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# Synthesis and characterization of new polyimides and polyamide-imides containing azomethine group in the polymer backbone*

**Susheela B. Idage, Bhaskar B. Idage, and Subhash P. Vernekar****

Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

## Summary

New aromatic polyimides and polyamide-imides containing azomethine linkages in the polymer backbone have been synthesized by reacting 4,4'-bis(isocyanato) benzylidene aniline (AZMI) with pyromellitic dianhydride (PMDA), 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and trimellitic anhydride (TMA) by one-step method. The AZMI was synthesized from 4,4'-bis(carboxy) benzylidene aniline (AZMA) by a Weinstock modified curtius rearrangement. All the polycondensation reactions were carried out in N-methyl-2-pyrrolidone (NMP) and the polymers obtained were characterized by infrared spectroscopy, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction.

## Introduction

Aromatic polyimides are well known for their chain stiffness and thermal stability (1). A number of aromatic polyimides containing various linking groups such as methylene (2), oxygen (2), oxyethylene (3), silicon (4), siloxane (5), sulfone (6), etc. in the polymer backbone have been synthesized and studied extensively. Aromatic azomethine linkage is well known mesogen in liquid crystalline polymers (7) and interesting due to its syn-anti isomerism and good thermal stability (8,9). Various polymers such as polyesters (10-12), polycarbonates (13-15), polyamides (16,17), copolyamides (18), and polyethers (19,20), etc. containing azomethine linkage in the polymer backbone are described in the literature. However, much information is not available in literature regarding polyimides containing azomethine linkage.

The present paper describes the synthesis and characterization of new aromatic polyimides and polyamide-imides containing azomethine linkage by the reaction of a new azomethine group containing diisocyanate namely 4,4'-bis(isocyanato) benzylidene aniline (AZMI) with PMDA, BTDA and TMA respectively and their characterization by elemental analysis, infrared spectra, intrinsic viscosity, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction.

## Experimental

Materials : 4-carboxybenzaldehyde (PCBA), 4-aminobenzoic acid (PABA) and p-toluene sulfonic acid (PTSA) (Fluka, A.G., Switzerland) were used as such without further purification. Pyromellitic dianhydride (PMDA), 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and trimellitic anhydride (TMA (Fluka, A.G., Switzerland) were purified

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** To whom offprint requests should be sent by recrystallization from appropriate solvents prior to use. All the solvents and other chemicals used were purified by following standard procedures.

Instrumental methods : The IR spectra were recorded on a Perkin-Elmer spectrophotometer. The $^1$H NMR spectra were recorded on a Bruker WH 90 MHz spectrophotometer with TMS as an internal standard. Ubbelohde viscometers were used to determine inherent viscosities of polymer solutions having concentration of 0.5 g/100 ml in conc. sulphuric acid. The DSC thermograms were recorded on a Perkin-Elmer DSC 2 equipped with thermal analysis data station (TADS). The rate of heating used was 20°C min$^{-1}$. Thermogravimetric analyses were obtained with a Netzsch STA 409 thermogravimetric analyzer in a flowing air environment. The heating rate used for the determinations was 5°C min$^{-1}$ and the temperature was measured by a Pt-Pt Rh (10% ) thermocouple. The X-ray diffractions were obtained with a Phillips X-ray unit (Phillips Generator, PW-1730) and a nickel filtered CuKα radiations.

Preparations :

4,4'-Bis(carboxy) benzylidene aniline (AZMA)

To a 250 ml three-necked round bottomed flask, equipped with a mechanical stirrer, thermowell and dean-stark trap, were placed 7.50 g (0.05 mole) of 4-carboxybenzaldehyde, 6.857 g (0.05 mole) of 4-aminobenzoic acid, 0.05 g of p-toluene sulfonic acid and 150 ml toluene. The reaction mixture was heated with stirring at the boiling temperature of toluene untill all water was evolved. The crude product was then filtered, washed with dry toluene and dried. The resulting solid was recrystallized from n-butanol to afford 12.78 g (95%) of pure AZMA, mp. 320-322°C.

IR (Nujol, $\nu$ cm$^{-1}$) : 2550 (-OH), 1685 ($>$C=O), 1600 (-C=N-)

$^1$H NMR (DMSO $d_6$, $\delta$ ppm): 7.33 (2Ha, d), 8.00 (2Hb, d), 8.00 (4Hc, d),

8.68 (1Hd, s), 10.06 (-COOH, s, exchanges with $D_2O$)

ANAL Calcd for $C_{15}H_{11}NO_4$(269): C, 66.91%, H, 4.09%, N, 5.20%

Found : C, 66.84%, H, 4.16%, N, 5.10%

Mass Spectrum : Molecular ion ($M^+$) peak at 269.

4,4'-Bis(azidocarbonyl) benzylidene aniline (AZMAZ)

To a 250 ml three-necked round bottomed flask, equipped with a mechanical stirrer, dropping funnel and thermowell, were placed 5.38 g (0.02 mole) of 4,4'-bis(carboxy) benzylidene aniline (AZMA) and 40 ml acetone. The suspension was cooled to 0°C and 4.04 g (0.004 mole) of triethylamine in 15 ml of acetone was added over a period of 10 min. The reaction mixture was stirred for further 10 min. and then a solution of 4.34 g (0.002 mole) of ethylchloroformate in 15 ml of acetone was added at 0°C over a period of 10 min. The resulting reaction mixture was stirred for 1 hr at the same temperature and then a solution of 2.60 g (0.04 mole) of sodium azide in 60 ml of water was added dropwise. Finally, the reaction mixture was stirred for 4 hr at 0°C and then poured into 200 ml ice-cold water.

The solid obtained was collected by filtration, dissolved in dichloromethane and dried over anhydrous sodium sulphate. After filtration, dichloromethane was removed under reduced pressure to obtain 4.52 g (84%) of pure AZMAZ, mp. 122-124°C (decomp.).

IR (Nujol ,$\nu$ cm$^{-1}$) : 2140 ($-N_3$), 1680 ($>C=O$), 1600 ($-\underset{|}{C}=N-$)

$^1$H NMR ($CDCl_3$,$\delta$ ppm) : 7.26 (2Ha, *d*), 8.02 (2Hb, *d*), 8·17 (4Hc, *d*), 8.25 (1Hd, *s*)

ANAL. Calcd. for $C_{15}H_9N_7O_2$(319) : C, 56.42%; H, 2.82%,

Found : C, 56.32%; H, 2.90%.

4,4'-Bis(isocyanato) benzylidene aniline (AZMI)

To a 100 ml round bottomed flask, equipped with a reflux condenser, calcium chloride guard tube, were placed 3.19 g (0.01 mole) of AZMAZ in 35 ml of dry benzene. The solution was refluxed for 6 hr and benzene was removed by distillation under reduced pressure. The residue after recrystallization from dry benzene gave 3.0 g (94%) of pure AZMI, mp. 110-112°C.

IR (Nujol,$\nu$ cm$^{-1}$) : 2300 (-NCO), 1600 ($-\underset{|}{C}=N-$).

$^1$H NMR ($CDCl_3$,$\delta$ ppm) : 7.05 (2Ha, *d*), 7.72 (2Hb, *d*), 7.05 (4Hc, *d*), 8.24 (1Hd, *s*).

ANAL. Calcd. for $C_{15}H_9N_3O_2$(263): C, 68.44%; H, 3.42%; N, 15.96%.

Found : C, 68.32%; H, 3.48%; N, 16.10%.

Mass spectrum : Molecular ion ($M^+$) peak at 263.

## Model Compounds

4,4'-Bis(phenylurea) benzylidene aniline (AZMU)

To a 50 ml three-necked round bottomed flask, equipped with a magnetic stirrer, nitrogen inlet tube, reflux condenser and calcium chloride guard tube, were placed 0.526 g (0.002 mole) of 4,4'-bis (isocyanato) benzylidene aniline (AZMI), 5 ml of aniline and 25 ml dry benzene. The reaction mixture was stirred at reflux temperature of benzene for 2.0 hr and was cooled to room temperature. The excess quantity of aniline was removed under reduced pressure by a rotary evaporator to give a pale yellow solid. Recrystallization of the solid from a mixture of acetone:pet-ether gave 0.494 g (94%) of AZMU, mp. 245-247°C.

IR (Nujol ,$\nu$ cm$^{-1}$) : 3300 (-NH), 1640 ($>C=O$), 1600 ($-\underset{|}{C}=N-$)

$^1$H NMR (DMSO $d_6$,$\delta$ ppm) : 7.00 (2Ha, *d*), 7.84 (2Hb, *d*), 7.20 (4Hc, *d*), 8.52 (1Hd, *s*), 8.97 (4H, *s*, urea protons), 7.48 (10H, *m*, aromatic protons).

ANAL. Calcd. for $C_{27}H_{23}N_5O_2$(449): C, 72.16%; H, 5.12%; N, 15.59%.

Found : C, 72.10%; H, 5.22%; N, 15.65%.

Mass spectrum : Molecular ion ($M^+$) peak at 449.

## Polymer Synthesis

A typical example of polyimide (8) preparation follows :

To a 50 ml three-necked round bottomed flask, equipped with a thermometer, nitrogen gas inlet and gas outlet connected to barium hydroxide solution, were placed 1.052 g (0.004 mole) of diisocyanate (7) and 10 ml of dry NMP. To this solution, 0.8724 g (0.004 mole) of PMDA was added in small quantities over a period of 15-20 min at 0°C. The reaction mixture was stirred at this temperature for 0.5 hr and then slowly heated to 40°C, at which temperature, it was held for 2.5 hr. The temperature was then slowly raised to 90°C and maintained for 2.0 hr. Carbon dioxide gas evolution was observed at this temperature. Finally, the reaction mixture was heated at 130-140°C for 24 hr after which the reaction mixture was poured into 100 ml water and the polymer was filtered off, washed several times with methanol and then dried at 100°C under reduced pressure. The same procedure was followed to prepare polyimide (9) and polyamide-imide (10) polymers.

## Polymer Solubility

The solubility of polyimide and polyamide-imide polymers was checked at 3% concentration in various solvents. All the polymers were insoluble in aprotic polar solvents and nonpolar solvents. These polymers were only soluble in conc. sulphuric acid and methane sulfonic acid.

## Results and Discussion

In the present work, a new diisocyanate namely 4,4'-bis(isocyanato) benzylidene aniline (AZMI) containing azomethine linkage has been synthesized in high yield from the corresponding new diacid namely 4,4'-bis(carboxy) benzylidene aniline (AZMA) by following the Weinstock modified curtius rearrangement. The scheme for the preparation of AZMI is shown in Fig.1.

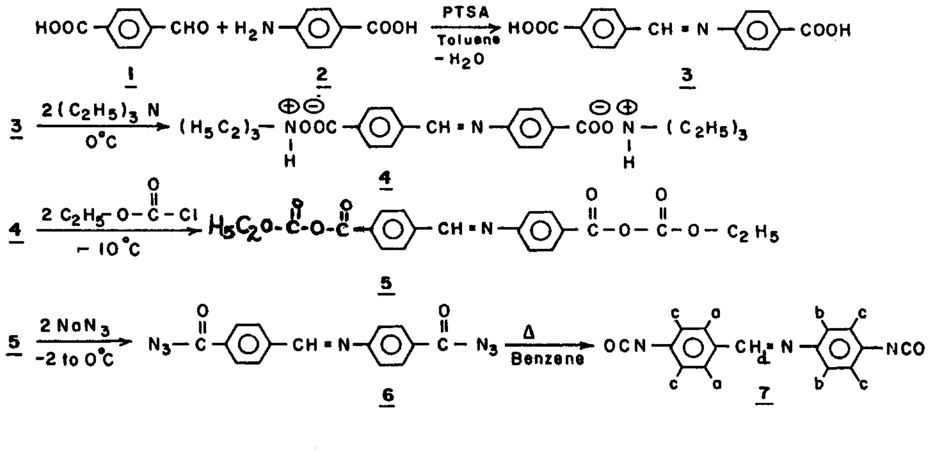
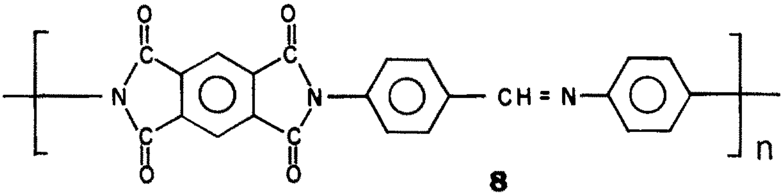


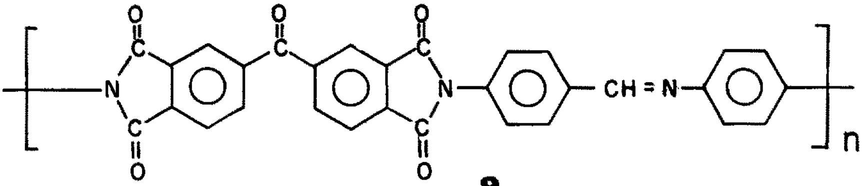
Fig.1 : Scheme for the preparation of 4,4'-bis(isocyanato)benzylidene aniline (AZMI)

The compounds such as diacid, diacylazide and diisocyanate prepared were characterized by IR, $^1$H NMR, mass spectroscopy and elemental analysis. The diisocyanate is a yellow coloured solid and sensitive to moisture. The structure of the diisocyanate was confirmed by preparing the phenylurea derivative of the diisocyanate and elucidating its structure by elemental and spectroscopic analysis.

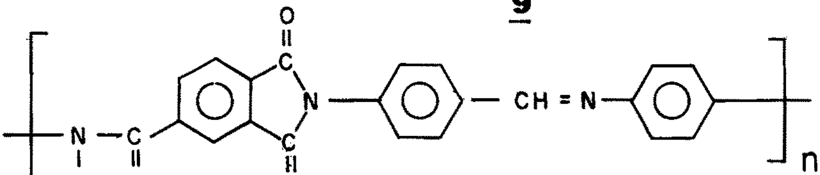
The diisocyanate, 4,4'-bis(isocyanato) benzylidene aniline (AZMI) was reacted with PMDA, BTDA and TMA in NMP under identical conditions in nitrogen atmosphere to give polyimides and polyamide-imide polymers of the following type.



**8**



**9**



**10**

The polymers are orange coloured powders which are insoluble in common aprotic polar and nonpolar solvents and soluble only in conc. sulphuric acid and methane sulfonic acid. The inherent viscosities in conc. sulfuric acid and elemental analysis of these polymers are tabulated in Table 1.

During condensation the polymer separates out from the solution, restricting the molecular built up of the polymer. This might be the cause for comparatively low inherent viscosities (0.32 to 0.41) of the polymers.

The thermal behaviour of these polymers was studied by TGA, DTA and DTG which were performed simultaneously by heating the samples in air at constant rate of 5°C min$^{-1}$. The temperature of ten percent weight loss ($T_{10}$), IDT and IPDT were determined from original TGA curves. Doyle's method (21) was used to calculate IPDT values. Tmax was calculated from DTG curve and the values are tabulated in Table 2.

Table 1

Properties of polyimides and polyamide-imides

| Sr. No. | Polymer Abbr. | Reactants | | $\eta_{inh}^{a}$ | Yield | Elemental analysis[b] | | |
|---|---|---|---|---|---|---|---|---|
| | | Dianhydride | Diisocyanate | dl.g$^{-1}$ | (%) | C% | H% | N% |
| Polyamides | | | | | | | | |
| 1. | 8 | PMDA | AZMI | 0.41 | 88.0 | 70.10<br>(70.23) | 2.72<br>(2.80) | 10.42<br>(10.68) |
| 2. | 9 | BTDA | AZMI | 0.32 | 89.5 | 72.36<br>(72.43) | 3.00<br>(3.02) | 8.32<br>(8.45) |
| Polyamide-imides | | | | | | | | |
| 3. | 10 | TMA | AZMI | 0.39 | 87.5 | 71.82<br>(71.93) | 3.50<br>(3.54) | 11.34<br>(11.44) |

a determined in conc. sulphuric acid at 30°C.

b values in parenthesis indicate the corresponding calculated values. PMDA - Pyromellitic dianhydride, BTDA - 3,3', 4,4'-Benzophenone tetracarboxylic dianhydride, TMA - Trimellitic anhydride, AZMI - 4,4'-Bis(isocyanato) benzylidene aniline.

Table 2

Thermal behaviour of polyimide and polyamide-imides

| Sr. No. | Polymer Abbr. | IDT (°C) | $T_{10}$ (°C) | IPDT (°C) | Tmax (°C) |
|---|---|---|---|---|---|
| Polyimides | | | | | |
| 1. | 8 | 446 | 485 | 576 | 545 |
| 2. | 9 | 418 | 449 | 508 | 516 |
| Polyamide-imides | | | | | |
| 3. | 10 | 466 | 519 | 588 | 594 |

IDT - initial decomposition temperature, $T_{10}$ - temperature for 10% weight loss, IPDT - integral procedural decomposition temperature, Tmax - temperature for maximum rate of decomposition.

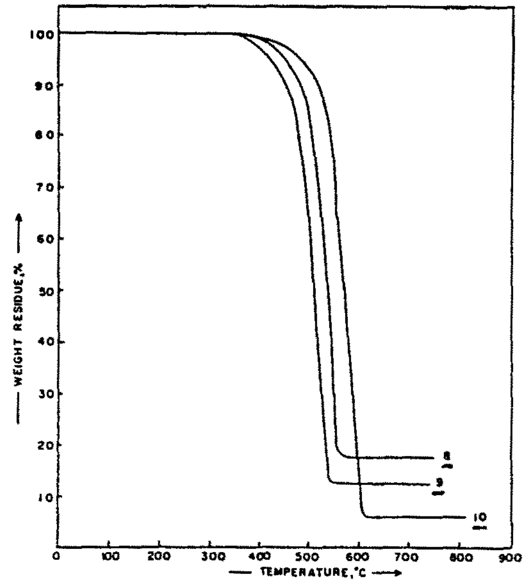


Fig.2: Thermogravimetric analyses of polyimide 8,9 & polyamide-imide 10

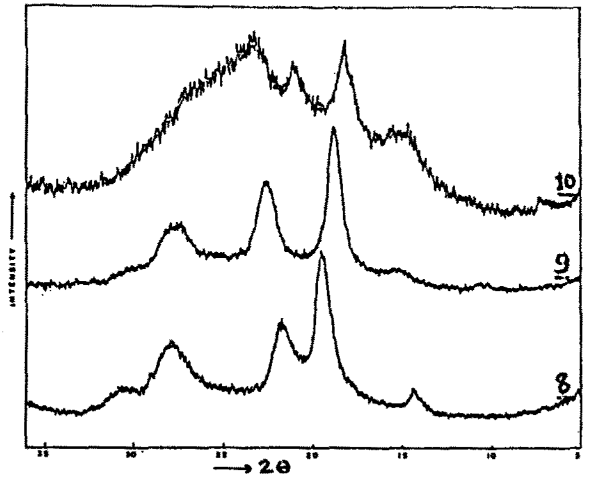


Fig.3 : X-ray diffractograms of polyimide 8,9 and polyamide-imide 10

The thermograms of polyimides 8, 9 and polyamide-imide 10 are illustrated in Fig.2.

Fairly good thermal stability was observed in all these polymers though polyamide-imides showed better stability than polyimides. As expected, PMDA based polyimide showed comparatively superior thermal stability.

The DSC thermograms of the polymers contained several endotherms indicating the possibility of liquid crystalline behaviour. Microscopic examinations of heated samples through crossed polarizing filters, however, did not reveal any optical anisotropy. In fact, the polymers darkened dramatically above 300°C without undergoing any significant flow.

The crystalline nature of these polymers was studied by X-ray diffraction. All the polymers showed partial crystallinity in their X-ray diffractograms. The representative X-ray diffractograms are shown in Fig.3.

## Conclusions

A new diisocyanate, 4,4'-bis(isocyanato) benzylidene aniline, containing aromatic azomethine linkage is synthesized from the corresponding diacid via Weinstock modified curtius rearrangement in good yields. New polyimides and polyamide-imides containing azomethine linkage in polymer backbone are synthesized by using this isocyanate and characterized by usual methods. The polymers show high thermal stability.

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