SYNTHESIS AND STUDY OF SOLUBLE POLY-(o-AMIDO)IMIDES*

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Poly-(o-acetamido)imides of high molecular weight that are soluble in organic solvents, have been obtained by treating the reaction solutions in DMF after preparation of poly-(o-amino-o-carboxy)amides, with excess of a pyridine-acetic anhydride mixture. The main characteristics of the poly-(o-acetamido)imides have been studied and the processes occurring during heat treatment of these polymers under various conditions are discussed. It is shown that the method developed here permits preparation of polyimides containing amide side groups of any structure, by varying the acid component of the cyclizing mixture.

THE most effective method of producing soluble polyimides is the introduction into the polymer molecules of bulky side groups attached to central carbon atoms [1] or in the *ortho*-position with respect to aryl imide rings in the main



FIG. 1. Infrared (a) and NMR (b) spectra of N-(o-acetamidophenyl)phthalimide (1) and the poly-(o-acetamido)imide from pyromellitic dianhydride (2).

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polymer chain [2]. The usual means of introducing side groups into polyimide molecules is the use of starting materials (diamines or aromatic tetracarboxylic acid dianhydrides) already containing these groups. In the present paper soluble, aromatic polyimides, containing amide groupings in the ortho-position with respect to the imide rings, are prepared by imidization of previously polymerized poly-(o-amino-o-carboxy)amides (PACA's) with dehydrating agents (acid chlorides and anhydrides) in the presence of tertiary amines [3]. The dehydrating agents also perform the function of acylating reagents, converting the free amino groups of the PACA to amide groups. The general scheme of preparation of poly-(oamido)imides can be represented in the following way:



where $B_N = C_5H_5N$; $(C_2H_5)_3N$; $R = CH_3$; C_6H_5 ; X = Cl; OCOR.

The imidization of the reaction solutions of PACA's in DMF with acetic anhydride in pyridine was studied in greatest detail. The products of this reaction are poly-(o-acetamide)imides of the type



Preparation of the polymers was preceded by study of a number of model reactions. The model reactions chosen for major study were those leading to imidization of N-(o-aminophenyl)phthalamic acid. When a solution of the latter in DMF was heated at 145° in the presence of excess of a 1:1 mixture of pyridine and acetic anhydride, N-(o-acetamidophenyl)phthalimide was obtained in high yield.

The same product was obtained when acetyl chloride was used in place of acetic anhydride.

It is interesting to note that when N-(o-aminophenyl)phthalamic acid is treated with a strictly equimolar quantity of the pyridine-acetic anhydride mixture the main product is N-(o-aminophenyl)phthalimide [4].

When a further quantity of the pyridine-acetic anhydride mixture is added to the solution of N-(o-aminophenyl)phthalimide so obtained, N-(o-acetamidophenyl)phthalimide was obtained in high yield. From this it may be concluded that in treatment of (o-amino-o-carboxy)amides with an excess of a pyridineacetic anhydride mixture, o-aminoimides are formed first and this is followed by acylation of the free amino groups.

Model compounds of more complex structure were obtained by treatment of bis-(o-amino-o-carboxy)amides with excess acetic anhydride and pyridine in DMF



The structure of all the model compounds was confirmed by infrared and NMR spectroscopy (Fig. 1), and by elementary analysis.

Poly-(o-acetamido) imides were prepared by treatment of PACA reaction solutions in DMF, obtained as in references [5] and [6], with an excess of the pyridine-acetic anhydride mixture at $140-150^{\circ}$ for 4-5 hr.

It is well known that degradation of polyimides occurs when they are heated at high temperatures in amide solvents. This is caused by hydrolysis, which is catalysed by amide solvents [7].

We found that polyimides do not degrade when heated in amide solvents in the presence of the pyridine-acetic anhydride mixture. For example when a reaction solution was heated for 8 hr in the presence of a five-fold excess of the pyridine-acetic anhydride mixture no change in the viscosity characteristics occurred. This is probably explained by the fact that in the presence of an excess of the cyclizing mixture only part of it is expended in cyclization, while the remainder is always present in the reaction medium, and it absorbs the moisture liberated. Moreover the cyclizing mixture can combine with dimethylamine, formed by decomposition of DMF at high temperatures and capable of reacting with the imide ring. Consequently to avoid degradation during preparation of the polyimides it is essential that the reaction system should contain an excess of the cyclizing mixture.

Study of the dependence of the viscosity characteristics of poly(o-acetamide) imides on the reaction conditions showed that they are practically independent of the concentration of the original solutions and of the quantity of cyclizing mixture.

The structure of the polymers was confirmed by infrared and NMR spectroscopic analysis (Fig. 1).

The main characteristics of the poly-(o-acetamide)imides are presented in the Table.

The poly-(o-acetamido)imides are soluble in a wide selection of organic solvents. The solubility of these polymers is attributable both to the presence of side groups that prevent the polymers from crystallizing (X-ray analysis shows that all these polymers are amorphous) and to the method of preparation used.



FIG. 2. TGA (1), DTA (2) and DTG (3) curves of poly(acetamido)imide IV in an inert atmosphere.

It is seen from the Table that these poly-(o-acetamido)imides have a fairly high viscosity, the only exceptions being the polymers based on 3,3',4,4'-tetraaminodiphenylsulphone and some poly-(o-acetamido)imides based on the dianhydride of 3,3',4,4'-tetracarboxydiphenylsulphone. This could be due to the low nucleophilic reactivity of this tetramine and too high an electrophilic reactivity of the dianhydride, because both these factors cause difficulty in production

CO CO R NHCOCH: H:CCONH $\eta_{\rm red}$, (0.5% Polymer €ъ, on. R' R solution No. kg/cm^a % in DMSO at 30°) I 0 1.6 1010 8.5 π 1.3 760 8.3 CH, ш so, 0.18 p-OC,HO-1070 18.2 IV 1.8 V Absent 1.1 VI o 0.54 1060 6.2 VII 0.3CH. 80, VIII 0.14 p-OC_H₄O 0.92 1330 6.9 IX х Absent 780 XI 1.72 8.5 0 XII 0.91 1130 9.8 CH, XIII SO. 0.26 XIV p-OC_H_O-0.7 1120 8.4 XV Absent 0.2 0 0.8 XVI CH. 0.3 XVII XVIII so, 0.16 $p \cdot OC_{\mathbf{s}} H_{\mathbf{s}} O$ 0.2XIX XX Absent 0.18

SOME CHARACTERISTICS OF POLY(0-ACETAMIDO)IMIDES*

• All the polymers except X are soluble in DMF, DMSO, dimethylacetamide, m-cresol, a 3:1 mixture of tetrachloroethane and phenol, and in hot formic acid; the polymers except VIII, X and XIII are soluble in hot nitrobenzene; polymer X is not soluble in any of the above solvents.

of PACA's of high molecular weight [8]. The low nucleophilic reactivity of 3,3',4,4'tetra-aminodiphenylsulphone results in a low rate of the main reaction. This can lead to the situation where the main and side reactions begin to proceed at comparable rates. On the other hand the high electrophilic reactivity of 3,3',4,4'- diphenylsulphonotetracarboxylic and dianhydride gives rise to vigorous occurrence of side reactions, leading to reduction in the molecular weight of the original PACA.

Poly-(o-acetamido)imides with the highest viscosity characteristics were obtained from the dianhydride of tetracarboxydiphenyl oxide and benzophenonetetracarboxylic acid. Clear, slightly coloured or colourless films were obtained from solutions of these polymers in dimethylformamide and the elongation and strength characteristics of these films are given in the Table.

Study of the thermal stability of the polymers by dynamic thermogravimetric analysis in an inert atmosphere showed that they begin to lose weight at 370-450°, depending on structure (Fig. 2).

The nature of the TGA curve shows that two processes occur when the polymers are heated, and this is confirmed also by the DTA and DTG curves. In all probability in the temperature interval of 370-450° cyclization of amido-imide to benzoylenebenzimidazole fragments occurs



The formation of benzoylenebenzimidazole rings in heat treatment of poly-(o-acetamido)imides was confirmed by infrared spectroscopic analysis of heattreated films and by synthesis of model bis-benzoylenebenzimidazoles by heat treatment of bis-(o-acetamido)imides.

The second process of degradation of poly-(o-acetamido)imides, occurring in an inert atmosphere at 450–600°, is evidently that of breakdown of the polybenzoylenebenzimidazole structure.

Thermal conversion of poly-(o-acetamido)imides to polybenzoylenebenzimidazoles is much more difficult than cyclization of poly-(o-amino)imides because of the lower nucleophilic reactivity of -NH- of the acetamide group and the difficulty of elimination of acetic acid. The rigorous conditions of cyclization of poly-(o-acetamido)imides gives rise to the possibility of the occurrence of a number of parallel degradative processes.

Analysis of the products of thermal degradation of a poly-(o-acetamide)imide under isothermal conditions showed that CO, CO_2 , CH_4 , C_2H_6 , H_2O and H_3 are present. The formation of most of these products can be explained by degradation of intermediate fragments of the polymer molecules of the type



at the sites indicated by the dotted lines. A similar mechanism of decomposition has been proposed before, to explain the results of cyclization of poly-(o-aceta-mido)imides [9].

When the thermal stability of the poly-(o-acetamido)imides was determined in air an additional maximum appeared in the TGA, DTA and DTG curves, corresponding to oxidation of the acetamide groups.

Our method of preparation enables a wide selection of poly-(o-acetamido)imides to be obtained, with higher viscosity characteristics than the polymers of similar structure prepared by reaction of aromatic diaminodiacetamides with aromatic tetracarboxylic acid dianhydrides [10].

Note that the reaction used here permits preparation of polyimides containing amide side groups other than acetamido groups. This is easily achieved by replacing acetic anhydride by the acid chlorides or anhydrides of other carboxylic acids, capable of fulfilling the function of dehydrating and acylating agents. Thus by using benzoyl chloride instead of acetic anhydride, polyimides containing benzamide groups in the *ortho*-position were obtained.

The polymers with o-benzamide groups, like the poly-(o-acetamido)imides, are soluble in various organic solvents and have film-forming properties.

EXPERIMENTAL

Starting materials. The aromatic tetramines and tetracarboxylic acid dianhydrides were prepared by methods described previously [5, 6].

N-(o-acetamidophenyl)phthalimide. A solution of 0.01 mole of phthalic anhydride in 40 ml of DMF was added dropwise over a period of 1 hr to a solution of 0.01 mole of o-phenylenediamine in 10 ml of DMF. The mixture was stirred for 3 hr at 20° in a current of argon. A previously prepared mixture of pyridine and acetic anhydride (0.1 mole of each) was added to the resulting mixture. The solution was then heated at the boiling point for 4–5 hr, after which it was cooled and poured into water. The white precipitate after recrystallization from alcohol had m.p. 202° (according to the literature, m.p. 202° [11]). Yield 87%. **Bis-N**-(o-acetamido)pyromellitimide. A solution of 0.01 mole of pyromellitic dianhydride in 30 ml of DMF was added dropwise, with stirring, in a current of argon, to a solution of 0.2 mole of o-phenylenediamine in 20 ml of DMF. The reaction mixture was stirred for 3 hr and then a previously prepared mixture of 0.2 mole of acetic anhydride and 0.2 mole of pyridine was added to it. The reaction solution was then heated at the boiling point for 4-5 hr, cooled and poured into water. The white precipitate after recrystallization from nitrobenzene had m.p. $386-387^{\circ}$. Yield 87%.

Found, %: C 64.00, H 3.86, N 11.77. C26H18N4O6. Calculated, %: C 64.73, H 3.76, N 11.60.

(3,3'-Diacetamide-4,4'-diphthalimido)diphenyl oxide. A solution of 0.02 mole of phthalic anhydride in 30 ml of DMF is added dropwise, with stirring, in a current of argon, to a solution of 0.01 mole of 3,3',4,4'-tetra-aminodiphenyl oxide. The reaction mixture was stirred for 3 hr and then a previously prepared mixture of 0.2 mole of acetic anhydride and 0.2 mole of pyridine was added. The solution was then heated at the boiling point for 4-5 hr, cooled and poured into water. After recrystallization from nitrobenzene the white precipitate had m.p. $312-313^{\circ}$. Yield 85%.

Found, %: C 66·1, H 3·74, N 9·2. C₃₂H₂₂N₄O₇. Calculated, %: C 66·9, H 3·85, N 9·75. (3,3'-Diacetamido-4,4'-diphthalamido)diphenylmethane. A solution of 0·02 mole of phthalic anhydride in 30 ml of DMF was added dropwise, with stirring, in a current of argon, to a solution of 0·01 mole of 3,3',4,4'-tetra-aminodiphenylmethane in 20 ml of DMF.

The reaction mixture was stirred for 3 hr, after which a mixture of 0.2 mole of acetic anhydride and 0.2 mole of pyridine was added. The solution was then heated at the boiling point for 4-5 hr, cooled and poured into water. After recrystallization from nitrobenzene the white precipitate had m.p. $268-269^{\circ}$. Yield 92%.

Found, %: C 68.72, H 3.88, N 9.59. $C_{33}H_{34}N_4O_6$. Calculated, %: C 69.25, H 4.19, N 9.89. The poly-(o-acetamido)imides were prepared by the following standard method. A freshly prepared solution of 0.01 mole of the tetracarboxylic acid dianhydride in 10 ml of dry, deoxygenated DMF was added slowly, with stirring, in an inert atmosphere, to a solution of 0.01 mole of the tetramine 10 ml of DMF.

In order to avoid formation of gel the last portions of the dianhydride were added very slowly. The resulting, viscous PACA solution was stirred for 2-3 hr, after which 0.2 mole of pyridine and 0.2 mole of acetic anhydride were added in separate portions or in the form of a previously prepared mixture. The resulting mixture was stirred at the boiling point in an inert atmosphere for 4-5 hr and was then cooled and poured into water. The poly-(o-acetamido)imide, which separated out, was filtered off, washed with water, acetone and ethanol, then extracted with acetone in a Soxhlet apparatus and dried *in vacuo* at 50-70°.

Poly-(o-benzamido)imides were prepared by a completely analogous method, the only difference being that benzoyl chloride was used as the dehydrating and acylating agent in place of acetic anhydride.

Dynamic thermogravimetric analysis of the polymers was carried out in a derivatograph in an inert atmosphere and in air, at a rate of heating of 4.5 deg/min.

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THE HYDRODYNAMIC PROPERTIES OF THE POLYIMIDE FROM THE DIANHYDRIDE OF 3,4,3',4'-TETRACARBOXYDIPHENYL OXIDE AND 9,9-BIS-(4-AMINOPHENYL)FLUORENE*

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The hydrodynamic properties of solutions of a polyimide from the dianhydride of 3,4,3',4'-tetracarboxydiphenyl oxide and 9,9-bis-(4-aminophenyl)fluorene have been investigated and the parameters of the equations relating $[\eta]$ to S_0 and \bar{M}_w have been determined. It was found that beginning at $\bar{M}_w = 400 \times 10^3$ the behaviour of the polymer molecules in solution is in accord with the theories of non-free-draining Gaussian coils. The length of the Kuhn segment characterizing the chain rigidity is A = 20-21 Å.

THE emergence in recent years of soluble polyimides with cyclic structures in the chain [1-7] has enabled us to study the hydrodynamic characteristics of solutions of narrow fractions of these polymers, namely the intrinsic viscosity $[\eta]$, the sedimentation constant S_0 , the molecular weight \overline{M}_w and the second virial coefficient A_2 , and on the basis of these to determine the parameters of the unperturbed chain dimensions.

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