

Polyimide Model Compounds

J. H. HODGKIN, *Division of Applied Organic Chemistry, C.S.I.R.O.,
Melbourne, Victoria, 3001, Australia*

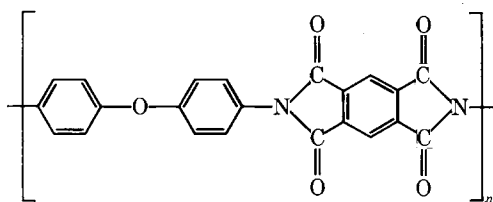
Synopsis

Pyromellitic dianhydride was reacted with various substituted aryl amines, under conditions similar to those used for polyimide formation. Yields of model imides have been greatly improved over those found in previous studies. The work has shown that the major impurities formed when the reactions were performed in solutions of *N,N*-dimethylformamide or *N,N*-dimethylacetamide were adducts containing chemically bound solvent residues.

INTRODUCTION

Polyimides formed by the reaction of pyromellitic dianhydride (PMDA) with aromatic diamines are among the most useful polymers available for extreme environments. There are many different forms commercially available, and a vast amount of research^{1,2} has been carried out on these materials.

In spite of this, there has been considerable uncertainty as to their true structure, e.g., the variation in the quoted figures for the degree of cyclization in the purely condensation type of polyimides such as du Pont "H film" (idealized structure I):



I

Results obtained from degradation studies^{3,4} indicate as little as 50% cyclization; techniques such as infrared spectroscopy have been interpreted to show greater than 85% cyclization.^{5,6} Differences such as these are important, as a knowledge of the polymer structure is vital to the understanding of its properties.

Perhaps the most important effect of defects⁷ in the polymer structure is on thermal and chemical stability, as most of the noncyclized groups have less resistance to heat or chemical degradation than the cyclized imide structure.

Considering this, it is surprising that most of the work on polyimide model compounds has been with very simplified and unrepresentative models, e.g.,

the use of phthalic anhydride instead of PMDA.^{8,9} Our previous work¹⁰ with model polyimides has indicated the pitfalls of considering simplified models for the diamine component of the polymer. In this paper, we consider the problems of the anhydride part of the polymer using model compounds.

Previous reports^{11,12} on the reactions of PMDA with aromatic monoamines in solvents normally used for polymerization have been published. In one case,¹¹ the yields of model compound were relatively high (between 77% and 87%), although purity and structures were inadequately determined. Because the three anilines used contained other reactive groups (*p*-hydroxy, *p*-carboxy, and *p*-carboxymethyl groups) and the products were nonmelting and insoluble, it is very probable that reactions other than imide formation were taking place.

In the second paper,¹² a large number of aromatic amines with ortho, meta, and para substituents were reacted with PMDA in dimethylformamide (DMF). The yields of the desired model compounds ranged from 17% to 76%. This is very low, as it is generally assumed that for most practical step-growth polymerizations, yields should be above 95%. For six-membered imides such as those obtained from 1,4,5,8-naphthalenetetracarboxylic dianhydride, high yields are common.¹⁰

Because of the varied results previously obtained for PMDA model imides, a number of the experiments were repeated, and also the reactions were carried out in different solvents and under different conditions. An effort was made to relate the cyclization conditions used to those generally encountered in polymerization experiments. Even where films of polyamic acids are cyclized in inert atmospheres, large amounts of the polar solvents remain in the films during the cyclization.^{1,5} Thus, it was hoped that our results would be applicable in studies of polyimide thermal stability.

EXPERIMENTAL

Materials

The reagents used during this study were commercial materials of the highest available purity. The diamines were purified by recrystallization to constant melting point. The pyromellitic dianhydride (PMDA) was purified by sublimation. The solvents employed were B.D.H. AnalaR-grade reagents and, where applicable (DMF, DMAC, DMSO), they were stored over 4A molecular sieves.

General

Melting points were determined in capillary tubes in a Fisher-Johns apparatus for temperatures up to 350°C; above this temperature, a Rigaku Thermogravimetric analyzer with simultaneous differential scanning calorimetry was used to determine melting points and decomposition temperatures. Microanalyses were carried out by the Australian Microanalytical Service, CSIRO, Melbourne. Infrared spectra were recorded on a Unicam SP200 spectrophotometer in potassium bromide discs or as evaporated films on sodium chloride plates. Proton magnetic resonance (PMR) spectra were recorded on a Varian HR 100 instrument.

TABLE I
Major Infrared Peaks for N,N'-Bis(R)-1,2,4,5-benzenetetracarboxydiimides (KBr Disc)

R	Infrared peaks cm^{-1}	
	Carbonyl ^a	Other major peaks
4-Chlorophenyl	1780(w), 1721	1125, 818, 723
4-Nitrophenyl	1775, 1734	1532, 1357(nitro), 854, 838, 748, 722
3-Nitrophenyl	1772, 1720	1551, 1358(nitro), 845, 820, 742, 726
4-Methoxyphenyl	1782(w), 1720	1252(methoxy), 819, 729
4-Methylphenyl	1784(w), 1720	1410, 810, 726
Phenyl	1720	1132, 751, 730

^a (w) = Weak.

For the work reported in this paper, the yields shown were determined primarily by physical separation. The cyclized imides with para substituents are extremely insoluble in cold DMF, unlike the various side reaction products.¹² The presence of small amounts of imides remaining with the impurities or with the recrystallization solvents were detected by nuclear magnetic resonance spectroscopy. Infrared spectroscopy was used to monitor the reaction progress, but it was found to be an unreliable method for determining total yield of model imide in a mixture, as a number of the other reaction products have similar spectra. This may be one of the factors contributing to the controversy arising over the degree of cyclization of polyimides.

The reactions were carried out in three-necked flasks equipped with a nitrogen inlet and outlet, a dropping funnel, and a condenser. The reagents were first mixed slowly at room temperature and then heated on an oil bath with vigorous magnetic stirring. All the model imides synthesized have been previously described.¹² Their structures were verified by analysis, infrared spectra (Table I), melting points, and decomposition temperatures.

RESULTS AND DISCUSSION

Imide Formation

Repetition of some of the work of Mosher and Chlystek¹² gave very good agreement with the yields and properties of the products they obtained. However, their experimental conditions are not very similar to those used in polymer formation. Their conditions consisted of heating the monomers at 150–160°C in DMF for only 10–15 min with some extra heating time as the solution was concentrated under vacuum. Also an important factor in their experiments was the use of a large excess (50–100%) of the substituted aniline.

In our experiments, stoichiometric quantities of the purified reagents were used, and, in general, the conditions were designed to approximate those in polymerization systems.^{1,2} Variations in the low-temperature treatment of the two monomers were tried as this is a feature of the polymerization technique,^{1,2,13} but it had no noticeable effect on the yield of imide. Such a result is consistent with the work of Dror and Levy¹⁴ which showed that with PMDA the first stage of imide synthesis—formation of amidoacid (II)—is a

fast, highly favored reaction even at low temperatures. This is in contrast to the cyclization step to the imide (III); which only occurs slowly at high temperatures:

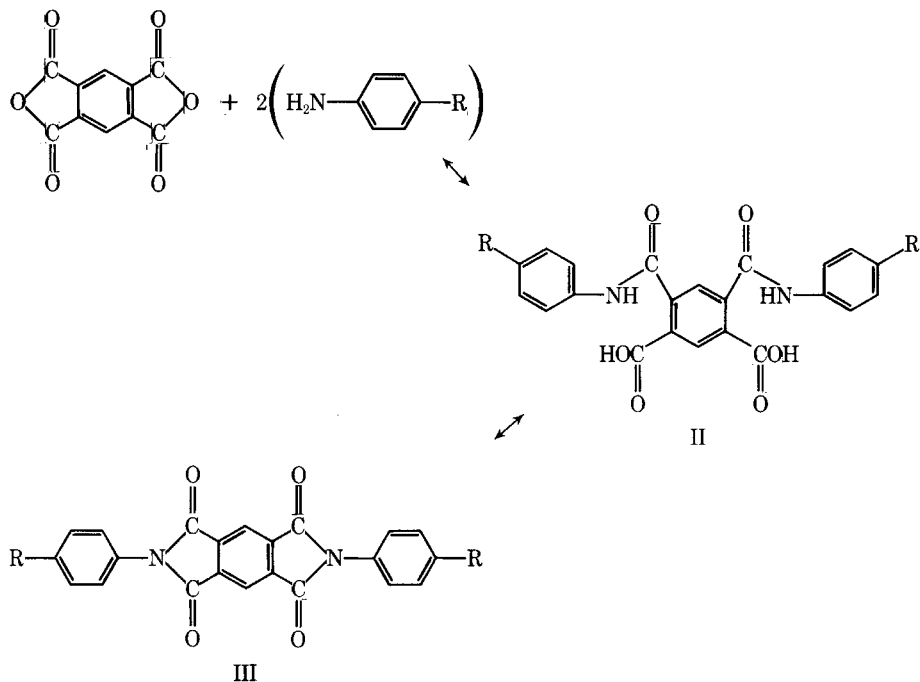


Table II illustrates the difference in product yield caused by variations in the reaction conditions during imide formation. This is an extreme example as the *para*-nitro group is strongly electron withdrawing and hence deactivating.

Similar but not such extreme examples of improvements were obtained with other substituted anilines, and it was apparent that the rates of formation of the imides were strongly influenced by the electronegativity of the non-amino functional group on the ring. Although the kinetics of each reaction were not studied in detail, some optimization of yields was attempted for the various aniline derivatives shown in Table III. In this case, all the reactions were carried out in DMF under conditions indicated by infrared spectroscopy to be the best for that particular amine. For reasons discussed below, these yields are probably close to the best possible obtainable in polymerization type of conditions where evaporation to dryness under nitrogen and then high temperature baking are common.

As other solvents are commonly used in polyimide preparation, further experiments were done with these model compounds using a variety of solvents. Some of these, like dimethyl sulfoxide (DMSO) and dimethylacetamide (DMAC), are commonly used in polymerization experiments, and others such as glycerol are not. Table IV shows the results of these experiments.

The reaction progress was followed qualitatively by continual monitoring with infrared spectroscopy, and so it was possible to get close to the optimum conditions. For example, the reaction of *p*-anisidine with PMDA in glycerol

TABLE II
Reaction of 0.02 mole *p*-Nitroaniline and 0.01 mole PMDA in DMF (40 ml)

Exp. no.	Yield (III), R = NO ₂ , %	Reaction conditions (time at 150–160°)	Recovery method ^a
1	18	10–15 min (ref. 12)	no filtrate treatment
2	21	4 hr plus vacuum evaporation to 50%	no filtrate treatment
3	29	12 hr	no filtrate treatment
4	70	17 hr	filtrate evaporated to dryness under nitrogen, then washed with cold DMF
5 ^b	85	22 hr	as above

^a The solutions were cooled overnight and the crystalline product filtered. The filtrate was treated as shown.

^b Further heating did not increase yields.

TABLE III
Reaction of 0.02 mole of Substituted Aniline and 0.01 mole of PMDA in DMF

Aniline used	Yield III, %		Reaction conditions (time at 150–165°)
	Ref. 12	This work ^a	
<i>p</i> -Chloraniline	28	71	12 hr
<i>p</i> -Nitroaniline	18	85	22 hr
<i>m</i> -Nitroaniline	19.5	69	5 hr
<i>p</i> -Anisidine	76	84	2 hr
<i>p</i> -Toluidine	58	83	4 hr
Aniline	52	68	8 hr

^a The recovery method included filtration of the bulk of the product from the cold DMF solution and then evaporation of the filtrate under N₂ and extraction of impurities from the remaining imide using cold DMF.

at 140°C gave a quantitative yield in 3 hr, whereas similar conditions with *p*-toluidine only gave a 80% yield. At 180°C for 5 hr, the yield of the *p*-toluidine imide increased to 91%, but higher temperatures or longer times did not improve the yield.

Solvents such as glycerol and DMSO cannot be removed completely by evaporation, but quantitative evaluation of the products was obtained by precipitation with water and crystallization of the imides from DMF. The yields of imide in DMSO were surprisingly low for a polymerization solvent, but this may have been caused by decomposition of the solvent at higher temperatures.

Side Reactions

The yields of the desired imide model compounds shown in Tables III and IV, although a considerable improvement on those quoted in previous work, are, in general, far from that expected (or hoped for) in a normal step-growth polymerization.¹⁵ For this reason, it was important to determine the other types of products formed in these model reactions, particularly in the commonly used solvents DMAC and DMF.

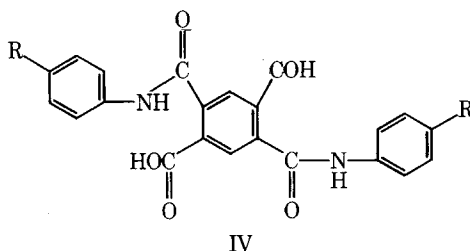
TABLE IV
Imide Yields Obtained by the Reaction of PMDA (0.01 mole) and a Substituted Aniline (0.02 mole) in Solvent (40 ml)

Solvent	Yield of aniline derivative, %, and (reaction time), hr				
	<i>p</i> -Chloro-aniline	<i>p</i> -Nitro-aniline	<i>p</i> -Anisidine	<i>p</i> -Toluidine	Aniline
Glycerol	81 (8)	18 (12)	100 (3)	91 (5)	85 (8)
Acetic acid ^b	67 (48)	—	72 (10)	—	—
DMSO	15 (12)	—	40 (5)	—	—
DMF ^b	71 (12)	85 (22)	84 (2)	83 (4)	68 (8)
DMAC ^b	74 (4)	85 (17)	81 (3)	—	—

^a Time required to reach maximum yield.

^b These solvents were used at or near reflux, the others, at 140–180 °C.

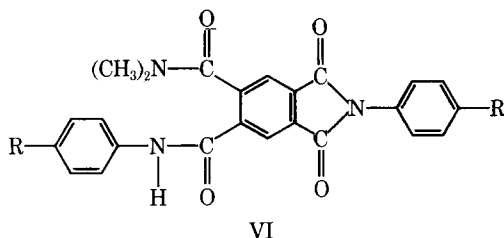
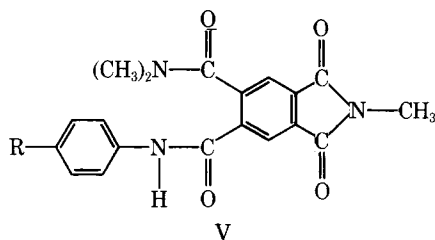
With all the DMAC and DMF experiments, the side reaction products were obtained as waxy solids from the mother liquors. Provided the reaction had been carried out to completion, as shown in Table III, further heat treatment (under vacuum or nitrogen) of these residues did not produce more diimide, thus precluding amido acid residues such as II and IV:



The infrared spectra of residues from all the preparations had strong imide and amide peaks at ≈ 1780 , 1720 , and 1630 cm^{-1} , with only low OH or NH bands, and were unlike any amido acid spectra (see Fig. 1). The broadness of some of these bands showed that there were complex mixtures of products, and this was confirmed by proton magnetic resonance spectroscopy (PMR). The most notable feature of the PMR spectra, for example, Figure 2, was the presence of a number of sharp and strong amide N-methyl peaks apart from those from the solvent (DMF or DMAC). Again in the aromatic proton region, there were always complex patterns in both the imide and para-substituted aromatic amine areas.

Attempted isolation of pure fractions of the various reaction products using either column chromatography or solvent extraction were unsuccessful. The only pure products obtained were small amounts (1–3%) of the acetanilides and formanilides of the respective amines. No one major product by-product was formed.

Thus, there is limited evidence for structures such as V, VI, and many isomeric variations, but the results are not consistent with materials which will be readily cyclized to the correct imide model compounds:



N-Methylimides such as V have been found among the impurities obtained in the reactions of naphthalic anhydrides in DMF.¹⁶ Other possible structures include various isoimides, amidines (cf., work on aromatic polyamides formed in DMF¹⁷), and decarboxylated compounds.

The results of the model compound work in this paper indicate that cyclization to the correct imide structure during the formation of a PMDA-type of polyimide would, at best, be not much greater than about 75% complete. Furthermore, a mixture of many different impurity structures are formed, some of which contain chemically bound solvent residues. These impurities do not have strong OH or NH peaks in the IR, so the normal spectroscopic methods,^{1,6} based on determining the amounts of cyclizable amidoacids, etc., would give erroneous results for imide formation. An adequate knowledge of

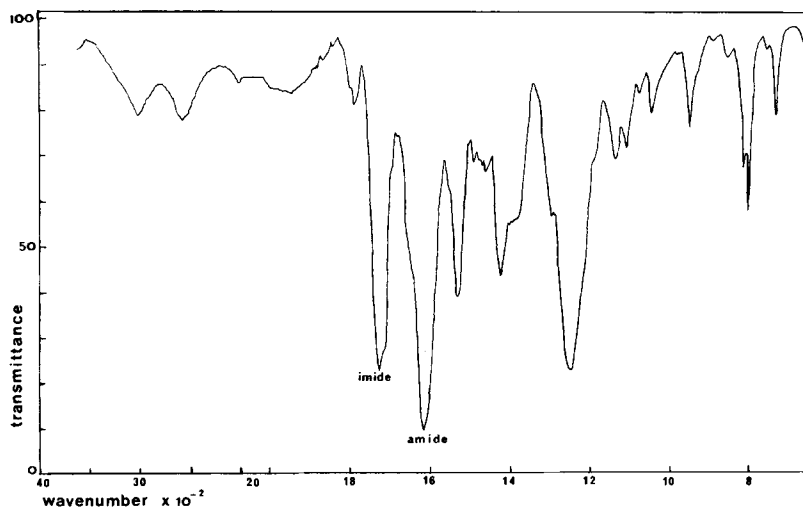


Fig. 1. Infrared spectrum of side reaction product from the interaction of PMDA and *p*-anisidine (KBr disc).

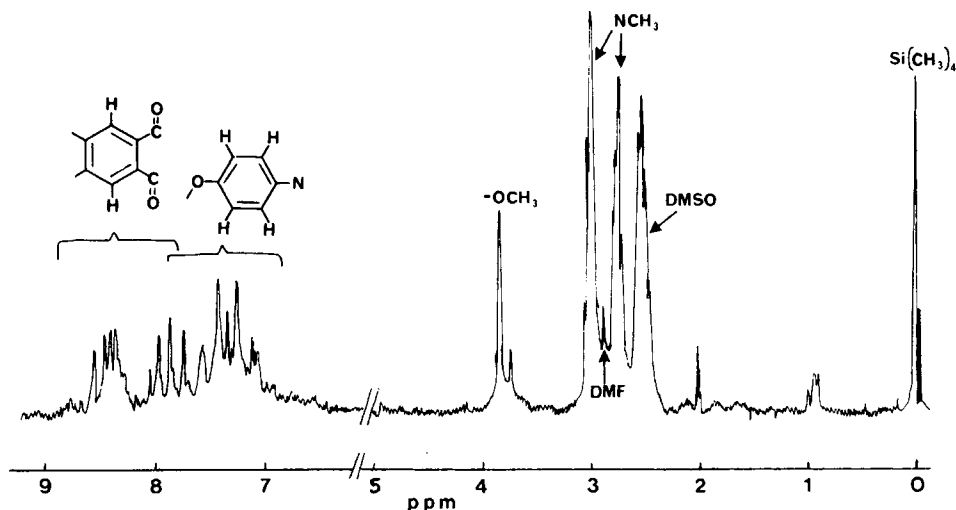


Fig. 2. Proton magnetic resonance spectrum of side reaction product from the interaction of PMDA and *p*-anisidine (100 MHz).

the type of impurities and their concentration is necessary for the determination of mechanisms of thermal degradation of commercial polyimides and could lead to methods of improving their stability.

References

1. N. A. Androva, M. I. Bessonov, L. A. Laius, and A. P. Rudakov, *Polyimides, a New Class of Heat-Resistant Polymers*, Israel Program for Scientific Translations, Jerusalem, 1969.
2. R. J. Cotter and M. Matzner, *Ring-Forming Polymerizations*, Vol. B-2, Academic Press, New York, 1972.
3. S. D. Bruck, *Polymer*, **6**, 319 (1965).
4. K. N. Vlasova, M. L. Dobrokhtova, L. N. Suvorova, and I. N. Emelyanov, *Soviet Plast.*, **10**, 26 (1971).
5. M. Lee, D. Stoffey, and K. Neville, *New Linear Polymers*, McGraw-Hill, New York, 1967, Chap. 8.
6. E. Sacher and D. G. Sedor, *J. Polym. Sci. A-2*, **12**, 629 (1974).
7. V. V. Korshak, *Russian Chem. Rev.*, **42**, 303 (1973).
8. P. H. Hermans and J. W. Streef, *Makromol. Chem.*, **74**, 133 (1964).
9. K. Kurita and R. L. Williams, *J. Polym. Sci. A-1*, **11**, 3125 (1973).
10. J. H. Hodgkin, *J. Polym. Sci.*, in press.
11. S. S. Gitis, U. M. Ivanova, S. A. Nemleva, and Z. N. Seina, *Zh. Org. Khim.*, **2**, 1261 (1966).
12. W. A. Mosher and S. J. Chlystek, *J. Heterocyclic Chem.*, **9**, 319 (1972).
13. E. L. Johnson, *J. Appl. Polym. Sci.*, **15**, 2825 (1971).
14. M. Dror and M. Levy, *J. Chem. Soc., Perkin II* (12), 1425 (1974).
15. R. W. Lenz, *Organic Chemistry of Synthetic High Polymers*, Interscience, New York, 1967.
16. P. H. Grayshar, A. M. Kadhim, and A. T. Peters, *J. Heterocyclic Chem.*, **11**, 33 (1974).
17. S. N. Kharkov, V. P. Kabanov, and L. P. Grechushrikava, *Vysokomol. Soedin., Ser. A*, **16**, 2045 (1974).

Received July 29, 1975

Revised October 15, 1975