

Polyimides from Diisocyanates, Dianhydrides, and Tetracarboxylic Acids

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Synopsis

High molecular weight polyimide resins have been prepared by the reaction of diisocyanates and a mixture of dianhydrides and their acids in the presence of a tertiary amine catalyst. The polyimides thus formed can be made into tough flexible films similar to those polyimides prepared by the conventional method of reacting a dianhydride with a diamine. The preparation of high molecular weight polymer is affected by the purity of reagents, the anhydride-acid ratio, temperature, and moisture. Evidence from model compound studies is presented regarding the nature of the reaction mechanism.

INTRODUCTION

Because of their growing commercial importance, several processes have been developed for the preparation of polyimides:

1. The reaction of a diamine and a dianhydride in a polar solvent to provide a polyamic acid that, on subsequent heating, loses water and forms a polyimide. This is of the most commercial importance.

2. The reaction¹ of a diester of a tetracarboxylic acid and an aromatic diisocyanate to provide a polyamic acid ester that on heating, forms a polyimide with the loss of alcohol.

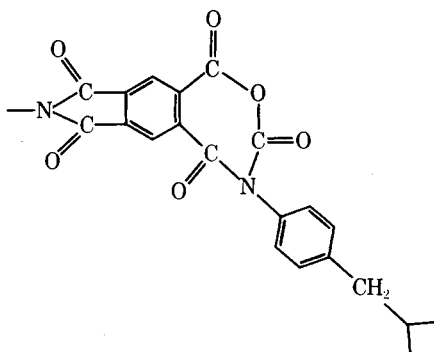
3. A Netherlands patent² discloses the reaction of dianhydrides and/or tetracarboxylic acids with diisocyanates in a polar solvent, but reports production of only low molecular weight or insoluble polymers. These investigators did succeed in making films from the lower molecular weight material, but only with long, involved curing schedules.

R. A. Meyers³ also investigated the dianhydride-diisocyanate reaction in solution and under melt-fusion conditions and obtained insoluble polyimides. In solutions, he did obtain a dimethylformamide (DMF) soluble-fraction that he postulated to be a seven-membered ring adduct (see page 2962).

Recently, P. S. Carleton, et al.⁴ have found that the rate of imide formation from the reaction of anhydrides and isocyanates is enhanced by the presence of water. This, they say, holds true for both mono- and difunctional reagents. They suggest that the water hydrolyzes the isocyanate to urea which reacts with anhydride to form imide.

Alberino⁵ reports on the preparation of moldable powders from the reaction of benzophenonic tetracarboxylic acid dianhydride (BTDA) + NCO

compound. The inherent viscosities of these polymers, however, are quite low (0.2 to 0.3 dl/g), suggesting a low molecular weight polymer. Miller⁶ reported on the preparation of polyimides, ester, urethane-imide copolymers by the reaction of carboxylic acid diaryl sulfones with isocyanates containing at least one pair of vicinal carboxyl groups.



All the polyimides prepared via the isocyanate route described above were either produced as a precipitate in the reaction medium or as low-viscosity solutions. High temperatures $\sim 150^{\circ}\text{C}$ and long reaction times were needed to produce the polymer, and supported films and/or coatings were obtained only after extended cure cycles at elevated temperatures. Self-supporting films were not prepared, apparently because a high enough molecular weight could not be obtained for the precursor polymer.

In the following study we wish to report our work on this reaction via model compound studies, to shed some light on the nature of the reaction. In addition, we have examined the effects of time, temperature, concentration, catalyst, etc., to determine their roles in the reaction leading to high molecular weight polymer formation. Furthermore, we wish to report on the mechanical and thermal properties of film made from the above polymer-forming reaction.

EXPERIMENTAL

Properties

Inherent viscosity measurements were made on 0.5% solutions of the polymers in dimethylacetamide (DMAC) at 24°C with the use of a Cannon-Fenske Viscometer (size 75). Infrared (IR) spectra were recorded on a Beckman IR-12 instrument. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were made with the du Pont 900 and 950 Analyzers in air at $10^{\circ}\text{C}/\text{min}$ and a flow rate of 0.2 l./min. The tensile strength and elongation of polymer films were measured as per ASTM-D882. Flexibility was determined as per ASTM-D2176 (MIT Fold Endurance—1 kg-load).

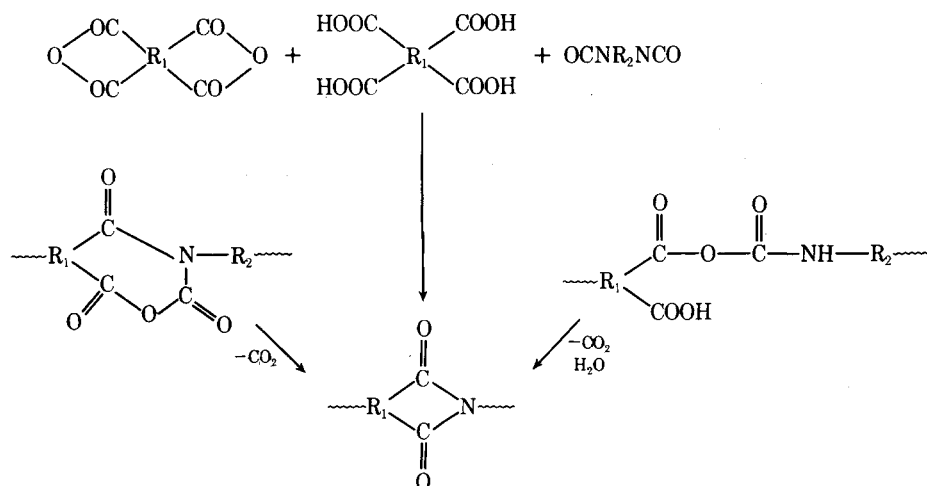
Films were prepared by casting the polymer solution on a suitable substrate; a coating bar with a gap adjustment for the wet film was used. The films were cured to $150\text{--}200^{\circ}\text{C}$, removed from the substrate, and clamped on metal frames for further curing to 300°C .

Materials

All reagents are commercially available and were used in purified form. Solvents were used as received and also after distillation.

Polymer Preparation

The diisocyanates were condensed at both ambient and elevated temperatures with a mixture of dianhydride and acid, either in the presence or absence of a tertiary amine catalyst such as triethylamine, benzyldimethylamine, etc. The acid portion was obtained either by direct addition of the tetracid or by hydrolysis of the anhydride with the appropriate amount of water. A generalized scheme illustrating the reaction that takes place with diisocyanate, dianhydride, and tetracid is shown below.



A typical procedure for preparing high molecular weight polyimide is as follows:

To a heated mixture (50–60°C) of 6.54 g (0.03 mole) of pyromellitic dianhydride (PMDA) and 5.08 g (0.02 mole) of pyromellitic acid (PMA) in 75 g of dry DMAC, are added five drops of benzyldimethylamine (BDMA). Then 12.6 g (0.05 mole) of 4,4'-diisocyanato diphenyl ether (DIPE) is added in increments while the reaction temperature is maintained between 50–60°C. The reaction begins very soon after the first addition of the isocyanate, and copious amounts of CO₂ are evolved. When all the isocyanate is added, the reaction mixture is maintained at temperature until maximum viscosity is reached and the CO₂ evolution subsides. The reaction mixture is cooled to room temperature and can be diluted with additional solvent to adjust the viscosity of the solution. Inherent viscosities range from 0.50 to 1.2 dl/g for creasable films.

Chemical analysis of PMDA to determine the anhydride and acid content involved two acid-base titrations: (1) After conversion of PMDA to the dimethyl ester, a reaction in which PMA is unaffected; and (2) after hydrolysis of PMDA to PMA.⁷

RESULTS AND DISCUSSION

Model Compounds

It has been reported that isocyanates react with carboxylic acid anhydrides to yield the corresponding imide and carbon dioxide.⁴ Recently, the reaction between phthalic anhydride and phenyl isocyanate has been repeated, and a yield of 63% for N-phenylphthalimide was obtained when heating occurred for 5 hr at 121°C with pyridine as catalyst. We have also run this reaction as well as several others at various temperatures, in order to gain some insight into the product distribution. The data for these reactions are reported in Table I.

TABLE I
Model Compound Reactions

No.	Reactants	Catalyst	Solvent	Temp., C	Time, hr	CO ₂ , %	Comments ^a
A	C ₆ H ₅ NCO + PA	BDMA	DMAC	150°	1	79	46% yield C ₁₄ H ₉ N ₁ O ₂ ; mp: 206°C
B	C ₆ H ₅ NCO + PA	BDMA	NMP	200°	1	98	80% yield C ₁₄ H ₉ N ₁ O ₂ ; mp: 207°C
C	C ₆ H ₅ NH ₂ + PA	—	DMAC	150°	1	—	43% yield C ₁₄ H ₉ N ₁ O ₂ ; mp: 206°C
D	C ₆ H ₅ COOH + C ₆ H ₅ NCO	BDMA	DMAC	160°	1	—	42% yield C ₁₃ H ₁₁ N ₁ O ₂ ; mp: 154°C
E	2C ₆ H ₅ COOH + MDI ^b	BDMA	DMAC	160°	1	91	50% yield C ₂₇ H ₂₂ N ₂ O ₂ ; mp: 240°C

^a Elemental analysis for A, B, and C

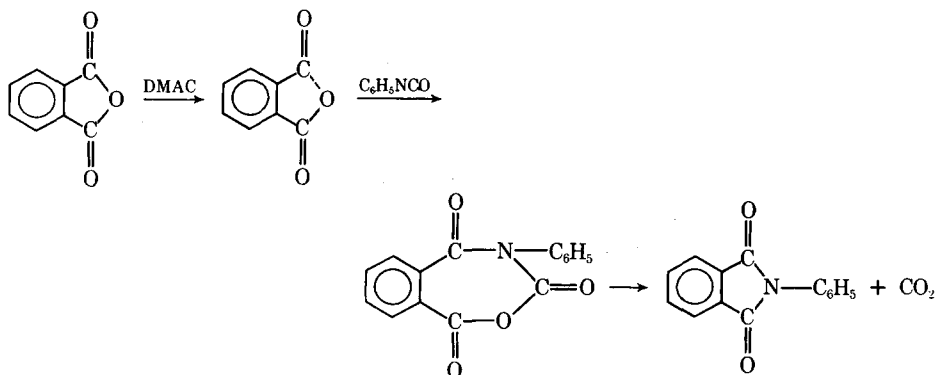
	C	H	N	O
Calc	75.35	4.03	6.27	14.32
Found	75.68	4.08	6.53	13.51
Elemental analysis for D				
Calc	79.25	5.58	7.11	8.13
Found	79.34	5.46	7.16	8.17

Elemental analysis for E

Calc	79.80	5.43	6.91	7.90
Found	79.84	5.39	6.93	7.93

4,4'-Diisocyanato diphenyl methane.

In all cases, reaction does proceed to the designated product, but the stoichiometric amount of CO₂ evolution is not obtained until a temperature of about 200°C is reached. The product of the amine-anhydride reaction and the isocyanate-anhydride reaction are the same. In the former reaction, the amine adds to the anhydride to form an amide-acid that is dehydrated to the imide. On the other hand, it has been proposed⁸ that the isocyanate-anhydride reaction proceeds by the addition of a partially polarized anhydride to the isocyanate, followed by decomposition of the intermediate-cyclic mixed anhydride with loss of CO₂ and formation of imide as shown below:



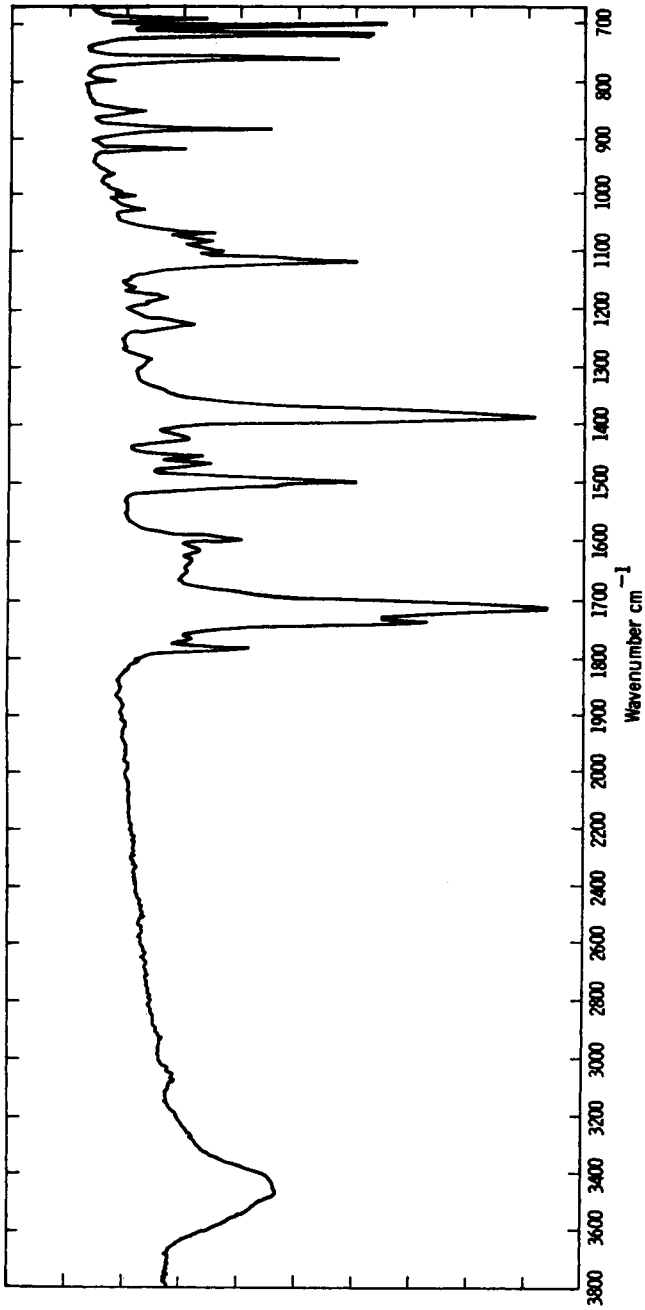


Fig. 1. IR spectrum of N-phenylphthalimide.

Figure 1 is the IR spectrum of the product of $C_6H_5NCO + PA$ reacted at $200^\circ C$. It is identical to an authentic sample of *N*-phenylphthalimide (Sadtler reference spectra #16607).

Polymer Systems—Initial Studies

Initial attempts by us to prepare high molecular weight polyimides from diisocyanates and dianhydrides were unsuccessful. One obtains a precipitate early in the reaction when the dianhydride or its corresponding acid is reacted with a diisocyanate in presence of a *t*-amine catalyst. Rapid carbon dioxide evolution also occurs during the reaction to the extent of 75% for the anhydride-NCO reaction and about 64% for the acid-NCO reaction. This precipitate was isolated, and its IR spectrum is shown in Figure 2. Examination of the spectrum indicates the presence of the imide (absorptions at 1780, 1730, and 720 cm^{-1}). It is worth noting that a considerable amount of imide formation is apparent, as evidenced by the intensity of these bands. It seems possible that because of this imide formation, the product precipitates out

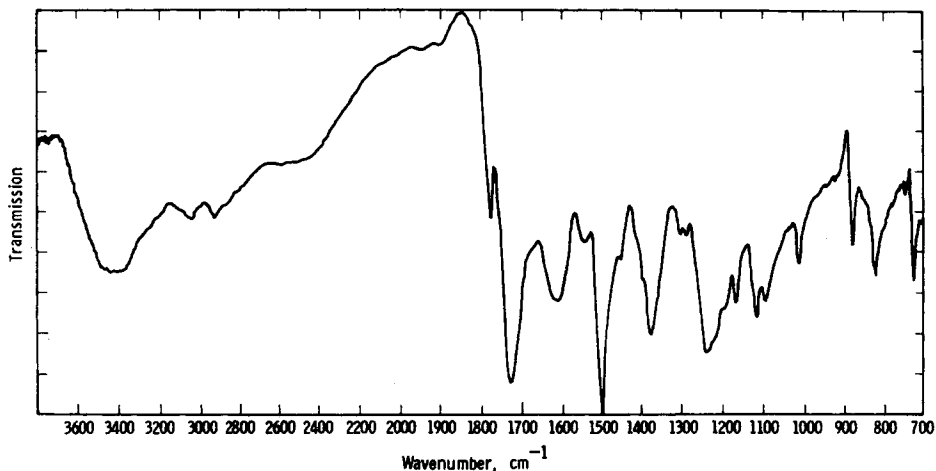


Fig. 2. IR spectrum of gelatinous precipitate from PMDA + DIPE reaction.

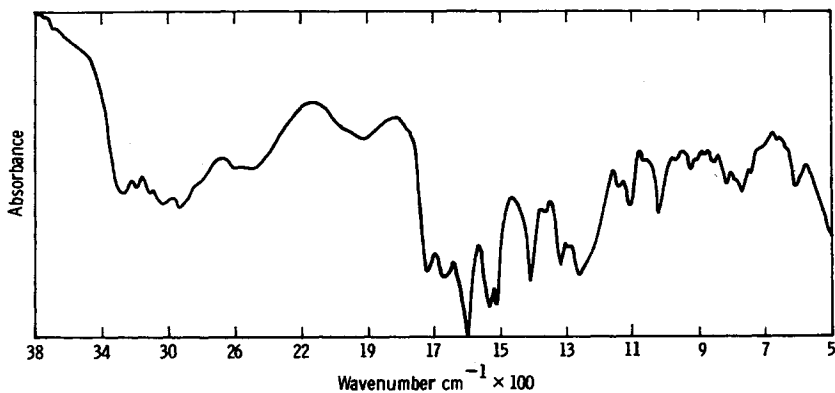


Fig. 3. IR spectra of PMDA + MDA cured 40 min at $100^\circ C$.

TABLE II
Reaction of PMDA + PMA + MDI^a

Run no.	PMDA/PMA ^b	CO ₂ evolution, %	Gardner Viscosity and comments
A	100/0	78	Precipitate—brittle film
B	80/20	80	<D-brittle film
C	78/22	79	Z2-flexible film
D	70/30	88	Z-flexible film
E	65/35	85	Z-flexible film
F	60/40	89	Z3-flexible film
G	55/45	89	K-flexible film
H	50/50	90	F-flexible film
I	45/55	89	<A-brittle film
J	30/70	83	<A-brittle film
K	20/80	75	<A-brittle film
L	0/100	65	Brittle film

^a 21% solids in DMAC, with BDMA used as catalyst. Reaction temperature between 60° and 75°C.

^b Uncorrected ratio (PMDA used as received).

before molecular weight can be built up. In the corresponding dianhydride reaction between PMDA and methylene dianiline (MDA), very little, if any, imide formation is apparent, even after 40 min at 100°C (see Fig. 3).

High Molecular Weight Polymer

We further explored this reaction by employing a mixture of the dianhydride and its corresponding acid. A series of reactions was run by varying the

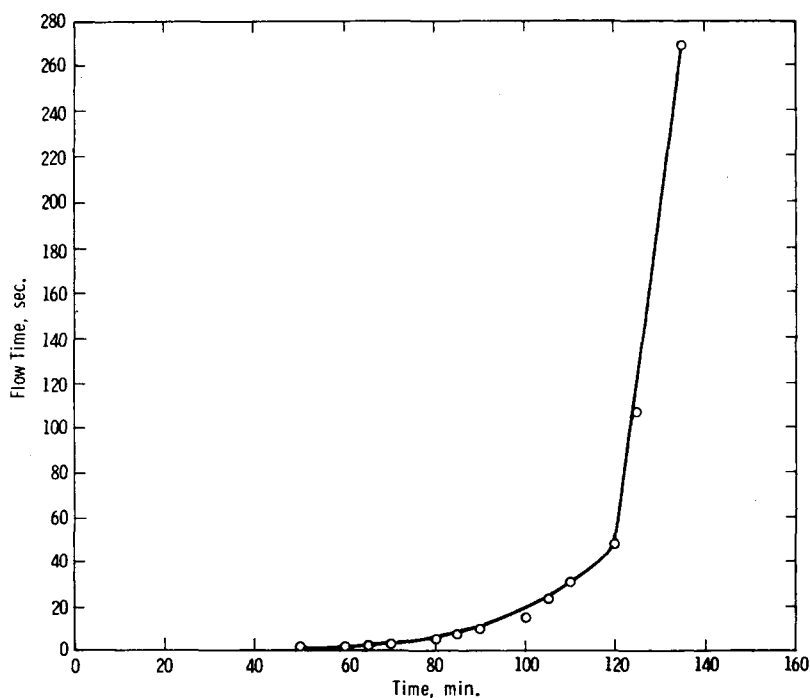


Fig. 4. Viscosity change vs. time for the reaction PMDA₆₀ + PMA₄₀ + MDI at 60°C.

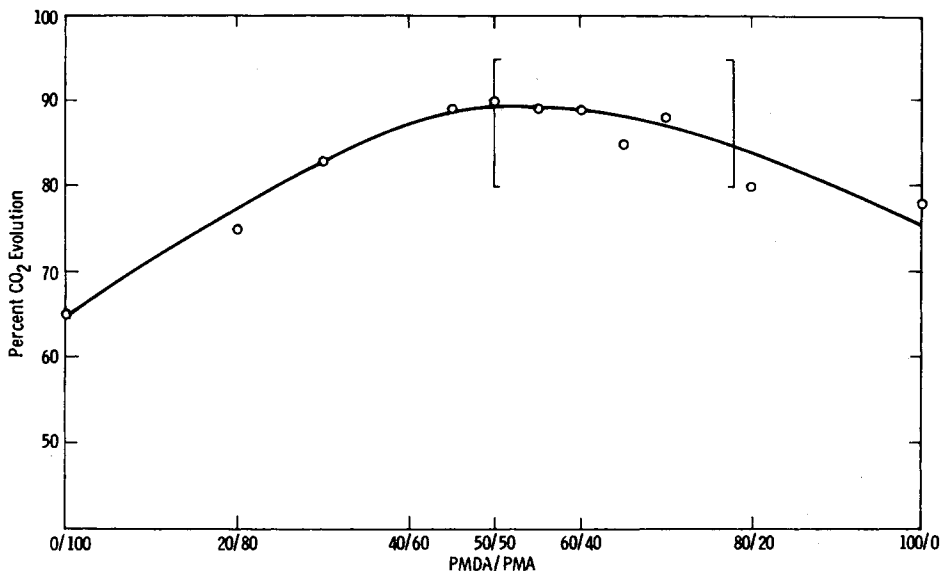


Fig. 5. Carbon dioxide evolution for the reaction PMDA + PMA + MDI at 60–75°C.

anhydride/acid ratio from 100/0 to 0/100 mole-%. Within specified limits, the reaction proceeds with a loss of CO₂ and the reaction medium increases substantially in viscosity. This viscosity increase with time is similar to that obtained with the reaction of a dianhydride with a diamine; however, reaction time to reach maximum viscosity is much shorter (see Fig. 4). Table II presents the data on these reactions. The carbon dioxide evolution is plotted in Figure 5. The amount of CO₂ was measured by passing the gas through an ascarite and barium hydroxide trap connected in series. The quantitative amount of CO₂ is not obtained, but neither does it drop below 65%—and it peaks at about 90%, which corresponds to a 50/50 PMDA to PMA ratio. The bracketed portion of the curve is the area within which film of sufficient flexibility can be prepared and creased without cracking. We have not made a detailed study of the significance of the CO₂ evolution, but since only 90% of it is evolved, either it is bound in an intermediate product requiring further heat to expel the remaining CO₂, or there is unreacted isocyanate. A higher-percentage CO₂ evolution is obtained at a PMDA/PMA ratio of 100/0.

Effect of Catalyst

As previously mentioned, the reaction between PMDA and MDI (4,4'-diisocyanato diphenyl methane) in the presence of a catalyst results in precipitate formation. This reaction was repeated in the absence of a catalyst in DMAC and NMP (N-methyl pyrrolidone) solvents. No precipitate formed, and an increase in viscosity was not observed. This precipitate formation manifests itself by the formation of a cloudy solution and eventually forms a pasty mixture. If, however, the reaction between PMDA₆₀ + PMA₄₀ + MDI is run without a catalyst, the reaction mixture tends to gel. In the presence of a catalyst, the tendency for gelation is suppressed and a high molecular weight polymer is formed and no precipitate is observed. Apparently, the

catalyst provides a route whereby polymer growth is preferred over gelation and precipitate formation when a mixture of the anhydride-acid is used.

Effect of Moisture

In addition to the anhydride-acid balance and catalyst, the presence of water can inhibit high polymer formation. If water is present, it can upset the anhydride/acid ratio and also react with isocyanate to form a urea. Films cast from resins containing an excessive amount of water become black and almost brittle after aging 15 min at 250°C in air. Films cast from resin solutions free from excessive water do not discolor or become brittle, even after 80 hr at 325°C. If the reaction between PMDA + PMA + MDI is run by carefully controlling the water content, a higher molecular weight polyimide is formed (compare reactions A and B in Table III below).

TABLE III
Effect of Solvent

Run no.	PMDA/PMA	Solvent	Solids, %	Gardner Viscosity	Inherent viscosity
A ^a	60/40	NMP ^b	19	Z	0.73 dl/g
B ^a	60/40	NMP ^c	19	Z5	1.21 dl/g

^a Both of these resins yield creasable films.

^b Solvent *N*-methyl pyrrolidone used as received.

^c Solvent *N*-methyl pyrrolidone distilled and stored over molecular sieve 5A.

Addition of Ingredients

There does not appear to be any difference in polymer formation whether one adds the isocyanate in increments or all at once. Adding the isocyanate in increments allows one to control the exotherm and to keep the CO₂ evolution under control; otherwise, considerable frothing will occur. In small batches, this has not been a problem, but in scaling up, it could present some difficulties.

It is preferable to add the solid isocyanate to a solution of the anhydride-acid. It has been observed that when the anhydride-acid mixture is added to the dissolved isocyanate, a highly colored solution is produced and high molecular weight is not obtained. A similar result is obtained if a solution of the anhydride is added to a solution of the isocyanate and vice versa. When the solid isocyanate is added to the anhydride-acid solution, a less highly colored solution is obtained and the desired molecular weight can be achieved. As will be shown later, the color of the reaction-solution is also affected by temperature.

Effect of Solids

In Table IV we present data on the effect of concentration on the reaction PMDA + PMA + MDI. In all cases, molecular weight was high enough for creasable films to be obtained. At high solids, there is a tendency for the reaction to gel, which could prevent high molecular weight formation. In addition, the viscosity of the reaction-mixture as the polymerization proceeds in-

TABLE IV
Effect of Solids on Reaction PMDA + PMA + MDI

Run no.	PMDA/PMA	Solvent	Solids, %	Gardner Viscosity	Inherent viscosity, dl/g
A	70/30	DMAC	22	gel	0.58
B	70/30	DMAC	12	K	1.21
C	70/30	DMAC	10	N	0.96
D	55/45	DMAC	25	Z	0.78
E	55/45	DMAC	15	E	0.52

creases substantially, and this causes diffusion problems with the escaping carbon dioxide.

Addition of Water

Since a prerequisite to flexible films is the presence of a mixture of a dianhydride and its acid, it was of interest to determine if the dianhydride/acid ratio could be obtained by adding water to the dianhydride alone in the solvent. In this way, one could hydrolyze a portion of the anhydride with the appropriate amount of water. Toward this end, we carried out a series of reactions by adding various amounts of water to a solution of the dianhydride in a suitable solvent. This was then heated to reaction temperature, and the isocyanate was added. The reaction proceeded just like the anhydride-acid system reaction, and viscous solutions were obtained from which flexible films could be produced. Table V details the properties of these anhydride/water systems. The PMDA/PMA ratio corresponds fairly well with that reported in Table II where both anhydride and acid were mixed together. The differences can be accounted for by the fact that moisture was not rigorously excluded from the reaction. In fact, samples E and G in Table V were repeated under dry conditions, with the use of distilled solvent (NMP). The Gardner Viscosity increases from U⁺ to Z4 for sample E and from T to Z2⁺ for sample G. In addition, the inherent viscosities were 0.65 and 0.60 dl/g,

TABLE V
Reaction of PMDA + MDI + H₂O^a

Run no.	H ₂ O, g	H ₂ O, moles	PMDA/PMA	Gardner Viscosity	Inherent viscosity	Comments
A	0.8	0.044	73/27	Z4	0.82	Flexible film
B	0.9	0.049	70/30	Z5	1.0	Flexible film
C	1.0	0.055	67/33	Z5	1.0	Flexible film
D	1.1	0.061	65/35	Y ⁺	0.83	Flexible film
E	1.2	0.067	61/39	U ⁺	0.56	Brittle film
F	1.3	0.072	59/41	U	0.50	Brittle film
G	1.4	0.078	55/43	T	0.49	Brittle film
H	1.5	0.083	53/47	0	0.46	Brittle film
I	1.7	0.094	48/52	J	0.34	Brittle film
J	1.9	0.105	42/58	I	0.30	Brittle film

^a Reaction based on 0.1 mole of PMDA + MDI. 20% solids in NMP. Reacted at 70°C for 1 hr.

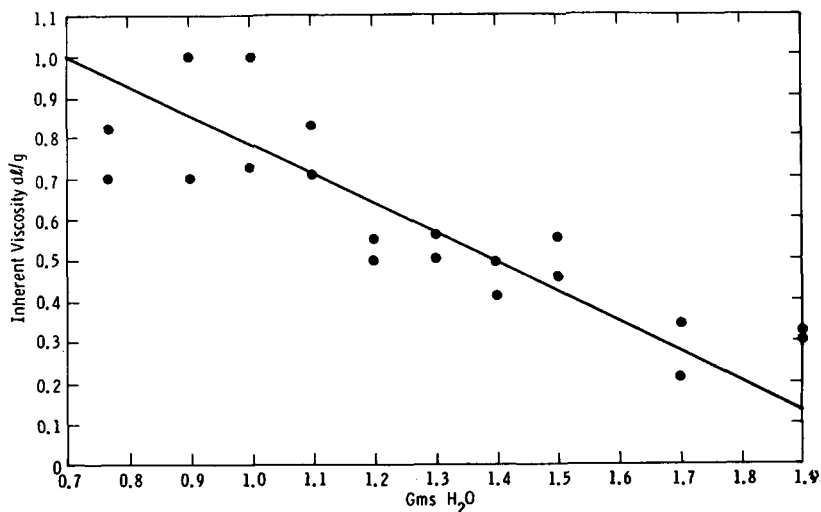


Fig. 6. Effect of water on the reaction of PMDA + MDI.

respectively; and flexible films were obtained. In general, the addition of water to the PMDA-MDI reaction has the effect of decreasing the molecular weight as the amount of water increases and/or as the PMDA/PMA ratio decreases (see Fig. 6 based on the 0.1-mole batch). PMDA is hydrolyzed very rapidly at room temperature,⁹ as is indicated by the curve shown in Figure 7, so that conversion to the acid is assured by the addition of water. The water must be added to a solution of the anhydride in a solvent in the absence of isocyanate. Otherwise, competing reactions between the anhydride and isocyanate with water would occur. Carleton, et al. have found that a mixture of phthalic anhydride, phenyl isocyanate, water, and pyridine, when refluxed, gives a 96% yield of diphenyl urea.⁴

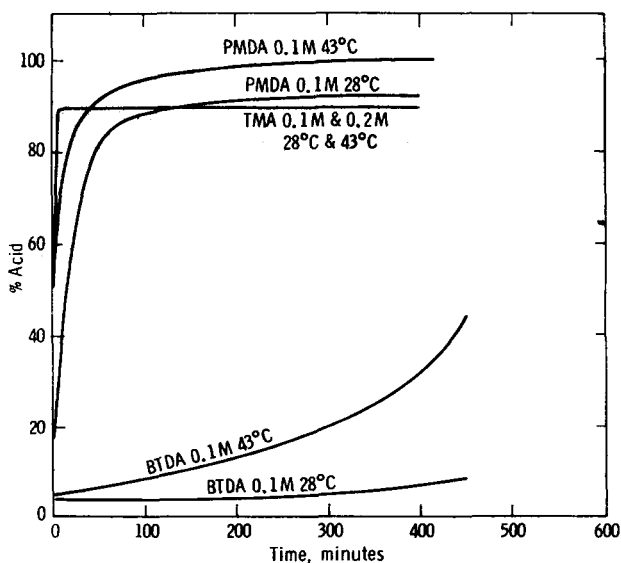


Fig. 7. Hydrolysis rate of BTDA, PMDA, and TMA in aqueous solution.

Effect of Temperature

The reaction of (0.1 mole) PMDA + MDI + (1 g) H₂O was examined with respect to temperature. Inherent viscosity increases with temperature over the range 5–90°C (see Fig. 8). At temperatures between 5° and 10°C, only a cloudy suspension was obtained.

The IR spectrum (Fig. 9) of the precipitate isolated from the reaction mixture contains absorptions indicative of the —CONHCO— group at 1780, 1730, and 720 cm⁻¹. These absorptions are not so intense as to indicate the presence of a large amount of imide formation. However, there are more intense absorptions at 1660 and 1640 cm⁻¹ which indicate amide functionality.

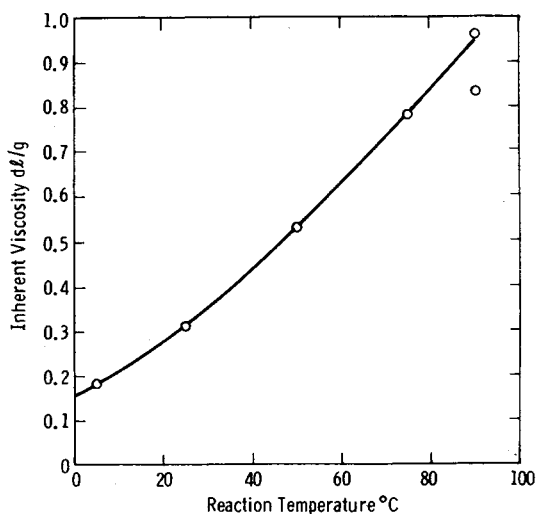


Fig. 8. Inherent viscosity as function of temperature for the reaction PMDA + MDI + (1 g) H₂O.

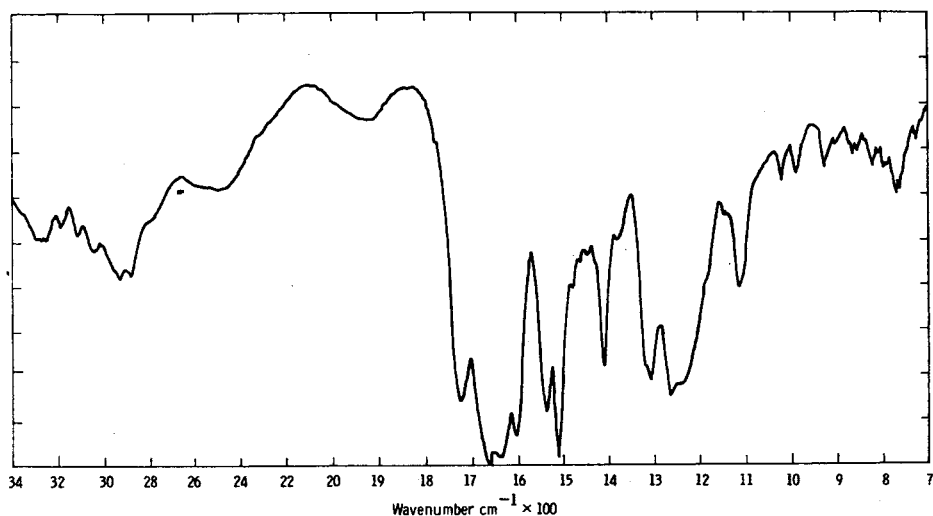


Fig. 9. IR spectrum of precipitate from low-temperature reaction of PMDA + PMA + MDI.

TABLE VI
Effect of Heating 7 Hr at 80°C on the Inherent Viscosity
of the Reaction PMDA + MDI + H₂O (0.1-Mole Batch)

H ₂ O, g	$\eta_{inh_o}^a$	η_{inh_f}
1.0	0.78	0.46
1.1	0.72	0.37
1.3	0.57	0.34
1.5	0.43	0.32

^a Inherent viscosity 0.5% in DMAC at 25°C.

These data suggest that the precipitate contains the amide-acid and imide structure.

When the initial reaction is carried out at 5–10°C, no increase in viscosity can be obtained by subsequent heating at a higher temperature. Apparently, the rate of reaction with free carboxyl groups is substantially faster than the reaction rate with anhydrides at low temperature. Since the free acid is tetrafunctional, most of the isocyanate reacts with the carboxyl groups, and this precludes the formation of imide and of high molecular weight. Above room temperature, the solution viscosity increases with time, with maximum viscosity being reached in shorter times as the temperature is raised. Furthermore, as the temperature is raised, the color of the resin-solution becomes more intense, ranging from a light amber to a deep cherry-red color. The effect of heating the resin-solution after maximum viscosity has been

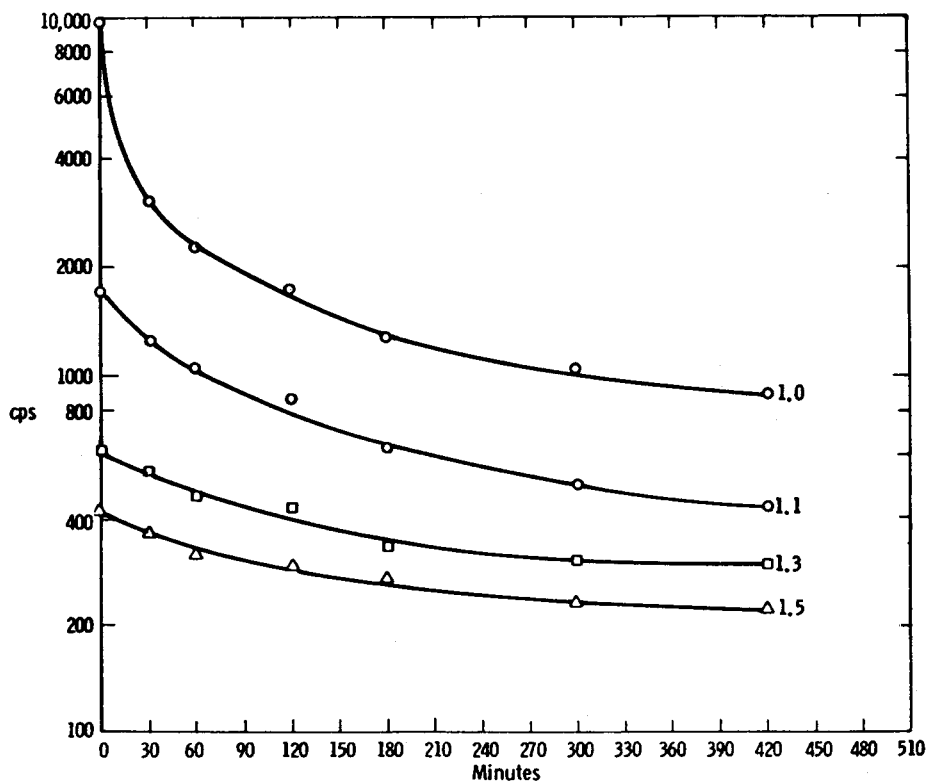


Fig. 10. Viscosity vs. heating time at 80°C for the reaction PMDA + MDI + (1.0 to 1.5 g) H₂O.

TABLE VII
Mechanical Properties of Film

Composition	Tensile strength, psi	Elongation, %	Fold endurance, ^a cycles
PMDA 0.72 PMA 0.28 DIPE ^b 1.0	10,300	8	85,000
PMDA 0.60 PMA 0.40 DIPE 1.0	11,000	8	385,000

^a Film thickness 0.9–1.0 mil.

^b 4,4'-diisocyanato diphenyl ether.

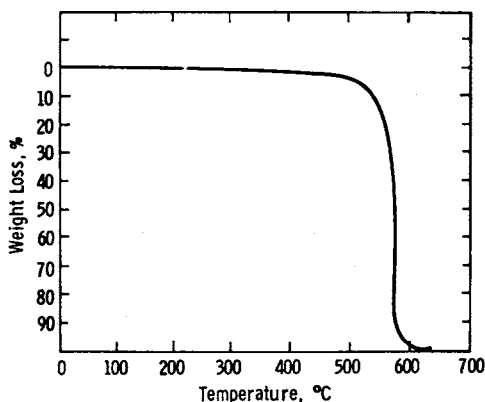


Fig. 11. TGA curve in air at 10°C/min for imidized polymer.

reached, is to reduce the viscosity and molecular weight of the polymer. (See Table VI and Fig. 10.)

Film Properties

The mechanical properties of hand-cast films of these type polymers prepared from PMDA + DIPE + PMA are good and are reported in Table VII.

TGA and DTA in air for the imidized polymer are shown in Figures 11 and 12 and are similar to the polyimide prepared from PMDA and p,p'-diamino-

TABLE VIII
Reaction of BTDA + BTA + MDI^a

Run no.	BTDA/BTA	Gardner Viscosity	Inherent viscosity	Comments
A	0/100	A	—	Brittle film
B	78/22	H	0.52	Flexible film
C	60/40	J	0.52	Flexible film
D	50/50	B	—	Brittle film
E	45/55	A	0.26	Brittle film
F	100/0	A	—	Brittle film

^a 22% solids in NMP using BDMA as catalyst. Reaction temperature, 70–80°C.

phenylether (DAPE) reported by Sroog.¹⁰ These curves indicate stability up to the 500–600°C range, which is typical of the polyimides.

In addition to being used in film, these isocyanate-prepared polyimide resins were recently tried as wire enamels. We have no extensive data yet, but

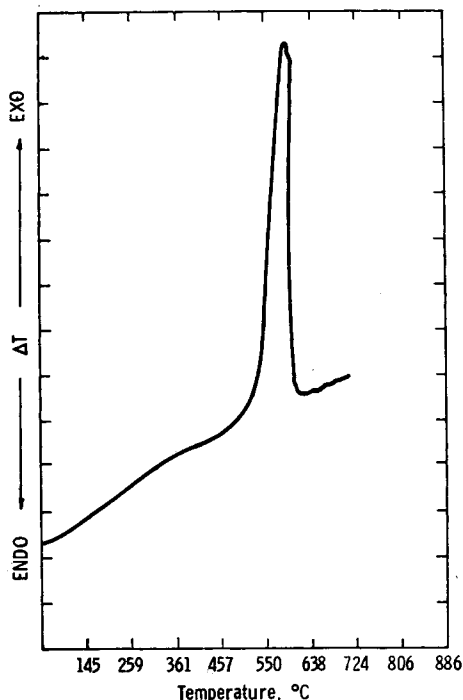


Fig. 12. DTA curve for PMDA + PMA + DIPE imidized polymer in air at heating rate of 10°C/min.

initial test results indicate good coatability and properties for the enameled wire. Tests are continuing in this area.

Reaction of Other Anhydrides

A similar series of reactions, but not so extensive as those listed in Table II, were run for the reaction BTDA + BTA + MDI. [Benzophenonetetracarboxylic acid (BTA)]. These are listed in Table VIII.

The reactions proceeded smoothly with rapid CO₂ evolution but only low viscosities were obtained. Flexible films were obtained only after the films were given an additional cure at 200°C. When the appropriate amount of water was substituted for the BTA acid, similar results were obtained as reported in Table VIII. Even extended reaction times at elevated temperatures (185°C) would not increase the viscosity of the reaction-solution. However, when PMDA or PMA was mixed with BTDA or BTA, the viscosity of the reaction-solution increased substantially to a Gardner value of X. Flexible films could be obtained from these mixed solutions. We do not know why the BTDA reactions do not yield high molecular weight polymers, but it seems that the PMDA is a more reactive system.

Mechanistic Implications

Although a reaction occurs between a diisocyanate and a dianhydride and their acids, high molecular weight polymer is obtained only when a mixture of anhydride and acid is used. In each of the above cases, CO_2 evolution is noted; but with the anhydride or acid alone, a sustained exotherm does not occur and only a low molecular weight product is obtained. On the other hand, when a mixture of anhydride and acid is used, copious amounts of CO_2 are evolved along with a sustained exothermic reaction.

In the case of the dianhydride–diisocyanate reaction alone, one obtains a precipitate very early in the reaction. This precipitate is gelatinous in substance. This precipitate is identified as containing the imide structure because of the absorption bands at 1780, 1730, and 720 cm^{-1} which are characteristic of the $-\text{CONHCO}-$ group. (See Figures 2 and 13.) This precipitation occurs regardless of whether the diisocyanate and dianhydride are dry blended or added to a solution of the other. Prior to precipitation, rapid CO_2 evolution takes place.

Model compound studies (Table I) show that reaction between isocyanates and anhydrides and/or acids yields the imide and amide product, respectively. Neither high temperatures nor long reaction times are needed to obtain up to 50% yields of the amide or imide product. At temperatures $\leq 160^\circ\text{C}$, about 80 to 90% CO_2 is evolved, which is in the same range as the CO_2 lost in the polymerization reaction. Complete CO_2 evolution is not obtained until a temperature of at least 200°C is reached. In the catalyzed reaction of a dianhydride and a diisocyanate, a precipitate is formed. No precipitate is obtained in the non-catalyzed reaction. However, CO_2 evolution is noted in both cases, being more rapid in the former reaction; and this suggests that the catalyst enhances the rate of reaction between anhydride and isocyanate.

In a similar fashion, the all-acid–isocyanate reaction precipitates before high molecular weight can be attained. The precipitate isolated in both cases

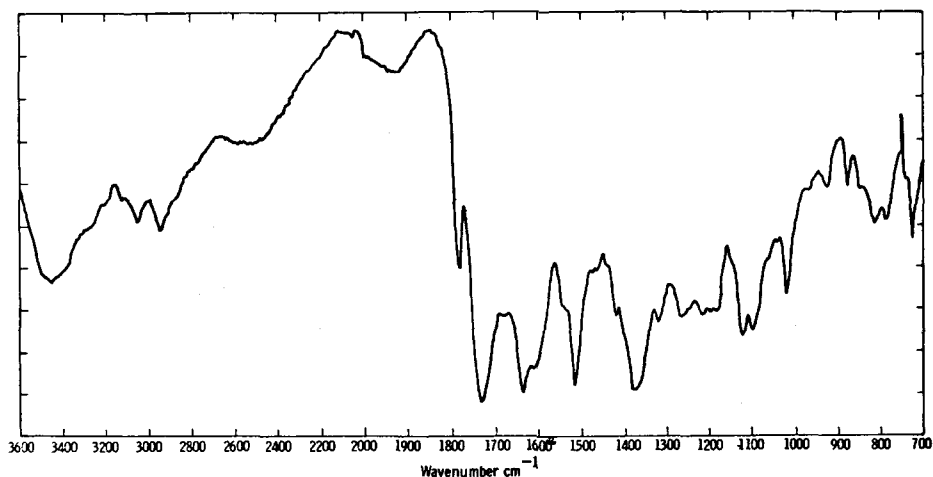


Fig. 13. IR spectrum of precipitate from catalyzed reaction of PMDA + MDI.

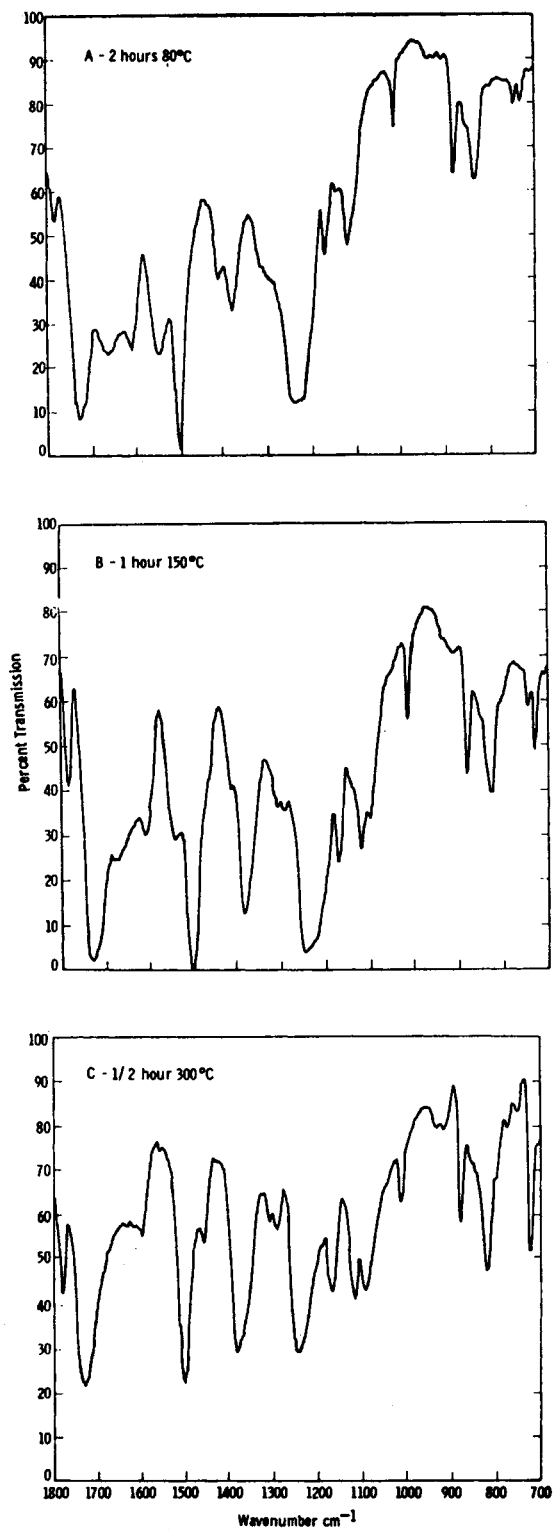


Fig. 14. Spectra of polymer from PMDA-PMA-DIPE at various stages of cure.

can be identified as having the imide structure by examining its IR spectrum (Figs. 2 and 13). There may also be some acid functionality present, but the imide structure is dominant.

Note the imide's bands at 1780, 1730, and 720 cm^{-1} . It is almost identical to that of B in Figure 14 which represents the infrared spectrum of the polymer from PMDA + PMA + DIPE isolated by precipitation. Spectra A, B, and C represent different degrees of imidization. It can be seen that there is an increase in the imide absorption bands at 1775, 1725, and 720 cm^{-1} as well as a disappearance of the amide band in the 1660 cm^{-1} region.

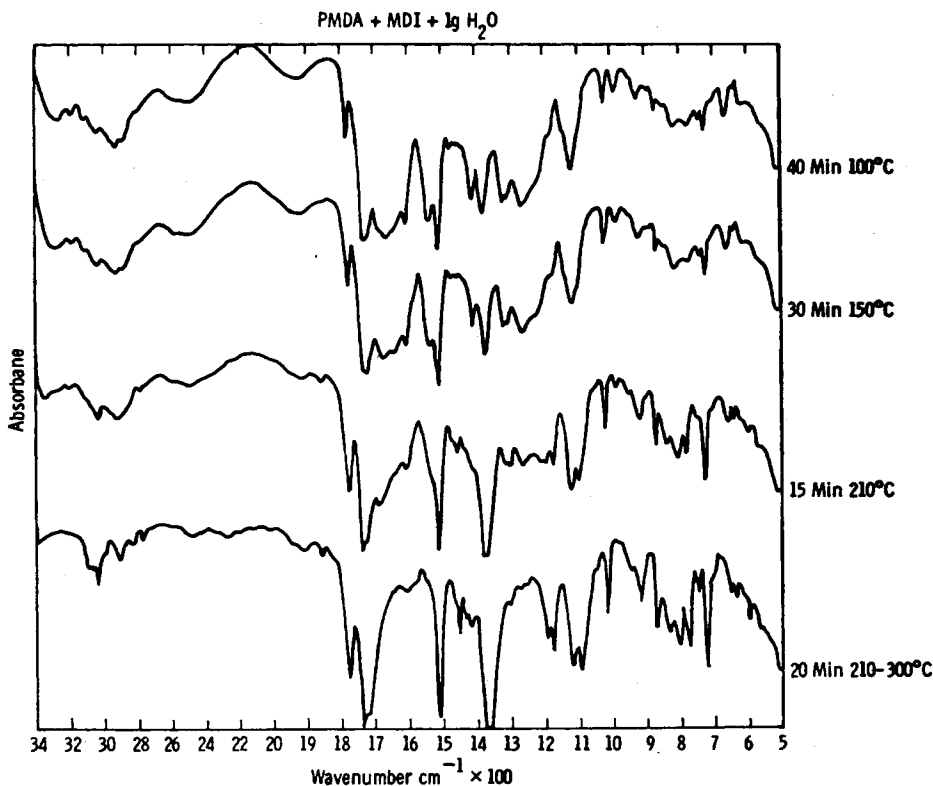


Fig. 15. IR spectra of the curing reaction in PMDA + MDI + H_2O .

When a mixture of anhydride and the acid is reacted with an isocyanate, the reaction proceeds smoothly to yield a high molecular weight polymer. The acid-anhydride combination might impart solubility to the growing chain, enabling it to increase in molecular weight. The IR spectra of the intermediate, the partially imidized, and the completely imidized polymer are shown in Figure 14 (A, B, and C, respectively). These spectra are identical to those reported for the authentic poly(diphenyl ether) pyromellitimide synthesized by the usual dianhydride-diamine reaction reported by Sroog.¹⁰

Furthermore, a comparison of the IR spectra of the curing or imidization reaction between PMDA + MDA and PMDA + MDI + H_2O shows that both reactions follow essentially the same pathway toward imidization. However, it appears that imide formation is faster in the isocyanate-anhydride reaction

because of the early appearance of the imide bands at 1780 and 720 cm^{-1} . (See Figures 15 and 16.)

We have not been able to identify the intermediate product, nor do we know the exact role the acid plays in the reaction between isocyanates and

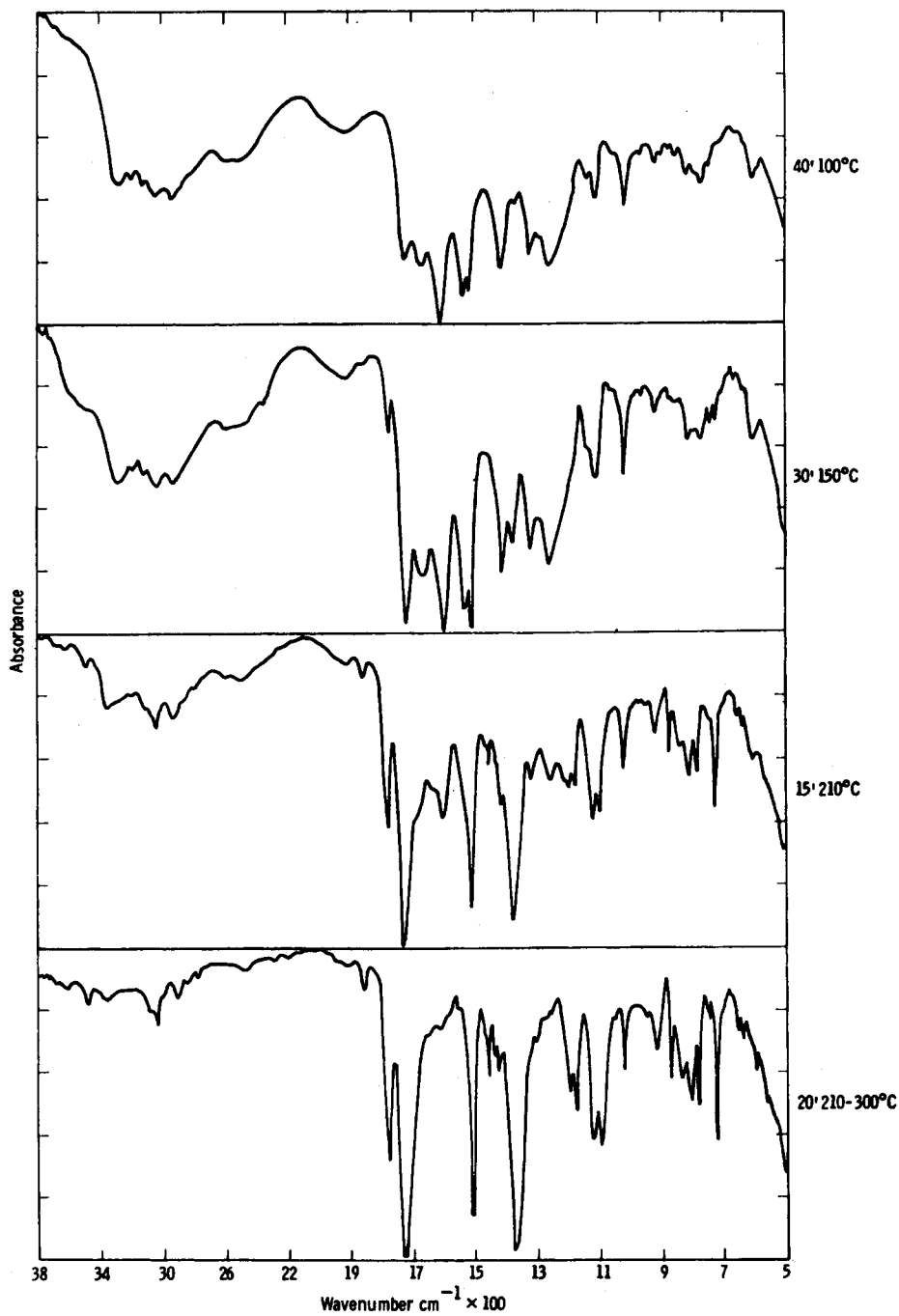


Fig. 16. IR spectra of curing reaction between PMDA + MDA.

anhydrides. Surely, the mechanism is complex and the partial explanations suggested by various authors^{3,4,8} in their examinations of the anhydride-isocyanate system alone confirm this fact. Work is continuing in this area.

CONCLUSIONS

High molecular weight film-forming polyimide resins have been prepared by the polymerization of diisocyanates and a mixture of dianhydrides and their acids. These polymers are identical to, and exhibit the same characteristics as, polyimides derived from dianhydrides and diamines. The preparation of high molecular weight polymer depends on using a tertiary amine catalyst, with the proper anhydride/acid ratio, and the exclusion of moisture. Tough flexible films can be obtained from these polymers which have good mechanical properties.

The authors would like to thank L. A. Cargnel and W. R. Koryak for their assistance in this study.

References

1. Furukawa Electric Co., Jap. Pat. 676-7/67 (*Derwent Jap. Pat. Report*) (1967).
2. Societe Rhodiaceta, Netherl. Pat. 6,690,214 (1967).
3. R. A. Meyers, *J. Polymer Sci. A-1*, **7**, 2757 (1969).
4. P. S. Carleton, W. J. Farrissey, Jr. and J. S. Rose, *J. Appl. Polym. Sci.*, **16**, 2983 (1972).
5. L. M. Alberino, W. J. Farrissey, Jr., and J. S. Rose, to The Upjohn Co. U.S. Pat. 3,708,458 (1973).
6. G. W. Miller, to Mobay Chemical Co. U.S. Pat. 3,622,525 (1971).
7. *Du Pont Bull. on PMA and PMDA*, November 1955, C. F. Robinson, Penns Grove, New Jersey.
8. C. D. Hurd and A. G. Prapas, *J. Org. Chem.*, **24**, 388 (1959).
9. Gulf Oil Corp., Chemical Division, R. E. Clark, 6/13/68, Pittsburgh, Pennsylvania.
10. C. E. Sroog, *J. Polym. Sci. C*, **16**, 1191 (1967).

Received October 18, 1974

Revised March 17, 1975