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THE PREPARATION BY A SOLID–SOLID INTERACTION ROUTE OF AROMATIC POLYAMIDE MATERIALS CONTAINING SULPHONE, ETHER AND KETONE LINKAGES

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Abstract

The polycondensation reactions between 4,4′-[sulphonyl bis(*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid (I) and *p*-phenylenediamine (II), 1,5-diaminonaphthalene (III), 4,4′-sulphonyldianiline (IV), 4,4′-diaminodiphenylsulphide (V) 4,4′-methylenedianiline (VI) and 4,4′-oxydianiline (VII) to form aromatic polyamides containing sulphone, ether and ketone linkages were attempted by a solid–solid interaction route. A stoichiometric 1:1 molar ratio of solid reactants was dynamically heated directly in a TG/DSC apparatus, and simultaneous TG/FT-IR was performed to interpret the mechanism of reaction. The results suggest that the polycondensation is dependent on the diamine used. The formation of polyamide was successful when I interacted with II, III, VI and VII. The interaction with IV and V was in part successful because partial decarboxylation of the diacid, made unstable by the diamine, occurred before the condensation reaction.

Keywords: aromatic polyamide materials containing sulphone, polycondensation reactions, solid–solid interaction

Introduction

Many recent papers report the synthesis of new aromatic polyamide materials containing sulphone, kentone or ether groups because of their potential commercial utility as polymers having good thermomechanical properties and thermooxidative stability [1 –6].

In previous work we prepared several aromatic polyamides from 4,4′-sulphonyl bis(*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid with various diamines, by the phosphorylation route [7].

With regard to our previous experience on solid–solid interactions to obtain (in the absence of solvent) molecules oligomeric or polymeric products [8–10], we set out to examine the possibility of obtaining, by interaction between the

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solid reagents, the previously prepared aromatic polyamides, as reported above. In solution, the molecules of the reactants are known to be scattered in the solvent, and the predominant initial reaction is the formation of dimers and trimers. If long chains are required, the reaction must be pushed towards completion by the correct use of appropriate solvent, time and temperature.

In the solid state, the polycondensations are normally carried to in the bulk, using melted reactants, often with the addition of acidic or basic compounds as catalysts, to encourage fast reactions and to eliminate low molecular mass condensation products.

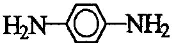
In the preparation of polymeric materials by interaction at high temperatures between solid reactants (and not in the bulk), the results are not always favourable because of the great number of variables involved, the experimental contrasts of extrapolations and the impossibility of explaining many forms of behaviour related to the material properties.

Therefore, considering that a great variety of chemical processes can originate from numerous chemical situations of the system which have been intentionally programmed or have taken place by chance, we believed that it would be interesting to establish the independent process variables by learning the physical properties and chemical reactions and also the material correlations involved in such a reaction process.

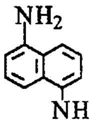
The interactions attempted in this work, involving 1:1 molar ratios of the solid reactants, were between:

4,4′-[sulphonyl bis (*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid (DAC) and

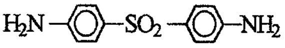
– *p*-phenylenediamine (PPD):



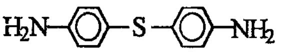
– 1,5-diaminonaphthalene (DAN):



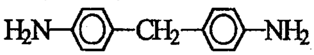
– 4,4′-sulphonyldianiline (DAS):



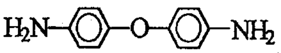
– 4,4′-diaminodiphenylsulphide (AS):



– 4,4′-methylenedianiline (MDA):



– or 4,4′-oxydianiline (ODA):



In a consideration of the linear polycondensation interaction of solid reactants to form the polymeric species, as previously reported, we suppose that all functional groups can be regarded as being equally reactive.

To interpret the mechanism of the reactions and to support the results, simultaneous TG/DSC and TG/FT-IR measurements were performed, registering the thermal effects relating to the reactions and the IR spectra of the gaseous products evolved.

The reactions were performed by introducing finely-powdered stoichiometric mixtures into the pan of the TG apparatus, and the evolved gaseous product was simultaneously determined by FT-IR.

Experimental

Materials

4,4′-[Sulphonyl bis(*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid (DAC) was synthesized according to the literature [11].

Reagent grade aromatic diamines (Aldrich Co.) were used; 4,4′-sulphonyldianiline (DAS) and 1,5-diaminonaphthalene (DAN) were crystallized from ethanol; *p*-phenylenediamine (PPD) and 4,4′-oxydianiline (ODA) were purified by sublimation; 4,4′-methylenedianiline (MDA) was crystallized twice from benzene; and 4,4′-diaminodiphenylsulphide (AS) was crystallized from ethanol/water.

Thermal measurements

The DSC measurements were performed with a DSC 30 Mettler apparatus, the TG-DTG measurements with a TG 50 Mettler apparatus, and the DSC-TG measurements with a POLYMER STA 625 apparatus. All thermal measurements were carried out in a dynamic nitrogen atmosphere (2 l h^{-1}) at 5°C min^{-1}, in aluminium (DSC, DSC/TG) or alumina pans.

In all DSC and DSC/TG measurements, the reference was an empty open aluminium pan.

The ΔH data concerning the thermal processes were evaluated by using the ΔH_{melt} value of indium (6.79 cal g^{-1}) as standard.

TG-FTIR simultaneous measurements

The spectra of the evolved gases consequent to the reaction were recorded with a TGA Du Pont 951, assembled with an FT-IR Nicolet 730 spectrophotometer (4000–400 cm^{-1}). Nitrogen was used as carrier (2.5 l h^{-1}).

Results

Thermal behaviour of (DAC)

DSC-TG simultaneous measurements

The DSC curve of the dicarboxylic acid exhibits an endothermic peak in the temperature range 270–320°C, with T_{max}=305°C, followed by a very broad incomplete endothermic effect due to decomposition.

The enthalpic value of the first process is ΔH=114.76 J g^{-1}, but the shape of the peak, with a shoulder at 300°C, indicates that it is probably the sum of different processes, as an α-β plus an S–L transition (Fig. 1).

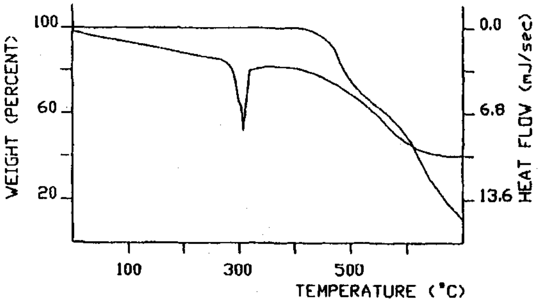


Fig. 1 Simultaneous TG and DSC curves (POLYMER STA 625 apparatus) of DAC

The TG curve of the dicarboxylic acid shows two consecutive processes: the first between 400 and 540°C, with a mass loss of 37%, and the second in the temperature range 540–700°C, with a mass loss of about 53%.

Thermal behaviour of (PPD) (Fig. 2a)

DSC measurements

This product becomes unstable at 60°C and the DSC curve reveals an endothermic effect up to 135°C.

Above this temperature, the curve assumes a sharp endothermic shape (T_{max}=140°C), characteristic of a melting process, followed by a broad endothermic effect (145–180°C).

These thermal effects are not separated from each other, and the total ΔH value is 938.46 J g^{-1}.

TG measurements

The TG curve shows, between 60 and 180°C, a continuous mass loss of about 95%. A comparison of the TG and DSC curves allows the interpretation that the calorimetric processes described in the DSC curve are due to: i) an S–V transition (60–135°C); ii) an S–L transition (135–145°C); and iii) an L–V transition (145–180°C).

Thermal behaviour of (DAN) (Fig. 2b)

DSC measurements

DAN becomes unstable at 140°C, showing a slight endothermic effect up to 185°C.

Above this temperature, the DSC curve assumes a sharp endothermic shape ($T_{\max}$=190°C), characteristic of a melting process, followed again by a large endothermic effect (195–260°C).

These effects are not separated from each other, and the total ΔH value is 808.13 J g^{-1}.

TG measurements

The TG curve shows, between 140 and 270°C, a continuous mass loss of about 98%. A comparison of the TG and DSC curves allows the interpretation that the calorimetric processes described in the DSC curve are due to: i) an S–V transition (140–185°C); ii) an S–L transition (185–195°C); and iii) and L–V transition (195–260°C).

Thermal behaviour of (DAS) (Fig. 2c)

DSC measurements

The DSC curve of DAS displays three effects.

The first effect is observed between 70 and 80°C, with $T_{\max}$=74°C and ΔH= 9.01 J g^{-1}; the second occurs in the range 170–180°C ($T_{\max}$=174°C) and the relative ΔH=85.804 J g^{-1}; the last effect, registered between 300 and 350°C, is due to the sum of several processes, as shown by the endo-exo shape of the curve.

TG measurements

The TG curve of DAS shows only one step in the temperature range 320–350°C, with $T_{\max}$=340°C and a mass loss about of 55%.

Thermal behaviour of (AS) (Fig. 2d)

DSC measurements

The DSC curve of AS contains a sharp endothermic process due to melting which occurs in the range 85–115°C ($T_{\max}$=105°C); the relative ΔH is 94.12 J g^{-1}. This process is followed by broad and irregular endothermic effects in the temperature range 120–700°C.

TG measurements

The TG curve shows two consecutive steps, between 140 and 320°C and between 320 and 700°C, with a mass loss of 80%.

Thermal behaviour of (MDA) (Fig. 2e)

DSC measurements

The DSC curve reveals two consecutive endothermic effects: the first effect (80–90°C, T_{max}=89°C) is due to melting (ΔH=130 J g^{-1}), while the second occurs in the temperature range 90–270°C (T_{max}=248°C) and is due to the L–V transition.

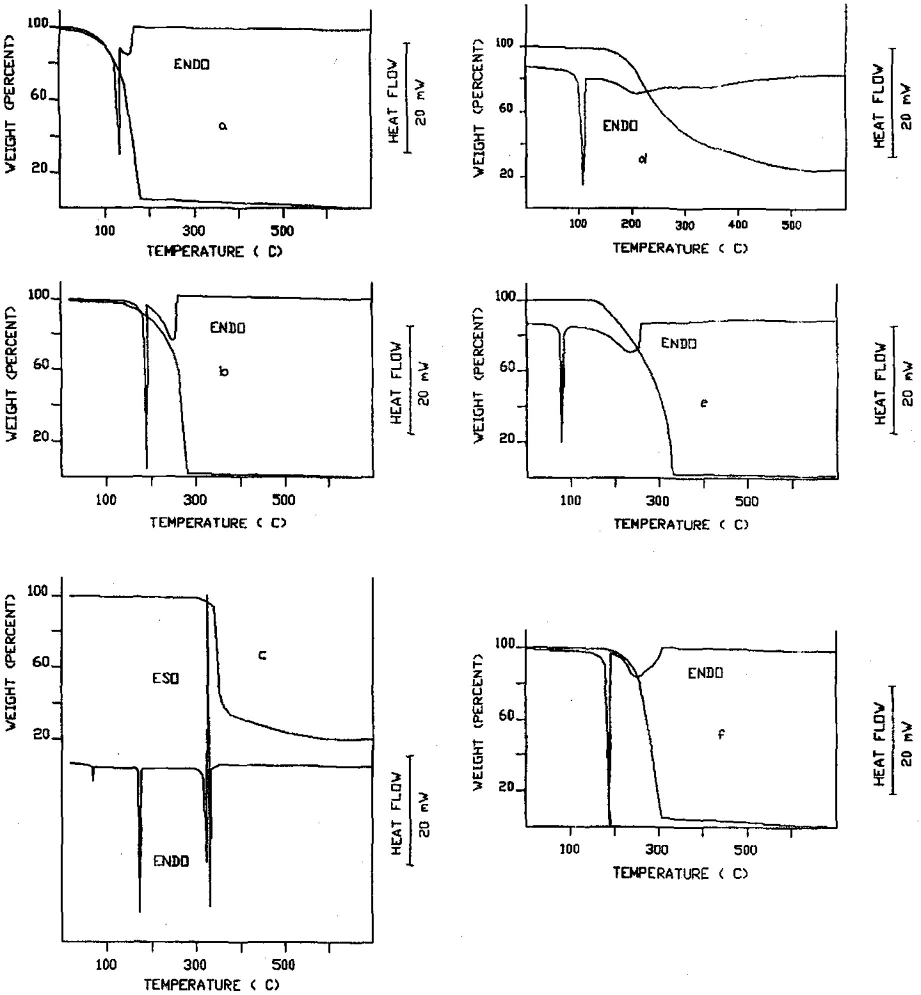


Fig. 2 Simultaneous TG and DSC curves (POLYMER STA 625 apparatus) of: a) PPD; b) DAN; c) DAS; d) AS; e) MDA; f) ODA

TG measurements

The TG curve includes only one step between 170 and 270°C, with a mass loss of 95%.

Thermal behaviour of (ODA) (Fig. 2f)

DSC measurements

ODA becomes unstable at 145°C and gives a weak endothermic effect up to 180°C. After this temperature, a sharp endothermic effect, due to melting, occurs between 180 and 190°C (T_{max}=187°C), followed by another large endothermic effect between 190 and 300°C (T_{max}=250°C), due to the L–V transition.

The three thermal effects are not separable, and the total ΔH value is 803.77 J g^{-1}.

TG measurements

The TG curve displays only one step between 185 and 300°C, with a mass loss of 99%.

Thermal behaviour of a 1:1 DAC:PPD mixture (Fig. 3a)

DSC measurements

The DSC curve of the 1:1 mixture exhibits two endothermic peaks. The first process is registered in the temperature range 70–150°C; the relative ΔH is 72.14 J g^{-1} referred to the mixture, but about 538.7 J g^{-1} if referred to the total amount of PPD present in the mixture. The second sharp peak occurs between 265 and 315°C, with ΔH=105.073 J g^{-1} if referred to the mixture, but 121.4 J g^{-1} if referred only to the total amount of the dicarboxylic acid present in the mixture.

TG measurements

The TG curve agrees with the results reported above: on heating of the 1:1 mixture, we observe a first step in the temperature range 70–180°C, with a mass loss of about 5%, and a second step between 320 and 700°C, which is the sum of several processes.

TG/FT-IR measurements

The IR spectrum reveals the release of H_2O during the first TG step In the temperature range 180–320°C, the release of small amounts of H_2O and CO_2 (not quantitatively registered by TG) is evidenced.

At temperatures higher than 320°C (second TG step), the release of CO_2 is observed.

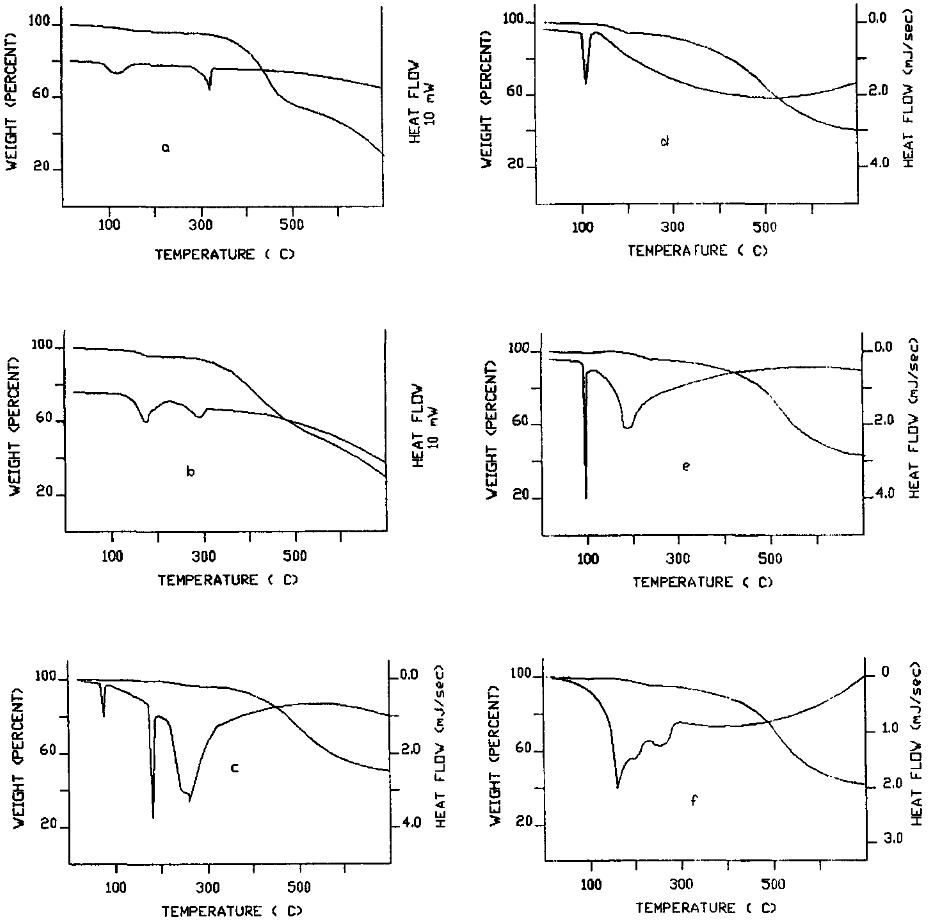


Fig. 3 Simultaneous TG and DSC curves (POLYMER STA 625 apparatus) of 1:1 ù DAC mixture with: a) PPD, b) DAN; c) DAS; d) AS; e) MDA; f) ODA

Thermal behaviour of a 1:1 DAC:DAN mixture (Fig. 3b)

DSC measurements

The DSC curve of the 1:1 mixture shows two endothermic peaks.

The first process is registered in the temperature range 140–225°C. The shape of this peak clearly indicates that at least two thermal effects are involved. The overall ΔH is 72.5 J g^{-1} if referred to the mixture, but about 392.6 J g^{-1} if referred only to the total amount of DAN present in the mixture.

The second sharp peak occurs from 225 and 320°C, but the relative ΔH is not evaluable because it is inside a broad endothermic effect.

TG measurements

The TG curve agrees with the results reported above: on heating of the 1:1 mixture, we observe a first step in the temperature range 120–225°C, with a mass loss of about 6%; a second step occurs between 225 and 700°C, which is the sum of several processes.

TG/FT-IR measurements

The continuous IR spectrum registered between 120 and 225°C reveals increasing quantities of H_2O; after 225°C (up to 320°C), CO_2 is released, with a small residual quantity of water.

At temperatures higher than 320°C, decomposition of the compound occurs.

Thermal behaviour of a 1:1 DAC:DAS mixture (Fig. 3c)

DSC-TG simultaneous measurements

The DSC curve of the 1:1 mixture exhibits three endothermic processes: the first between 80 and 90°C, with the relative ΔH=2.72 J g^{-1} if referred to the mixture and 10.38 J g^{-1} if referred to the amount of DAS present in the mixture; this process can be attributed to the irreversible α-β transition of DAS.

The second effect is due to a melting process that occurs in the temperature range 170–190°C, with ΔH=20.12 J g^{-1} if referred to the mixture and 76, 78 J g^{-1} if referred to the amount of DAS present in the mixture; the third process is registered in the range 215–285°C and the enthalpic value is ΔH=98.03 J g^{-1}.

Considering the ΔH data, it is reasonable to attribute the first process to the α-β irreversible transition of DAS present in the mixture; the second process is due to the melting of DAS (the lower value found can be related to the solution of the solid dicarboxylic acid in the melted DAS); the third process can be attributed to a decomposition of the mixture or a compound if formed.

The TG curve shows a first step in the same range as the third DSC peak, with a mass loss of about 3.9%, followed by a second step between 390 and 560°C, with a mass loss of about 34%.

Above this temperature, decomposition occurs.

TG/FT-IR measurements

Continuous scanning of the IR spectrum between 200 and 350°C reveals that the mass loss corresponding to the first TG step is due to the release of relevant quantities of CO_2 first and then H_2O. Above 350°C, only CO_2 is released.

Thermal behaviour of a 1:1 DAC:AS mixture (Fig. 3d)

DSC-TG simultaneous measurements

The DSC curve indicates an endothermic process between 100 and 115°C, with ΔH=21.9 J g^{-1} if referred to the mixture, but about 92.7 J g^{-1} if referred only to the amount of AS present in the mixture.

The simultaneous TG curve shows a step between 140 and 250°C, with a mass loss of about 5%, followed by another step between 250 and 400°C, with a mass loss of 6.5%. Above this temperature, decomposition occurs.

TG/FT-IR measurements

Continuous scanning of the IR spectrum demonstrates that in the range corresponding to the first TG step, first CO_2 is released, followed by H_2O; at temperatures higher than 300°C, the release of CO_2 is observed.

Thermal behaviour of a 1:1 DAC:MDA mixture (Fig. 3e)

DSC-TG simultaneous measurements

The DSC curve of the 1:1 mixture exhibits two sharp endothermic peaks: the first occurs in the temperature range 85–100°C and the relative ΔH=29.90 J g^{-1} if referred to the mixture, but about 135.4 J g^{-1} if referred to the total amount of MDA present in the mixture. The second thermal effect is very broad and the relative ΔH value is 164 J g^{-1}.

The simultaneously registered TG curve of the 1:1 mixture shows one step in the range 140–230°C, with a mass loss of 4.5%, followed by another step between 280 and 400°C, with a mass loss of about 5%. After this temperature, decomposition of the residual product occurs.

If the mixture is cooled after the first TG step and then reheated up to 700°C, the DSC curve does not contain the first endothermic effect reported above, and the TG curve indicates thermal stability up to 250°C.

TG/FT-IR measurements

Continuous scanning of the IR spectrum under dynamic conditions reveals that the mass loss between 140 and 230°C is due to the release of H_2O; between 280 and 400°C, CO_2 is released.

In the temperature range between 100 and 140°C, a small and quantitatively unimportant release of CO_2 is evidenced.

Thermal behaviour of a 1:1 DAC:ODA mixture (Fig. 3f)

DSC-TG simultaneous measurements

The DSC curve of the 1:1 mixture shows an irregular endothermic effect due to the sum of several different processes between 140 and 220°C.

The TG curve of the 1:1 mixture points to two steps. The first step, between 140 and 230°C, presents a mass loss of 4.5%; a second step, between 280 and 400°C, involves mass loss of about 5%. Above this temperature, decomposition of the residual product occurs.

TG/FT-IR measurements

While the TG curve, between 140 and 230°C, contains only one step, continuous scanning of the IR spectrum reveals that the in this temperature range the mass loss is due to the release of H_2O and a small quantity of CO_2; between 280 and 400°C, CO_2 is released.

Discussion

The results obtained as regards the condensation by the solid–solid interaction route agree satisfactorily with the results obtained by the phosphorylation route for DAN, PPD, MDA and ODA.

When AS or DAS is used, the results do not reveal simple behaviour and condensation can possibly be achieved in an intermediate reaction.

To confirm that the condensation was completed, we dissolved part of the product, obtained after the release of water molecules, in an appropriate solvent to eliminate a possible excess of diamines, and the other part in dioxane to eliminate a possible excess of DAC.

The purified compounds were successively analysed by DSC and TG analysis.

The observed thermal behaviour was in each case similar to that of the original product, obviously with the disappearance of the thermal effects exhibited up to condensation.

For all the obtained products, the considerable quantity of CO_2 released during the second TG step clearly shows that the predominant reaction is the formation of oligomers of low molecular weight, so a high number of free carboxylic groups are present. This was also evidenced by the low value of η_{inh} (~0.1 dL g^{-1}) of the condensation products relative to those obtained by the phosphorylation route (η_{inh}=0.7 dL g^{-1}).

The thermal behaviour and the IR data reported in the Results section allow some considerations depending on the diamine used.

Interaction of DAC with DAN, PPD, MDA or ODA

The thermal behaviour of DAN, PPD, MDA and ODA exhibits a noteworthy difference in thermal stability relative to DAC (140°C for DAN, 60°C for PPD, 200°C for MDA, 160°C for ODA and 400°C for DAC).

The TG/DSC and TG/FT-IR analyses of the 1:1 mixtures of DAC with these four diamines show that a condensation reaction occurs.

Furthermore, the ΔH values found when the thermal effect is referred to the total amount of diamine in the mixtures clearly demonstrate that the interaction occurs in the melted diamine, so the condensations can be considered to take place in the bulk and not by a solid interaction.

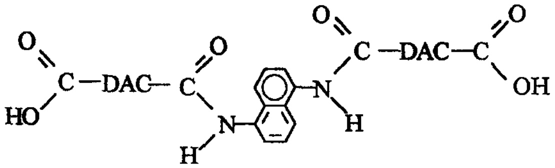
Therefore, it is reasonable to assume that DAC is soluble in melted DAN, PPD, MDA or ODA.

The dissolved DAC probably behaves as an acidic catalyst and allows the condensation. The product obtained at temperatures higher than that of condensation becomes unstable an releases CO_2.

The proposed reactions are:

1:1 DAN:DAC mixture

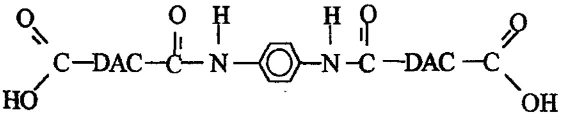
1) 140–225°C: DAN melting (DSC endothermic peak), condensation (1° TG step) with release of H_2O (TG/FT-IR) and formation of



2) 225–320°C: decarboxylation (2° TG step) with release of CO_2 (TG/FT-IR)
3) 320–700°C: decomposition

1:1 mixture PPD:DAC

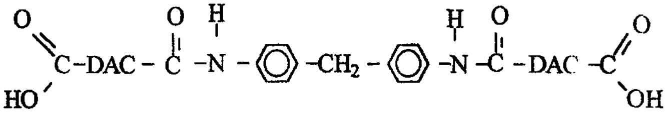
1) 70–180°C:
PPD melting (DSC endothermic peak), condensation (1° TG step) with release of H_2O (TG/FT-IR) and formation of



2) 180 –320 °C: release of CO_2 (TG/FT-IR)
3) 320 –700 °C: decomposition

1:1 MDA:DAC mixture

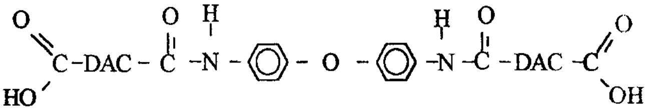
1) 85–100°C: MDA melting (DSC endothermic peak)
2) 140–230°C: condensation (1° TG step) with release of H_2O (TG/FT-IR) and formation of



3) 280–400°C: decarboxylation (2° TG step) with release of CO_2 (TG/FT-IR)
4) 400–700°C: decomposition

ODA:DAC mixture

1) 140–190°C: ODA melting and condensation (DSC irregular peak, 1° TG step)
190–220°C: release of H_2O (TG/FT-IR) and formation of



2) 280–400°C: decarboxylation (2° TG step) with release of CO_2 (TG/FT-IR)
3) 400–700°C: decomposition

Interaction of DAC with DAS or AS

As concerns the interaction between DAC and DAS or AS, the TG curves, supported by the IR spectrum, show a significant loss in mass due to the release of CO_2 in the first step in the temperature range 140–250°C.

This indicates that the first decomposition step is due to the partial decarboxylation of DAC (made unstable by the presence of the diamine).

Similar behaviour, through quantitatively less evident, is registered before the condensation of DAC with MDA or ODA.

At temperatures higher than 250°C, the undecomposed DAC interacts with the diamine, as evidenced by the TG/FT-IR showing the simultaneous release of H_2O and CO_2.

The impossibility of distinguishing these two processes does not permit a quantitative evaluation of the condensation and decarboxylation.

The different behaviour exhibited by DAS and AS relative to the other diamines shows that the crystal structure of the reactants does not always permit the nucleation of the products if several conditions are not achieved.

In the studied case, the experimental conditions required for condensation are:

- the melting of the diamine
- the solubilization of DAC in the melted diamine
- the catalyst behaviour of DAC
- an appropriate temperature range.

The low value of η_{inh} found for the condensed product confirms the important role played by the solubility of the forming polymer in the polymerization medium [7].

The presence of S atom in AS or DAS probably makes these two diamines less reactive relative to DAC, which cannot behaves as a catalyst. The dissolved acid provides the experimental conditions for decarboxylation until the increasing temperature reaches the appropriate value for the condensation reaction, but part of the DAC is already decomposed.

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