride with the dianhydrides as 3-5 % solutions in PPA at 180°C under nitrogen with stirring for 12 to 14 hr. The PPA solution was then poured on to a stirred ice-water mixture; the polymer was then isolated, washed in boiling water three times, and dried at 100°C in a vacuum oven. The infrared spectra of the polymers showed the presence of absorption bands at 1765 and 720 cm^{-1} for imide and 1620 cm^{-1} for imidazole. The polymers prepared in PPA were not soluble in DMAC or dimethylformamide but were soluble in 97% sulfuric acid; these solubility characteristics indicated high cyclization. The intrinsic viscosity in 97% H_2SO_4 of polymer (V) was 0.631 dl/g and for (VI) from 1, 4, 5, 8-naphthalenetetracarboxylic acid anhydride it was 0.882 dl/g. Polymer (VI) is the triamino analogue of the bisbenzimidazophenanthroline polymer [5].

The thermal stabilities in nitrogen of (V) and (VI), shown in Fig. 1, were in excess of 540°C; the weight losses for (V) were 32% at 1000°C and 38% at 1176°C; and for (VI) they were 26% at 1000°C and 31% at 1176°C.



(V)



(VI)

Analysis for (V):

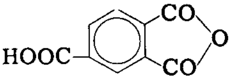
Calculated for $C_{16}H_5N_3O_3$: C, 66.90; H, 1.74; N, 14.63; O, 16.73.
Found: C, 67.12; H, 1.82; N. 14.58; O, 16.57.

Analysis for (VI):

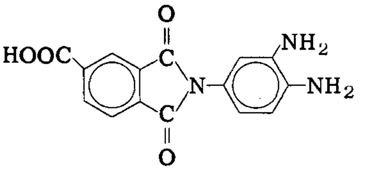
Calculated for $C_{20}H_7N_3O_3$: C, 71.22; H, 2.08; N, 12.46; O, 14.24.
Found: C, 71.62; H, 2.11; N, 12.44; O, 14.89.

Polymers (V) and (VI) may be described as condensation products of (a) an aromatic triamine, TAB, having attached to the nucleus (1) one pair of ortho-disposed NH_2 groups, and (2) an isolated amino group with (b) an aromatic dianhydride. Since TAB may condense in either a head-to-head, or a head-to-tail reaction, structures (V) and (VI) most probably are not the true overall structures of the polymers, but the lack of symmetry of TAB requires that imide and imidazopyrrolone structures alternate at each amine nucleus, and thus at least half of the repeating units in the chains are of types represented by (V) and (VI).

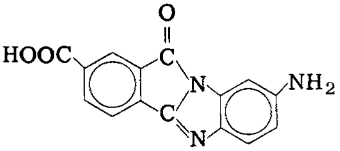
We have studied also the condensation of TAB with trimellitic anhydride (TMA),



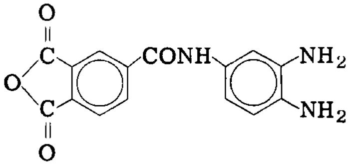
Reactions performed in DMAC yielded only very low molecular weight condensation products or salts, $[\eta] = 0.03$ dl/g in 97% H_2SO_4. The condensation in PPA, performed similarly to that described above, yielded a low molecular weight polymer, $[\eta] = 0.084$ dl/g. The initial product of the condensation of TMA with TAB can be written as head-head (VII), head-tail (VIII); tail-head (IX), and tail-tail (X).



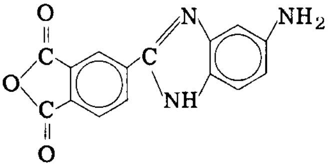
(VII)



(VIII)



(IX)

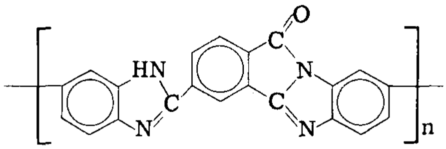


(X)

In PPA, the thermodynamic driving force in the polycondensations involving amines and carboxyl groups is the formation of stable rings [6]. On this basis structure (IX) would not be expected to be formed, although, if it did form, propagation to higher molecular weights could occur. Structures (VII) and (X), if formed, also would propagate as equivalents of the A-B types of monomers, which could form ring structures. In contrast, structure (VIII) would not be expected to form high polymers in a PPA medium. The low intrinsic viscosity of the product actually obtained, 0.03 dl/g, indicated that the major portion of the reaction yielded structure (VIII), and extended heating of TAB and TMA even at 220°C for 48 hr failed to increase the viscosity of the condensation product. Evidently, the reaction of the carboxyanhydride with the more basic 1, 2-amino groups is favored over the reaction with the isolated 4-amino group. However, polymers of higher intrinsic viscosities were obtained when TAB was condensed with (TMAC) trimellitic acid chloride, 4-ClOC-C_6H_3-(1-2)-$(CO)_2O$, either in PPA or DMAC with triethylamine as the hydrogen chloride acceptor. These reactions proceeded more readily due to the higher driving force of the acid chloride and the elimination of HCl as a gas in the PPA medium and as the amine hydrochloride in the DMAC solvent. The reaction product obtained from the DMAC solution yielded a hemipolymer soluble in DMAC; $[\eta] = 0.288$ dl/g in 97% H_2SO_4. The product, (XI), obtained from the PPA reaction was only partially soluble in DMAC but soluble in H_2SO_4, $[\eta] = 0.453$ dl/g; its thermal stability is shown in Fig.1.

The melt condensation of 4-phenyl trimellitate anhydride, (2.68 g, 0.01 mole), m.p. 150°C, with TAB (1.23 g, 0.01 mole) using Marvel's procedures [7-9] was performed at 300°C for 1 hr under nitrogen, then $1\frac{1}{2}$ hr at 300°C at approximately 0.5 mm Hg pressure. Then the mass was cooled, ground to a powder, and heated at 360°C at 0.3-0.5 mm Hg pressure for 2 hr. The polymer was slightly soluble in DMAC but soluble in 97% H_2SO_4, $[\eta] = 0.366$ dl/g. Its thermal stability was similar to (XI).

The studies with TMA were extended to the reaction with aromatic tetraamines such as, 3, 3′-diaminobenzidine, DAB. The reaction in DMAC, as in the case of the triamine, TAB, yielded only low molecular weight products. The condensation of DAB with TMA in PPA yielded a polymer, (XII), of intrinsic viscosity in 97% H_2SO_4 of 0.513 dl/g. Its infrared spectrum showed bands for imide at 1765 and 720 cm^{-1} and for imidazole at 1620 cm^{-1}; its thermal stability is shown in Fig. 1.



Analysis:

Calculated for $C_{21}H_{10}N_4O$: C, 75.44; H, 2.99; N, 16.76; C, 4.81.
Found: C, 74.84; H, 3.05; N, 16.72; O, 4.92.

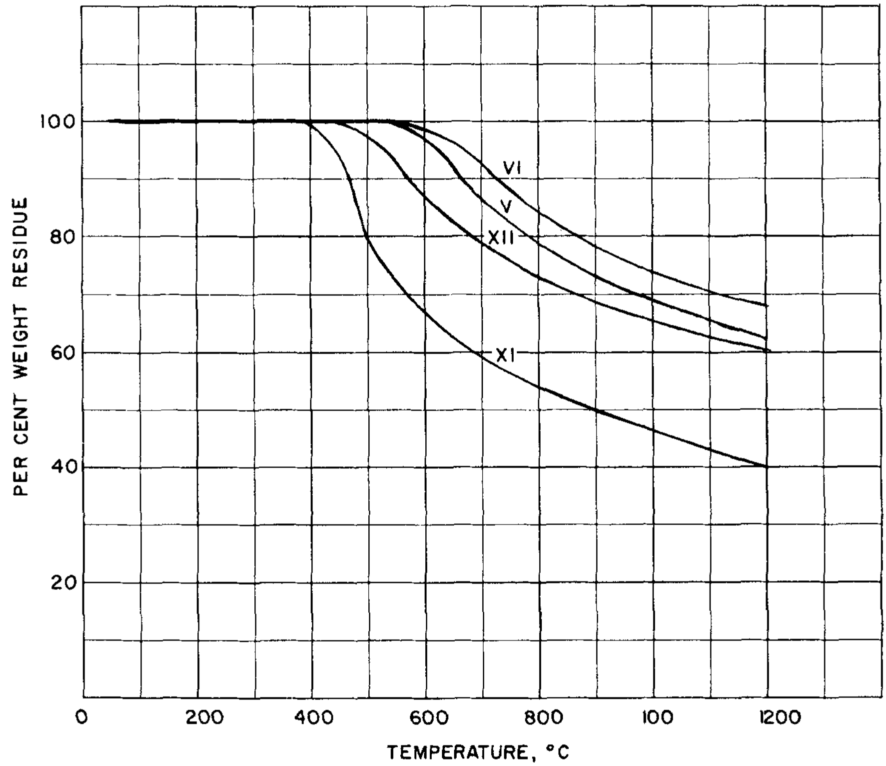


Fig. 1. Thermogravimetric analyses of the polymers under nitrogen at ΔT of 10°C/min.

The thermal stability in nitrogen of polymer (VI) was the highest of those prepared and similar to the bisbenzimidazophenanthroline polymers [5]; the thermal stabilities of (V) and (XII) were next in order and similar to the poly(1, 2-benzoylenebenzimidazoles) [3-4]; polymer (XI) had the lowest thermal stability of the polymers studied, most probably because of the linear disorder resulting from the random incorporation of two or more types of head-head, head-tail, tail-head, and tail-tail structures in the polymer chain. A future publication will describe the work more completely.

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