

*Studies in the Synthesis of Diisocyanates and Polyimides Therefrom**

INTRODUCTION

With enormous growth of polymer industries, the need for the development of new diisocyanates suitable for variety of applications, has increased considerably. In order to assess the field of applications for newly developed diisocyanates, it is essential to know their reactivity towards compounds containing an active hydrogen groups, such as alcohols, amines, etc. However, research workers and technologists have been showing a greater interest in the reaction of diisocyanate with alcohol because of its commercial importance from the polyurethane chemistry point of view.

Thermally stable heterochain polymers such as polybenzimidazoles, poly(amide-imides), poly(ester-imides), poly(ether-imides), polyamides, and polyimides have been the subject of research for a number of years. Among them polyimides are commercially important due to their outstanding thermal stability. Polyimides are conventionally prepared by the reaction of diamine and dianhydride in a polar aprotic solvent. The other method is where a diisocyanate is reacted with a dianhydride.

A Dutch patent¹ reported the reaction of aliphatic and aromatic diisocyanates with pyromellitic dianhydride (PMDA) in dimethyl acetamide (DMAC).

The reaction² of an aromatic diisocyanate and a tetracarboxylic diester provides a polyamic acid ester which on heating forms a polyimide with loss of alcohol. Naoya³ prepared polyimides by H transfer polymerization of pyromellitic acid diimide and diisocyanates in polar solvents with tertiary amine as catalyst.

Meyers⁴ reported a novel method for polyimide preparation. He investigated diisocyanate-dianhydride reaction in polar solvents and also under melt fusion conditions and suggested a possible mechanism that involved a seven-membered ring intermediate.

Carleton et al.⁵ have found that water enhanced the rate of imide formation from the reaction of dianhydride and diisocyanate.

Alberino and Farrissey⁶ and Farrissey and Andrews⁷ prepared soluble polyimides from the reaction of dianhydride and a mixture of diisocyanates.

Ghatge and Dandge⁸ have studied the synthesis and properties of polyimides obtained by the reaction of 3,3'-sulfonyl bis(phenyl isocyanate) with PMDA and BTDA and compared their properties with polyimides obtained from 4,4'-methylene bis(phenyl isocyanate) with PMDA and BTDA.

Alvino and Edelman prepared high molecular weight polyimides by the reaction of diisocyanate and a mixture of dianhydride and their acids^{9a} or a mixture of dianhydride and their dialkylesters.^{9b}

Under prepared soluble polyimides from a mixture of diisocyanates and dianhydride with alkali metal salt of alcohol^{10a} or alkali metal lactam^{10b} as catalyst.

Ghatge et al.^{8,11-13} have investigated the structure property relations by thermal study of polyimides from diisocyanates and dianhydrides.

EXPERIMENTAL

Materials

1. Pyromellitic dianhydride (PMDA) obtained from M/s Koch-Light Industries, United Kingdom, was purified by sublimation under reduced pressure prior to use.

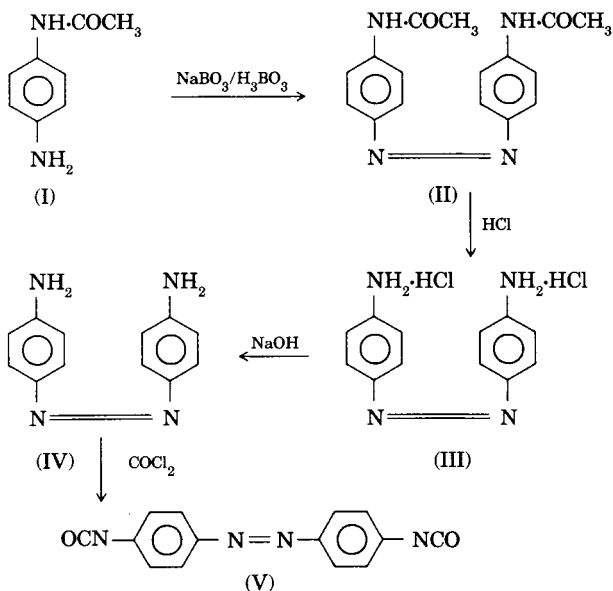
2. 3,3', 4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA) obtained from M/s Gulf Oil Chemical Co., Houston, TX was purified by sublimation under reduced pressure before use.

* NCL Communication No. 3481.

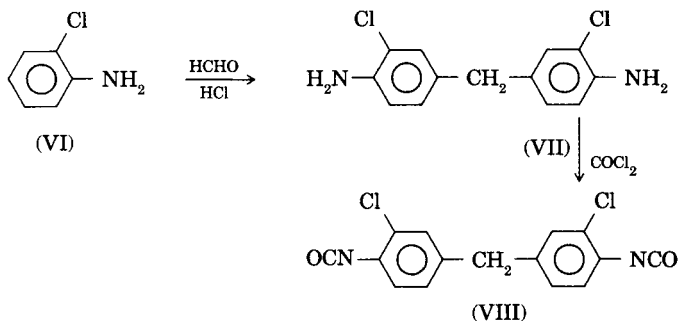
3. *N,N*-dimethyl acetamide (DMAC) obtained from M/s Fluka A.G., Switzerland, was dried over phosphorus pentoxide and then distilled.

4. Diisocyanates. The synthesis of 4,4'-diisocyanato azobenzene (DIAB) and 3,3'-dichloro-4,4'-diisocyanato diphenyl methane (DCMDI) is shown in the following schemes (1A and 1B):

Scheme 1A for synthesis of DIAB (V)



Scheme 1B for synthesis of DCMDI (VIII)



Synthesis of 4,4'-Diisocyanato Azobenzene (DIAB) (V)

4,4'-Diamino azobenzene (IV) was prepared by the same method as reported by Santurri et al.¹⁴ and was further purified by recrystallization from ethyl alcohol, mp 240°C (lit 238–241°C). The elemental analysis and IR and NMR spectra of this compound are well in accordance with the structure assigned to it.

Ten grams (IV) was suspended in 350 mL of monochlorobenzene and the slurry was cooled to 0°C. Dry phosgene gas was passed into the reaction mixture for 5–6 h at 0–5°C and was then kept overnight. The reaction mixture was then refluxed with phosgene gas bubbling till it became almost a clear solution. This was refluxed further for another 2–3 h and the excess of COCl_2 gas was removed by passing dry nitrogen gas through the reaction mixture. The solvent was removed, and the residual mass was crystallized from carbon tetrachloride and then this crystalline compound was subjected for sublimation under vacuum (mp 160°C) for further purification. Yield obtained was 9.0 g (90%).

ANAL. Calcd for $\text{C}_{14}\text{H}_8\text{N}_4\text{O}_2$: C, 63.64%; H, 3.03%; N, 21.21%. Found: C, 63.42%; H, 3.01%; N, 21.02.

Synthesis of 3,3'-Dichloro-4,4'-Diisocyanato Diphenyl Methane (DCMDI) (VIII)

3,3'-Dichloro-4,4'-diamino diphenyl methane (VII) was prepared by the same method as reported by Gorvin¹⁵ and was purified by crystallization from ethyl alcohol, mp 109°C (lit 108–110°C). The elemental analysis and IR and NMR spectra of this compound are well in accordance with the structure assigned to it.

The same experimental procedure mentioned for the synthesis of (V) was followed to synthesize DCMDI (VIII). The residual mass was purified by crystallization from carbon tetrachloride, mp 107°C. Yield obtained was 4.3 g (86%).

ANAL. Calcd for C₁₅H₈Cl₂N₂O₂: C, 56.43%; H, 2.50%; N, 8.78. Found: C, 56.81%; H, 2.90 %; N, 8.79%.

Polyimides from Diisocyanates

The polymerization was carried out by addition of equimolar dianhydride to a stirred solution of diisocyanate in aprotic solvent (Scheme 2). The experimental procedure was adopted as follows.

To a 100 mL round-bottom three-neck flask equipped with magnetic stirrer, a nitrogen gas inlet, a drying tube, and thermometer was added 0.01 mol of diisocyanate, and DMAC (about 20 mL). The mixture was stirred to form a clear solution and the temperature was brought to 0°C with the help of ice-salt mixture. To this solution 0.01 mol of dianhydride was added over a period of 15 min 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 heated at 90°C for about 2 h. The mixture was heated further at 130°C for 5–6 h. The polymer begins to separate after 5–6 h at 130°C. To ensure the complete separation, the reaction mixture was heated for another 24 h. The polymer thus obtained was filtered, washed with DMAC, and several times with methanol and then dried at 110°C for 5–6 h under reduced pressure.

Polymer Characterization

In spectra of the polymers were recorded in nujol mull on Perkin-Elmer Model E-137 spectrophotometer.

Inherent viscosity measurements were made with 0.5% solutions of polyimides in concd sulfuric acid, at 30°C using modified Ubbelohde viscometer.

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were made simultaneously in air at a heating rate of 10°C/min with Netzsch STA 409. Temperature was measured by platinum-platinum Rhodium (10%) thermocouple. Before their properties were determined, the polymer samples were dried for 4–6 h at 110°C under reduced pressure of 10⁻³ mm Hg.

RESULTS AND DISCUSSION

Monomers

4,4'-Diamino azobenzene (IV) was synthesized from *p*-amino acetanilide (I) by the same method as reported by Santurri et al.¹⁴ It was purified by recrystallization and it melted at 238°C (lit 238–241°C). The structure of this compound was confirmed by elemental analysis and IR and NMR spectral studies. The IR spectrum of IV showed a characteristic bands at 3225 cm⁻¹ and between 1630 and 1575 cm⁻¹ corresponding to amino group and azo (—N=N—) group, respectively. 4,4'-Diisocyanato azobenzene (V) was prepared by phosgenation of IV. The structure of V was confirmed by elemental analysis and IR and NMR spectral studies. The IR spectrum of V showed a characteristic bands at 2270 cm⁻¹ and between 1630 and 1575 cm⁻¹ corresponding to isocyanate (—NCO) group and azo (—N=N—) group, respectively.

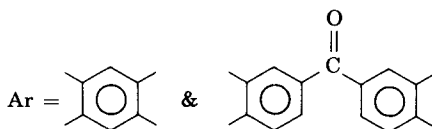
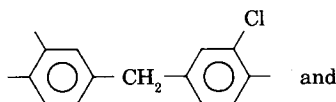
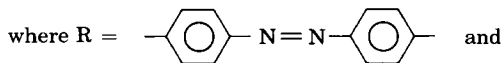
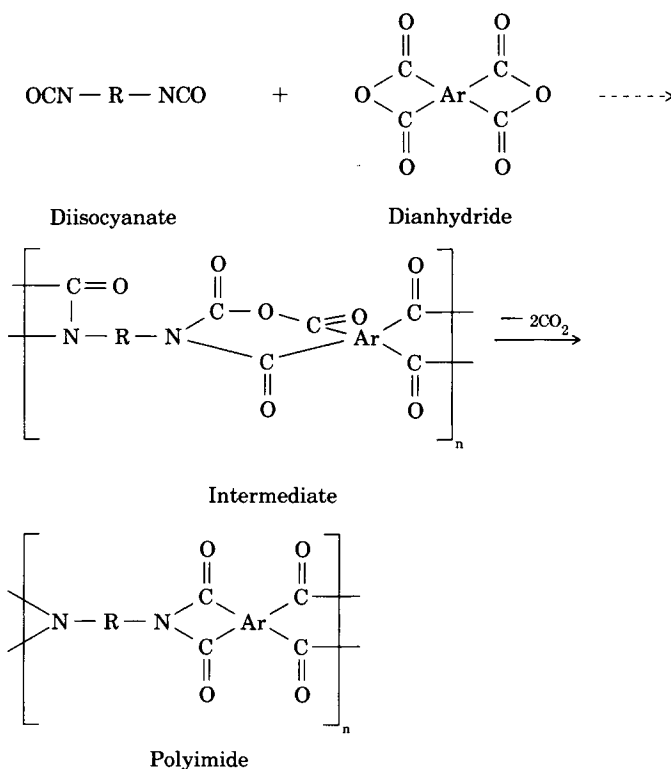
3,3'-Dichloro-4,4'-diamino diphenyl methane (VII) was synthesized from *O*-chloroaniline (VI) by the same method as reported by Govin.¹⁵ It was purified by recrystallization and melted at 109°C (lit 108–110°C). The structure of this compound was confirmed by elemental analysis and IR and NMR spectral studies. The IR spectrum of VII showed an absorption band at 3225 cm⁻¹ corresponding to the amino group. 3,3'-Dichloro-4,4'-diisocyanato diphenyl methane (VIII)

was prepared by the phosgenation of VII. The structure of VIII was confirmed by elemental analysis and IR and NMR spectral studies. The IR spectrum of VIII showed a peak at 2270 cm^{-1} corresponding to the isocyanate ($-\text{NCO}$) group in the compound.

Polyimide Polymers

Addition of dry anhydride to diisocyanate solution under nitrogen atmosphere and perfectly dry conditions was done to yield high molecular weight polyimide polymers. In 1854, Wurtz¹⁶ discovered that acetic anhydride and ethyl isocyanate react to form imide (*n*-ethyl diacetimide). Attempts have been made by several investigators⁹ to achieve high molecular weight polyimide polymers by the polymerization of diisocyanates and dianhydrides. To explain the formation of imide in this reaction, the investigators assumed that there is an initial addition of anhydride to isocyanate resulting from the partial polarization of both the molecules at the required temperature. The resulting mixed acid anhydride is unstable and loses carbon dioxide by readjustment of electrons in the molecule as given below:

Scheme 2: Synthesis of polyimides from diisocyanates and dianhydrides



All the polyimide polymers begin to separate out after heating at 130°C for 5–6 h. It was observed that the polyimides from the reaction of DIAB with PMDA and BTDA gave products (A and B) in the form of orange-red powder, while the reaction of DCMDI with PMDA and BTDA gave products (C and D) in the form of lemon-yellow powder.

Table I summarizes the analysis of all these polyimides synthesized in the present investigation. The elemental analysis of polyimides fairly corresponds to the calculated values for carbon and hydrogen. The elemental analysis obtained were 1–2% less for carbon. This may be due to the fact that while analyzing, some samples remained un-ionized even at higher temperatures. This is supported by earlier work^{12,17} and also by percentage weight losses in the thermogravimetric analysis (TGA), which are not more than 70% at 900°C.

Solubility

Polyimides are mostly inert to organic solvents and oils and are not affected by dilute acids. However, polyimides dissolve with degradation in strong acids like fuming nitric acid or concentrated sulfuric acid¹⁸ and the viscosity of the resulting solution drops with time.

Viscosity

On comparing the viscosity (η_{inh}) of polyimide polymers (Table I) prepared from diisocyanates and dianhydrides, it was found that in every case (i.e., PMDA and BTDA), polymers obtained with 4,4'-diisocyanato azobenzene (DIAB) have higher viscosities than the corresponding polyimides from 3,3'-dichloro-4,4'-diisocyanato diphenyl methane (DCMDI).

Because of the solution polymerization technique, the polyimide polymers separated out may be of low molecular weight having low viscosity.

Infrared Spectra

Infrared spectrum of polyimide obtained by reaction of 4,4'-diisocyanato azobenzene (DIAB) with BTDA is shown in Figure 1 (as a representative).

The imide group is characterized¹⁹ in the spectrum by strong absorptions at 1780 and 1720 cm^{-1} (amide-I), 1380–1370 cm^{-1} (imide-II), 1120 cm^{-1} (imide-III), and 720 cm^{-1} (imide-IV). Imide-I is attributed to the stretching vibrations of the two carbonyls which are weakly coupled. Imides-II, -III, and -IV are assigned to axial, transverse, and out-of-plane vibrations of cyclic imide structure.

Thus, the IR spectra of all polyimides exhibit characteristic absorptions corresponding to imide function and disappearance of the isocyanato group frequency. Further, it was also revealed from IR spectra of polyimides obtained from DIAB with PMDA and BTDA that there is presence of azo ($-\text{N}=\text{N}-$) linkage in the polymeric chain polymer (absorption in the region 1630–1575 cm^{-1}).

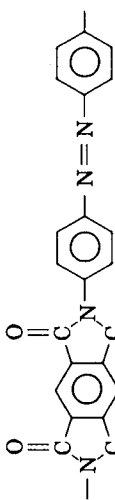
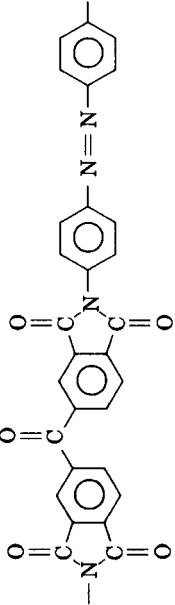
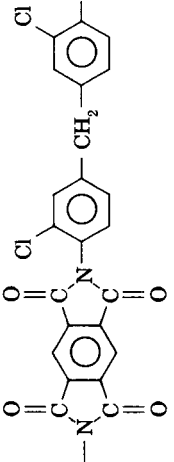
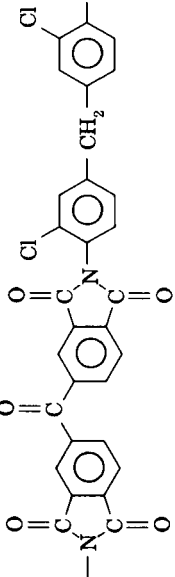
Thermal Stability

In order to study the effect of diisocyanate structure on the thermal properties of polyimides, the thermooxidative degradation of polymers was evaluated by dynamic thermogravimetry. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were made simultaneously in air at a heating rate of 10°C/min with derivatograph described by Paulik et al.²⁰ [Figs. 2(a) and 2(b)]

The quantitative determination is carried out on the basis of TGA curve. But with the help of DTG curve a higher accuracy can be attained. Qualitative evaluation is based on the DTG curve, which shows transformations accompanied by weight change and their characteristic temperatures more accurately than DTA curve.

TGA, DTA, and DTG curves for all the polyimides show more or less similar pattern. TGA curves for polyimides (A to D) are given in Figures 2(a) and 2(b). Loss in weight of the polymer at different temperatures was determined from the respective TGA and is presented in Table II. The small weight loss ($3 \pm 1\%$) can be attributed to the removal of absorbed moisture from the polymer. The initial decomposition temperature (taking the sharp drop in the curve as the onset of maximum decomposition reaction) (T_0), the temperature of maximum decomposition (T_{max}), 10% weight loss temperature (T_{10}), and exothermic peak position from DTA are listed in Table III.

TABLE I
Elemental Analysis and Some of the Characteristics of the Polyimide Polymers

Polyimide	Formula of the repeating unit	Elemental analysis		Viscosity ^a (η_{inh}) (dL/g)
		C (%)	H (%)	
A		Found:	3.15	0.2179
		Calcd:	2.54	
B		Found:	3.38	0.2015
		Calcd:	2.31	
C		Found:	3.35	0.2089
		Calcd:	2.23	
D		Found:	3.23	0.1914
		Calcd:	2.53	

^a The inherent viscosity (η_{inh}) of the polyimide (0.5% in concentrated sulfuric acid at 30°C) is reported.

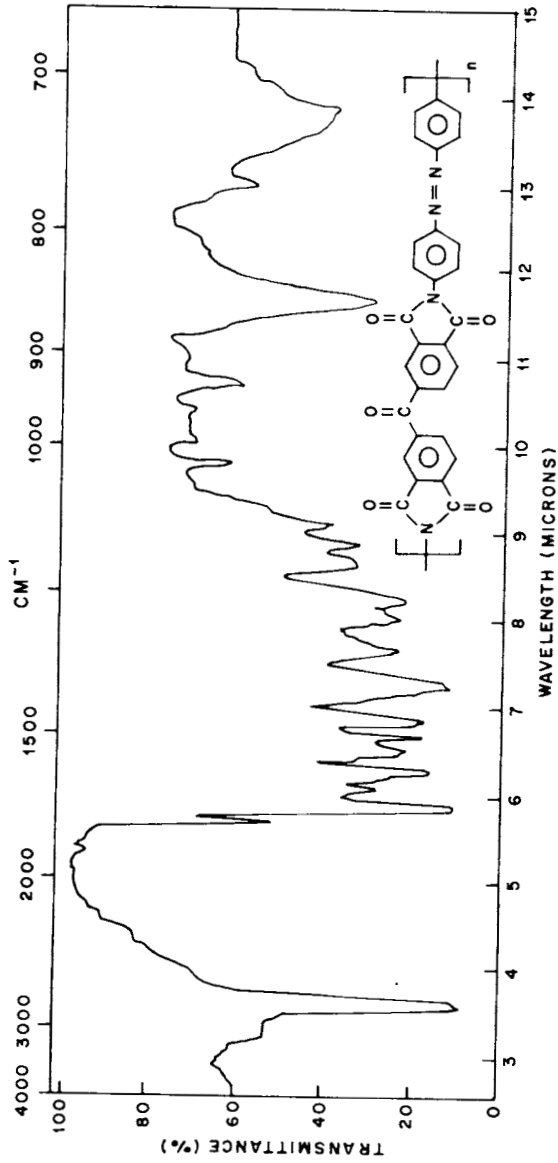


Fig. 1. IR spectrum of polyimide from DIAB and BTDA reaction.

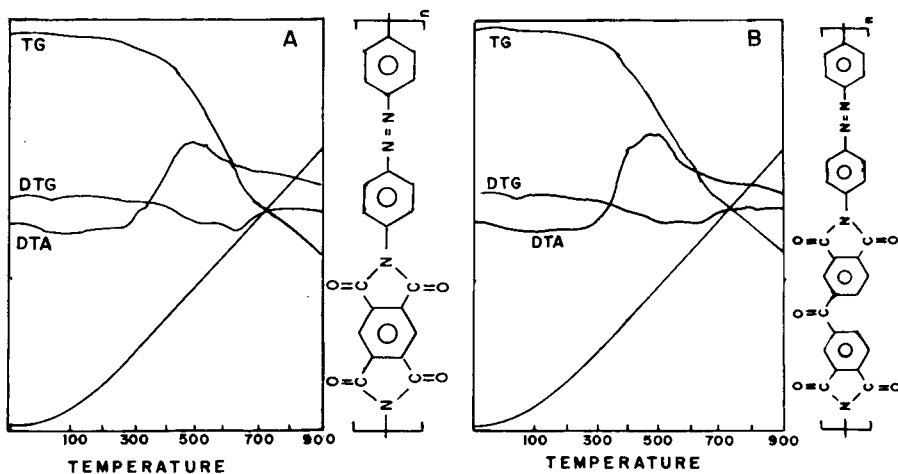


Fig. 2. Thermograms of polyimide polymer A and B.

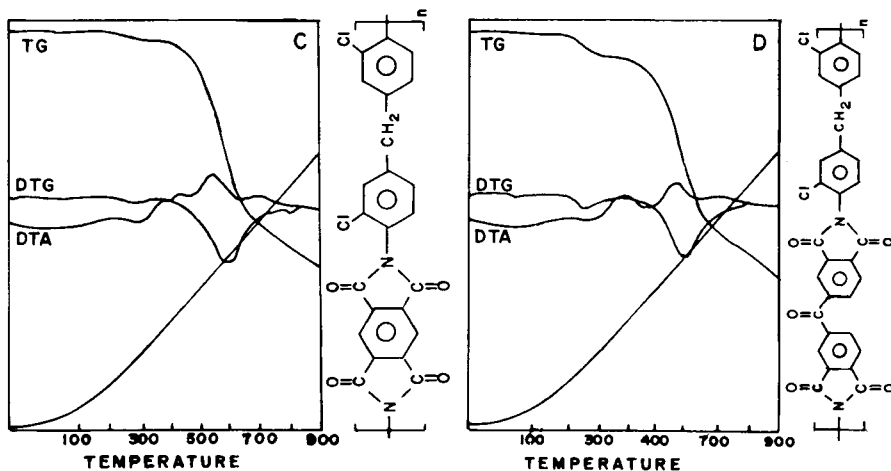


Fig. 2(b). Thermograms of polyimide polymer C and D.

TABLE II
Percentage Weight Loss of Polyimide Polymers at Different Temperatures

Temp (°C)	Percentage weight of polyimide polymers			
	A	B	C	D
100	0.47	0.66	0	0.65
200	0.88	0.95	0	0.86
300	4.19	4.26	1.08	6.48
400	8.59	10.40	3.68	7.99
500	17.18	22.93	9.52	12.09
600	30.84	37.83	34.63	34.55
700	44.93	48.23	50.87	52.48
800	52.64	52.36	56.49	58.32
900	59.91	63.83	61.47	64.36

TABLE III
Temperature Characteristics of Polyimide Polymers

Polyimide	T_0^a (°C)	T_{10}^b (°C)	T_{max}^c (°C)	Peak position ^d
A	260	437	637	490
B	243	411	637	480
C	202	478	271,600	555
D	196	473	248,600	545

^a Initial decomposition temperature (T_0).

^b 10% weight loss temperature (T_{10}).

^c Maximum rate of decomposition temperature (T_{max}).

^d Exothermic transition peak position from DTA.

TGA curves of polyimides (A and B) show that the heat resistance temperatures vary between 240 and 260°C, while the polyimides (C and D) show that the heat resistance temperatures vary between 195 and 205°C. Further, increase in the temperature causes rapid decomposition of the polymer.

The initial temperature of decomposition (T_0) and the temperature of 10% weight loss are some of the main criteria of the heat stability of polymers (with dynamic heating). The higher the value of T_0/T_{10} , the higher will be the stability of a given polymer.²¹ A comparison of T_0/T_{10} of the polyimides using PMDA and BTDA indicate that the polyimide polymers obtained using PMDA have the higher thermal stability than the polyimide polymer obtained using BTDA.

It is clear from the Figure 2(b) and the results obtained (Table III) that the temperature of maximum rate of decomposition (T_{max}) was observed twice in case of polyimide polymers obtained using 3,3'-dichloro-4,4'-diisocyanato diphenyl methane (DCMDI). This shows that the decomposition of polyimide polymers (C and D) occurs in two steps.

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