Polyimides from dianhydride and diamine: structure property relations by thermogravimetric analysis (t.g.a.)*

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Novel polyimides were synthesized from 1,4-benzenediamine, 2-methyl 1,4-benzenediamine, 2-pentadecyl 1,4-benzenediamine, pyromellitic dianhydride and 3,3',4,4'-benzophenone tetracarboxylic dianhydride. Polymers obtained with 2-pentadecyl 1,4-benzenediamine yield good flexible films. Physical and thermal properties of these polyimides are discussed in relation to the molecular structure. A well defined order of stability was observed for the polyimides studied.

(Keywords: polyimide synthesis; 1,4-benzenediamine substituted; dianhydrides; characterization; properties; thermal-stability)

INTRODUCTION

The aromatic polyimides are known to possess outstanding physical properties, notably a high degree of stability to heat as well as excellent mechanical properties of shaped articles. Polyimides can be prepared either by condensation of dianhydrides with diisocyanates[1] or by the reaction of an aromatic diamine with a dianhydride to give a poly(amic acid) followed by dehydration to give the polyimide. The polyimides formed from a variety of diamines have been reported and the dianhydride unit has been varied widely[2]. Unfortunately, total aromatic polyimides, due to their relatively high rigidity, are very nearly intractable, being insoluble in all but the strongest acids and very difficult to process into useful films and fibres.

These materials may be made tractable, however, by insertion of a limited number of atoms or groups chosen so as to impart a controlled amount of additional flexibility to the chain. For example, the introduction of oxygen atoms into a typical aromatic polyimide should decrease the rigidity of the chain. Another approach to the fabrication problems would be to retain as much aromaticity as possible, to preserve thermal stability while introducing a flexible aliphatic based unit to lower the transition temperature. William et al.[3] reported the preparation and polymerization of a series of novel diamines containing polyoxyethylene units which lowered the transition temperatures of polyimides.

Dine-Hart, Wright[4] and Bell[5,6] investigated the effect of diamine structure on the thermoxidative stability of aromatic polyimides. Ghatge et al. investigated the structure–property relations of polyimides by thermal analysis. Polymers were obtained either from diisocyanates[7–10] or diamines[11,12] and different dianhydrides.

In the present work, some novel polyimides (synthesis and characterization of these diamines will be reported elsewhere) made by reaction of diamines with dianhydrides are described and the physical and thermal properties of these polymers were studied to correlate the structure–property relations. Thus, polyimides have been prepared by reacting pyromellitic dianhydride (PMDA) with:

    (1) 1,4-benzenediamine (BDA)
    (2) 2-methyl 1,4-benzenediamine (MBDA), and
    (3) 2-pentadecyl 1,4-benzenediamine (PBDA).

Although pyromellitimides with BDA have been reported earlier, the polymer was again synthesized under identical conditions for the comparative study. Polyimides have also been obtained with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and diamines above. The scheme for the polyimide synthesis is represented in *Figure 1*.

EXPERIMENTAL

Materials

BTDA and PMDA were obtained from the Gulf Oil Company (Houston, Texas) and Koch-Light Laboratories (England), respectively. These dianhydrides were purified by crystallization from dry acetic anhydride and/or by sublimation under reduced pressure.

N,N-dimethylacetamide (DMAC) was dried with P_2O_5 and twice distilled before use.

All the diamines were synthesized in the laboratory.

Polymer synthesis

Diamine (0.01 mol) and DMAC (20 ml) were added to a 100 ml round bottom three neck flask with a magnetic stirrer, nigrogen gas inlet, a drying tube and thermometer. The mixture was stirred to form a clear solution and the temperature of the flask maintained 0°C. To this solution dianhydride (0.01 mol) was added over a period of 15 min
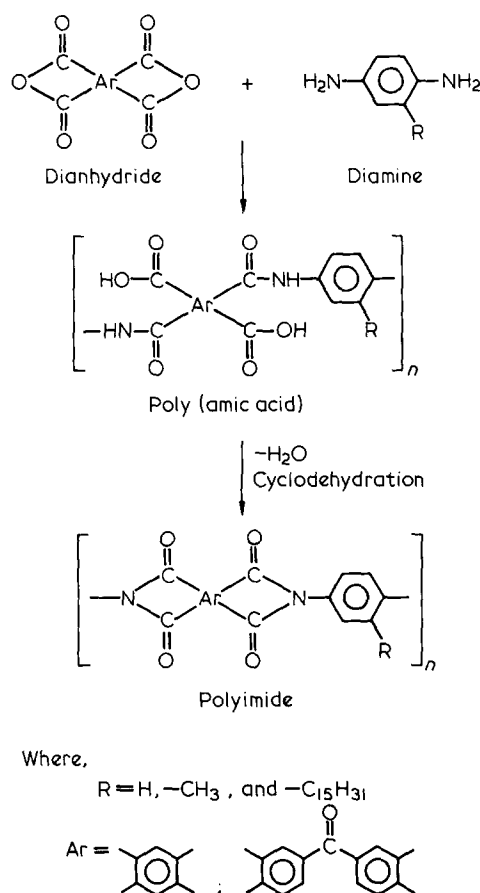

Figure 1 Scheme for polyimide synthesis

with vigorous stirring. Residual dianhydride was washed with 5–10 ml dry DMAC and 12% solution was made. The whole mixture was stirred for 1 h at 0°C, 1 h at 10–15°C and allowed to stand overnight at 25°C. A nitrogen atmosphere was maintained in the reaction flask throughout the course of reaction. A viscous poly(amic acid) solution obtained at this stage was used for the film preparation.

Poly(amic acid) films

Poly(amic acid) solutions were cast onto a dry glass plate to form a uniform film (approximately 0.005 cm). The solvent was removed in the inert atmosphere below 70°C. The resultant colourless-to-pale yellow films were only partly dry (70–75% solid content) and were peeled off gently after cooling to 25°C.

Polyimide conversion

The poly(amic acid) films were dried at 25°C at reduced pressure and then the temperature was uniformly raised up to 300°C over a period of 9 h. Yellow to red polyimide films were obtained. The polyimide obtained with BDA and PMDA was brittle, whereas flexible, transparent yellow films are obtained with PBDA. Polyimide films obtained with BTDA were more flexible than the corresponding polypyromellitimide film and increased flexibility was observed for PBDA–BTDA reaction product.

Characterization

Viscosity measurements were made with 0.5% solutions of poly(amic acid) in DMAC, at 30°C using modified Ubbelhode viscometer. The infra-red spectra were re-

corded on a Perkin–Elmer E-137 infracord spectrophotometer. Thermogravimetric analysis (t.g.a.), differential thermal analysis (d.t.a.) and derivative thermogravimetry (d.t.g.) were made simultaneously (in air at a heating rate of 9°C/min, using a Mom Budapest derivatograph type OD 102 as described by Paulik *et al.*[13]) on samples dried for 4 h at 110°C under reduced pressure of 10^{-3} mm of Hg.

RESULTS AND DISCUSSION

Table 1 summarizes the analysis of all the polyimides synthesized in the present investigation. Addition of dry dianhydride to the amine solution was shown to yield high molecular weight intermediate poly(amid acid), while the addition of diamine to the solution of dianhydride or mixing together in equimolar proportions of reactants gave low molecular weight poly(amic acid)[14]. Since moisture causes hydrolysis of poly(amic acid) and hinders its cyclodehydration, due care was taken to conduct the reactions under nitrogen atmosphere and perfectly dry conditions.

On comparing the viscosity (η_{inh}) of the poly(amic acid) (*Table 1*) prepared from different substituted 1,4 benzenediamines, it was found that in every case (i.e. with PMDA or BTDA), polymers obtained with BDA have higher viscosities than corresponding polymers from MBDA. Similarly polymers with MBDA have higher viscosities than poly(amic acid) prepared from PBDA. Using this data, the diamine series occupies the order of reactivity as:
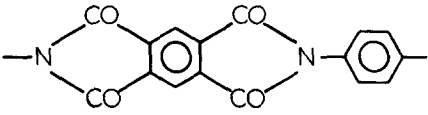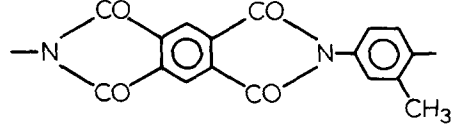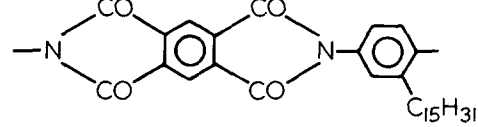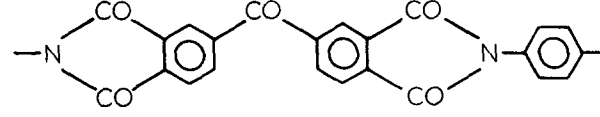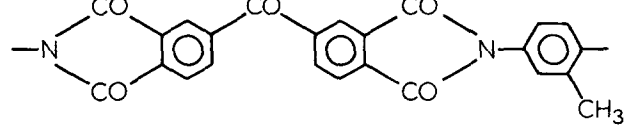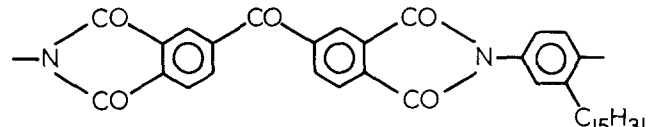
$$BDA > MBDA > PBDA$$

It was found by Dine-Hart *et al.*[4] that with several diamines the steric factors come into play and the presence of substituents *ortho* to the amino function prevented the formation of high molecular weight poly(amic acid). Thus, the relatively low molecular weight (inherent viscosity) of polymers with PBDA is due to the passivating influence of the bulky pentadecyl group on passing from BDA to PBDA.

It was also observed that the viscosities of poly(amic acids) prepared with PTDA (D–F) were lower than the corresponding poly(amic acid) obtained with PMDA (A–C).

Poly(amic acid) solutions were precipitated by water, filtered, dried to obtain the powdered poly(amic acid) and the i.r. spectra of these powdered poly(amic acids) were recorded in nujol mulls. I.r. spectra of the polyimide films were recorded directly without the use of any medium or mulling agent. The spectra of polymers agree well with that of model compounds and show characteristic absorptions. Thus poly(amic acid) spectrum showed NH bands at 3200–3400 cm^{-1}. Complete transformation of poly(amic acid) to polyimide was confirmed by strong absorptions at 1780, 1720, 1380 and 720 cm^{-1} (characteristic of imide structure) and the disappearance of NH bands at 3200–3400 cm^{-1}, in i.r. spectra of polyimide.

In general the elemental analysis (*Table 1*) of dried polyimides are in good agreement with the calculated values for carbon and hydrogen, although for some polyimides analysis obtained were 1–2% less for carbon. This may be due to the fact that while analysing, some samples remained unionized even at higher temperatures. This is supported by earlier work[4,12] and also by the

Table 1 The elemental analysis and some of the characteristics of the polyimides

Polyimide	Repeating unit	Analysis	C%	H%	Viscosity* (dl/g)
A		Found: Calcd:	6503 66.20	2.76 2.06	0.7755
B		Found: Calcd:	65.56 67.10	3.10 2.65	0.7288
C		Found: Calcd:	72.06 74.40	7.4 7.2	0.5573
D		Found: Calcd:	67.93 70.05	3.10 2.54	0.7686
E		Found: Calcd:	69.36 80.58	3.60 2.94	0.6279
F		Found: Calcd:	74.95 75.49	6.21 6.62	0.4891

* The inherent viscosity (η_{inh}) of the precursor poly(amic acid) (0.5% in DMAC at 30°C) is reported

percentage weight losses in thermogravimetric analysis (t.g.a.), which are not more than 70% at 900°C.

It has been shown by Koton and Sazanov[16] that the thermal stability of polyimides is affected greatly by the structure of the diamine t.g.a. curves obtained for the six polyimides (A–F) are given in *Figures 2* and *3*. Temperature characteristics such as T_0 (initial decomposition temperature), T_{10} (temperature for 10% weight loss), T_{max} (temperature for maximum rate of decomposition), T_s (half volatilization point temperature) and *IPDT* (integral procedure decomposition temperature) were calculated[15] and are given in *Table 2*.

T_0 and T_{10} are some of the main criteria of the heat stability of polymers (with dynamic heating). The higher the value of T_0 and T_{10}, the higher will be the heat stability of a given polymer[17]. A comparison of T_0 and/or T_{10} of polypyromellitimides (Polyimides A–C) indicates that polyimide (A) (obtained with BDA) has the highest thermal stability, as it contains only phenylene units in the diamine component. Alkyl group substitution in the benzene ring of the diamine component has a marked effect on the thermal stability of polyimides, as shown by a considerable clearance in T_0 and T_{10} values for polyimides (B) and (C).

Table 2 shows that temperature of maximum rate of decomposition T_{max} for polypyromellitimides studies varies within a narrow range of temperature 605 ± 20°C. T_{max} is highest for polyimide (A) (625°C) and decrease in series,

polyimide (C) being the lowest (590°). Polyimide (C) showed maxima at 470°C and 590°C. The T_{max} at 590°C was assigned to regular polyimide structure decomposition, whereas T_{max} at lower temperature may be due to loss of the bulky pentadecylbalkyl group.

T_0, T_{10} and T_{max} are single feature criteria and therefore, to get a quantitative picture of the relative stability of polypyromellitimides, T_s (half volatilization point) and *IPDT* (integral procedure decomposition temperature) were calculated. *IPDT* represents the overall nature of t.g.a. curve for the temperature range of 25–900°C. T_s is the temperature at which half of the ultimate weight loss has occurred. The ultimate weight loss was measured at 900°C.

It was observed that both T_s and *IPDT* values are highest for polyimide (A), suggesting its high thermal stability. The decreased thermal stability of polyimides (B) and (C) due to the presence of methyl (polyimide B) or pentadecyl (polyimide C) side chain in polymer backbone, were supported by decreases in T_s and *IPDT* values.

Sroog[18] and Nishizaki *et al.*[19,20] have also suggested that introduction of side-chain or main-chain aliphatic linkages such as benzidine and 3,3'-dimethyl benzidine sharply reduce thermal stability of wholly aromatic polyimides.

Results of the present investigation are in good agreement with the conclusions by above workers. Thus thermal stability of polyimides based on MBDA or
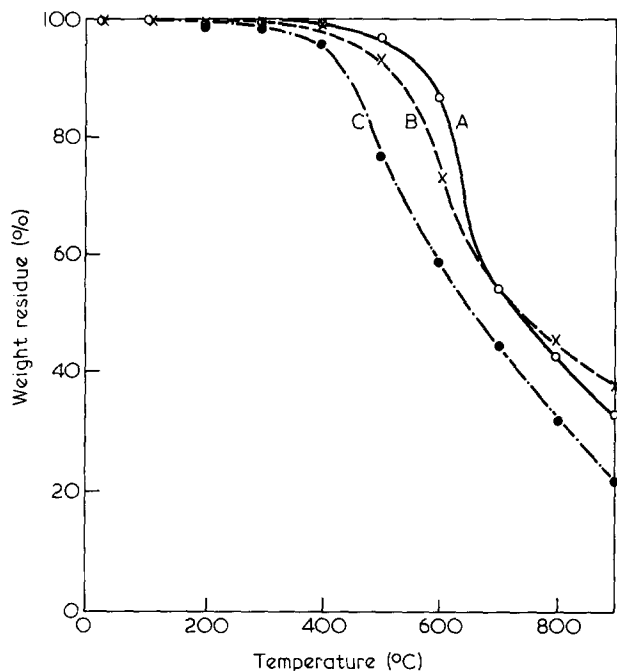
Figure 2 T.g.a. curve in air at 9°C/min for polyimides **A**, **B** and 3; A=BDA+PMDA, B=MBDA+PMDA and C=PBDA+PMDA
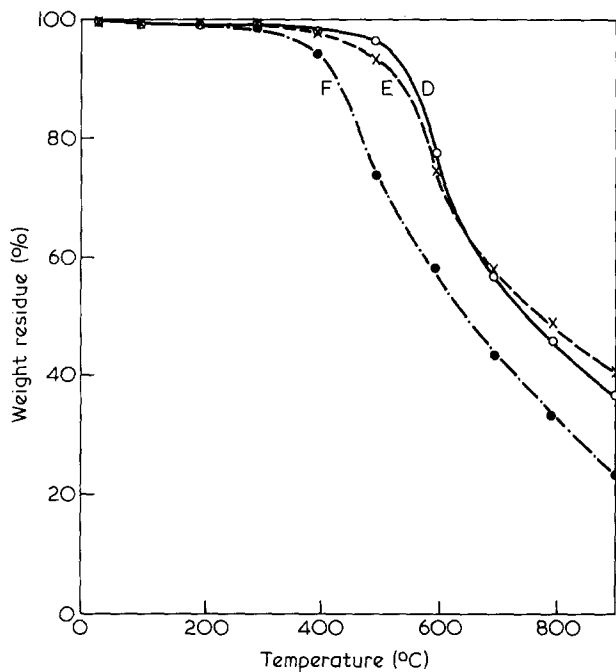

Figure 3 T.g.a. curve in air at 9°C/min for polyimides **D**, **E** and F; D=BDA+BTDA, E=MBDA+BTDA, F=PBDA+BTDA

PBDA is less than the corresponding BDA polymer. These studies were extended to the polyimides obtained with BTDA. Temperature characteristics (T_0, T_{10}, T_{max}, T_s and $IPDT$) derived from t.g.a. curves shown in *Figure 3* are given in *Table 2*. A good correlation was observed between the thermoxidative stability of polyimides and the structure of the diamine component used to obtain these polyimides. Thus in BTDA–polymer series of polyimides (**D**, **E** and **F**), polyimide (**D**) higher thermal stability, as supported by the characteristics at higher temperatures. An ordered descending trend was obtained from polyimide (**D**) to polyimide (**F**), through the polyimide (**E**).

Table 2 Temperature characteristics of polyimides

Polyimide	T_0	T_{10}	T_{max}	T_s	$IPDT$
A	420	580	625	630	648
B	400	540	585	600	612
C	340	430	470, 590	570	612
D	400	560	600	620	627
E	380	525	600	610	613
F	310	430	460, 580	655	550

T_0 = Initial decomposition temperature
T_{10} = 10% weight loss temperature
T_{max} = Maximum rate of decomposition temperature
T_s = Half volatilization point temperature
$IPDT$ = Integral procedure decomposition temperature

On comparing the thermal stability of polypyromelli-timides (polyimides A–C) and that of polyimides based on BTDA (D–F), it was observed that polypyromellitimides were thermally more stable than corresponding poly-imide with BTDA. These results are similar to those obtained by Dine-Hart et al.[4]

Thus these studies reveal the lower thermal stability of polyimides (**B, C, E** and **F**) as compared to an all aromatic polyimide systems (**A** and **D**). This is not unexpected in view of the aliphatic nature of the substituent linkages in the diamine component of polyimide systems studied. The gain in flexibility due to increased aliphatic chain length appears to be balanced by a lower thermal stability, attributable to the same increased chain length.

ACKNOWLEDGEMENT

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