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## SYNTHESIS AND ISOMERIZATION CYCLIZATION OF POLYCYANO-UREAS CONTAINING IMIDE UNITS\*

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Polycyano-ureas containing imide units have been synthesized by polycondensation of N,N'-bis-(o-amidocyanophenyl) di-imides with 4,4'-diphenylmethanediisocyanate. The thermal isomerization of the polycyanoureas into polymers of heterocyclic structure has been investigated. Verification of the structure of the polymers has been obtained by the synthesis of model compounds of anthranylonitrile and phenylisocyanate.

A two stage method is frequently used for the synthesis of a number of heterocyclic heat stable polymers, e.g. polyimides. However, difficulties are encountered in processing polymers of this type into industrial goods, primarily on account of high softening points of these polymers and owing to the evolution of volatile

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products at the stage of cyclization of prepolymers, which means that one has to develop new methods for the preparation of heat stable heterocyclic polymers. One of these methods is that of synthesizing heat stable polymers from fusible reactive oligomers that may be transformed into heterocyclic polymers without the evolution of volatile products. As examples of polymers that may be prepared by the foregoing method we have maleimides [1] as well as oligomeric polyimides containing acetylene [2, 3] or nitrile end groups [4] that may be thermally hardened by cyclotrimerization or through interaction with N, N'-dioxide of terephthalonitrile.

The present paper relates to our study of the feasibility of synthesizing heterocyclic heat stable polymers by reacting oligomeric imides containing o-aminonitrile end groups with aromatic dissocyanates. It is known [5] that the interaction of anthranylonitrile with phenylisocyanate in solution leads to the formation of N-phenyl-N'-(o-cyanophenyl) urea which may be thermally cyclized to 2-oxo-3phenyl-4-amino-1, 2, 3, 4-tetrahydroquinazoline (IV), and the melting together of the latter compounds at 130° yields 2-oxo-4-anilino-1, 2, -dihydroquinazoline (V) [6]



Since the foregoing transformations all take place without the evolution of volatile products, they may serve as a basis for hardening of the respective oligomers.

The reactive oligomers used in this investigation were N, N'-bis-(o-aminocyanophenyl) diimides obtained by reacting dianhydrides of tetracarboxylic acids with a two fold excess of 2,4- or 2,5-diaminobenzonitrile



I

Starting materials. The synthesis of 2,5-diaminobenzonitrile (2,5-DABN) was carried out in accordance with the procedure outlined in [7]; pale-yellow crystals were obtained from a mixture of benzene and petroleum ether (3:1), m.p. 89.5-90°. 2,4-Diaminobenzonitrile (2,4-DABN) was synthesized by the method of [8]: colourless needles were obtained from benzene; m.p. 104.5-105°. Dianhydride of 3,3',4,4'-benzophenonetotracarboxylic acid (BDA) and dianhydride of 3,3',4,4'-diphenyloxidetetracarboxylic acid (ODA) were recrystallized from acetic anhydride and sublimed under vacuum; m.p. 227-228° and 228-229° respectively. 4,4'-diphenylmethanediisocyanate (DMI) was twice distilled over residual pressure of 1 torr over 5 Å molecular sieves, m.p. 39-40.5°. N-methylpyrrolidone (N-MP) and m-cresol were purified in line with the method of [7]; tributylamine was twice distilled over sodium hydroxide under residual pressure of 10 torr. Di-imide of N,N'-bis-(4-amino-3-cyanophenyl) diphenyloxide-3,3',4,4'-tetracarboxylic acid (DIO-2,5-DABN) and di-imide of N,N'bis-(3-amino-4-cyanophenyl)diphenyloxide-3,3',4-4'-tetracarboxylic (DIO-2,4-DABN) were synthesized in m-cresol in line with the procedure described in [7] for the synthesis of di-imides of BDA and 2,4-DABN or 2,5-DABN (DIB-2,4-DABN and DIB-2,5-DABN respectively). The molecular weights of the di-imides based on BDA and ODA based on the results of mass spectrometric analysis (Varian-MAT-731) were respectively 552 and 540, which agreed with the theoretical values. A quantitative analysis of the number of amino end groups in the N,N'-bis(o-aminocyanophenyl) di-imides was carried out in N-MP solution by photometry using an SF-2U spectrophotometer and the method given in [9]. To plot the calibration curve we used a colourless solution of anthranylonitrile in N-MP (the amino group concentration was varied within limits of  $0.8 \times 10^{-4} - 2.5 \times 10^{-4}$  $\times 10^{-4}$  g-equiv/l.), the indicator being an alcoholic solution of N,N-dimethylamino-p-benzaldehyde. The results obtained are given in Table 1.

Di-imides	M.p., °C	MW*	Content of amino-groups, %	
			found †	calculated
DIB-2-4-DABN	312-315	552	5.97	5.80
DIB-2·5-DABN	370375	552	6.05	5.80
DIO-2·4-DABN	267 - 270	540	6.04	5.93
DIO-2-5-DABN	320-324	540	6.11	5.93

TABLE 1. PROPERTIES OF N,N'-BIS-(0-AMINOCYANOPHENYL) DI-IMIDES

\* Determined by mass spectrometry.

† Determined by photometry.

The model compounds. N-Phenyl-N'-(o-dyanophenyl) urea (III) was synthesized from anthranylonitrile and phenylisocyanate following the procedure of [5]; m.p. 186–188°. Isomerization of III to 2-oxo-3-phenyl-4-imino-1,2,3,4-tetrahydroquinazoline (IV) was carried out by the method of [5] m.p. 215–218°. Isomerization of IV to 2-oxo-4-anilino-1,2, dihydroquinazoline (V) was carried out in the melt in a sealed evacuated ampoule at 280° for 30 min. After recrystallization from alcohol the product obtained had m.p. 262–263°, 54% yield. The substance does not produce any depression of the melting point along with the reliable compound V prepared, as described in [6], by melting phenylisocyanate together with anthranylonitrile. Compound V was also obtained by isomerization of the diphenylcyano-urea III, whilst heating in an evacuated ampoule at 210–225°, 41% yield (from alcohol), m.p. 260–262°.

*Polycyano-ureas* (PCU) were prepared by polycondensation in N-MP medium, using tributylamine as catalyst. For instance, to a solution of 0.2700 g (0.5 mmole) of DIO-2,5-DABN in 4 ml of N-MP were added, whilst stirring, 0.1275 g (0.510 mmole) of DMI and

0.20 ml (5 vol.%) of tributylamine. The solution was stirred for 30 min at room temperature, and then for 3 hr with heating to  $60-70^{\circ}$ . After cooling some of the solution was decanted into water, while from the other portion translucent brittle films were cast on glass. Polymer yield 94%,  $\eta_{10g}=0.26$  (0.5% solution N-MP, 25°). The composition and some of the other PCU and polymers obtained after cyclization are given in Table 2.

Polymer	Starting di-imides	$\eta_{\log}^{\dagger}$ for PCU	T₅, °C	$\left  \begin{array}{c} T \text{ onset degrada-} \\  ext{tion}^{\ddagger}, \ ^{\circ} \mathrm{C} \end{array} \right $
PCU-I	DIB-2-4-DABN	0.20	335	415
PCU-II	DIB-2-5-DABN	0.25	355	440
PCU-III	DIO-2-4-DABN	0.22	330	395
PCU-IV	DIO-2-5-DABN	0.26	340	410

TABLE 2. PROPERTIES OF THE PCU AND OF CYCLIZED POLYMERS\* BASED ON THE PCU

\* Prepared by heating the respective PCU under vacuum for 1 hr at 300°.

† Measured for a 0.5% solution in N-MP at 25°.

**‡** Temperature of the onset of degradation determined from the TGA curves.

Thermogravimetric measurements of the polymers were carried out on a UVDT-1 thermobalance under vacuum  $(10^{-2} \text{ torr})$  whilst heating at the rate of 5 deg/min. To carry out the differential thermal analysis we used Heraus DTA equipment, heating rate 10 deg/min. The IR spectra were taken on a UR-10 spectrometer. Thermomechanical curves were plotted for pressed powders of the polymers with a constant load of 100 g on a plunger 4 mm in diameter, heating rate 2 deg/min.

Some properties of the synthesized N,N'-bis-(o-aminocyanophenyl) di-imides are given in Table 1. It can be seen that measurement data on molecular weights and the results of amino end group analysis tally with values calculated in line with anticipated structures. On a previous occasion [7] we showed that 2,4-DABN and 2,5-DABN react with dianhydrides through amino groups in position 4 (5), i.e. the resulting bis-imides contain o-aminonitrile end groups. N,N'-bis-(o-aminocyanophenyl) di-imides were reacted with DMI both in solution in N-MP and in the melt. As one would expect, polycyano-ureas are formed in solution, whereas the reaction in the melt leads to formation of partially cyclized structures. Table 2 gives the data on some properties of the PCU and of the polymers after cyclization, and it can be seen that the  $\eta_{\log}$  values for the PCU are relatively low, probably owing to the low reactivity of bis-(o-aminonitriles) containing imide units. The obtained PCU all dissolved in amide solvents and in conc. H<sub>2</sub>SO<sub>4</sub>. The IR spectrum of the PCU-III (Fig. 1) bears out the structure expected in the case of the latter: bands at 1390, 1730 and 1780  $\rm cm^{-1}$  relate to imide rings, and the band at 2220  $\rm cm^{-1}$ pertains to the nitrile group. Vacuum heating of PCU for 1 hr at 300° resulted in the practically complete disappearance of the band relating to the nitrile group (Fig. 1), which means that cyclization of the polymers takes place. The cyclized polymers are insoluble in amide solvents, and are only partially soluble in concentrated H<sub>2</sub>SO<sub>4</sub>.

Difficulties encountered when carrying out the reaction in the melt are due to

major differences in the melting points of bis-imides (see Table 1) and DMI (m.p  $39-40.5^{\circ}$ ). Thus when the most readily fusible of the bis-imides (DIO-2,4-DABN) is heated in a mixture with DMI in an argon atmosphere for 2 hr at 220–230° and for 1 hr at 250–260° this fails to produce complete melting of the reaction mass.



FIG. 1. IR spectra of the original PCU-III (a) and of PCU-III after heating in vacuo at  $300^{\circ}$  for 1 hr (b).

After softening has taken place the mixture congeals into a hard brittle product which is sparingly soluble only in concentrated  $H_2SO_4$ . The IR spectrum of the obtained product has weak bonds at 3380 and 3475 cm<sup>-1</sup> relating to amino groups as well as a well defined band at 2215 cm<sup>-1</sup> relating to the CN group which fails to disappear after the specimen has been heated for 1 hr at 300°. This points to the presence of unreacted *o*-aminonitrile end groups in the specimen and to the consequently low molecular weight of the polymer. The factor underlying the latter finding might well be side reactions of DMI taking place at 220° or more and impeding the course of the main reaction.

Processes taking place during heating of the stoichiometric amounts of DIB-2,5-DABN and DMI were investigated by DTA. The DTA curves have an exothermic peak in the region of  $325^{\circ}$ , which is absent from DTA curves of individual components of the mixture, and probably relates to interaction between the isocyanate and amino groups. Softening of the mixture of DIB-2,5-DABN and DMI apparently takes place at this temperature and factilitates the reaction. It is probable that apart from interaction between  $NH_{2}$ - and OCN groups involving urea bond formation under these conditions, there will in addition be a process of isomerization to heterocyclic structures.



Fig. 2. TGA curves (a) and thermomechanical curves (b) of polymers prepared by cyclization of PCU in vacuo at 300° for 1 hr (the figures denote the original PCU).

The method of TGA under vacuum was used to determine the thermal stability of the polymers after cyclization (Fig. 2a). Weight losses at temperatures above  $100^{\circ}$  are apparently due to the removal of adsorbed water. It can be seen from Fig. 2 that the thermal stability of the polymers having *p*-phenylene units in the amino component is slightly higher than that of the polymers containing *m*-phenylene units.

Figure 2b shows the thermomechanical curves for pressed powders of the polymers, which were used to determine the glass transition temperatures  $T_g$ .  $T_g$ values for the polymers containing benzophenone units in the chain are higher compared with the polymers with diphenyloxide units in the chain. A similar tendency comes to light in the case of polyimides based on BDA and ODA [10]. The discontinuity appearing on the thermomechanical curves at temperatures above 480° is apparently due to marked degradation occurring in the polymers, which is supported by TGA results.

To determine the nature of the hetero rings formed during cyclization of PCU a more detailed study was made of transformations of model compounds III, IV and V. Although it is thought in [6] that formation of compound V takes place via intermediate compound IV, the cited authors [6] were unable to isomerize IV to V. However, we have shown that a 54% transformation of IV to V takes place on heating IV to 280° for 30 min. Moreover compound V is obtainable by heating III for 30 min at 210–225°. In view of these results there are grounds for assuming that the cyclization of PCU takes place in two stages, the first being that of formation of the iminoquinazolone structure (VI), which at higher temperatures  $(300^\circ)$  undergoes regrouping resulting in the aminoquinazolone structure (VII)



This means that the presence of both structures is to be expected in the end polymer. These suppositions are supported by a comparison of the IR spectra of the cyclized polymers with those of the model compounds (Fig. 3). The band at 1650 cm<sup>-1</sup> in the spectrum of PCU-III after cyclization (Fig. 2a) points to the presence of aminoquinazolone structures [11]. Moreover, the presence of structure VII is substantiated by the results of hydrolysis of the cyclized polymers in a boiling dilute hydrochloric acid solution under conditions similar to those described for model V [6]. In the solution obtained as a result of hydrolysis one is able with the aid of a qualitative reaction with N,N-dimethylamino-p-benzaldehyde to detect the presence of primary amino-groups, whose formation is the result of hydrolytic breakdown of structures VII by the scheme



Clearly, a certain amount of iminoquinazolone units will remain in the cyclization of PCU, but the band at  $1703 \text{ cm}^{-1}$  relating to the imino group is unde-

tectable in the IR spectra on account of the strong band of the imide ring at 1730  $cm^{-1}$ .

A kinetic study of the isomerization cyclization of the PCU was based on the disappearance of the band at 2220 cm<sup>-1</sup> in the IR spectrum. The PCU specimens used for the measurements were in the form of films of thickness [10–15] cast from solutions of the polymers in N-MP on germanium plates.



FIG. 3. IR spectra of model compounds V (a), IV (b) and III (c).

Kinetic curves typical of the cyclization of two PCU are displayed in Fig. 4. It can be seen that the curves bear the "saturated" character that is associated with cyclization curves of other classes of polymers [7], and that stems, apparently,



FIG. 4. Kinetic curves of cyclization of PCU-III (1, 2) and PCU-IV (3-5).Cyclization temperatures: 1-300, 2,3-250, 4-220, 5-180°.

from the stiffness of the polymer chains increasing as the reaction advances. On comparing the cyclization curves of PCU based on N,N'-bis-(o-aminocyanophenyl) di-imides synthesized on the basis of one and the same dianhydride and different diamines (polymers PCU-III and PCU-IV), it is seen that the nature of the diamine has a certain significance. A PCU based on a diimide containing the *m*-isomeric diamine cyclizes rather more readily than a PCU based on a di-imide containing the *p*-isomeric diamine. It may well be that this results from a difference in the glass transition temperatures both of the starting PCU and of the forming partially cyclized polymers. Using initial portions of the kinetic curves of cyclization of the PCU-IV polymer at 180, 220 and 250° we calculated the first order cyclization rate constants, amounting respectively to  $0.108 \times 10^{-3}$ ,  $0.666 \times 10^{-3}$  and  $2.205 \times \times 10^{-3} \sec^{-1}$ . The activation energy for the cyclization process calculated from the foregoing data is  $20 \pm 1 \text{ kcal/mole}$ .

Translated by R. J. A. HENDRY

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