

## Calculation of activation energy for unsaturated polyamide using fumaric acid and 2,6-diaminopyridine by modified Higashi-Yamazaki phosphorylation method

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With a view to examine the modification of polymer characteristics by the introduction of heterocyclic units in the polymer backbone it was proposed to synthesize and characterize unsaturated polyamides involving 2,6-diaminopyridine and fumaric acid. Though the synthesis of these polyamide has been reported earlier by interfacial method, there is no systematic study seems to have been done to evaluate the kinetic parameters and biological activity. In the present paper phosphorylation technique was employed to prepare the unsaturated polyamide and the results compared with the maleic acid to show the effect of *cis-trans* isomerism in thermal studies.

Keywords: 2,6-Diaminopyridine, fumaric acid, phosphorylation, kinetic parameters.

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### Introduction

Amides are of fundamental chemical interest because conjugation between the nitrogen lone-pair and carbonyl  $\pi$ -bond result in distinctive physical and chemical properties like rigidity and thermal stability. A number of high molecular weight wholly aromatic and thermally stable polyamides have been reported in literature. Bajpai *et al.*<sup>1</sup> reported the unsaturated polyamides based on  $\beta$ -glutamic acid. These polyamides have amide and an unsaturated double bond. If such polyamides are prepared at higher ratio of diamine concentration, the polymer may have amino terminated group. Such terminated amino group and unsaturated double bond may participate into post curing reaction for wide industrial application<sup>2-4</sup>.

It has been reported that MA (Michel Addition) diamine reaction can be used to prepare unsaturated polyamides which are cross linkable by UV light. Carothers was one of the first to explore this type of unsaturated polyamides in interfacial polycondensation reaction between fumaroyl dichloride and diamines which provides polyamides giving tough infusible films, tough modulus fiber stable to 285°C<sup>5,6</sup>.

### Experimental

The polymer was prepared by modified phosphorylation method employing Higashi's conditions. A solution of NMP (65 ml), pyridine (10 ml), LiCl (1 g) and CaCl<sub>2</sub> (3 g) was added

to a mixture of 2,6-diaminopyridine (0.005 ml), diacid (0.005 ml) and triphenyl phosphite (0.01 mol). Mixture was stirred for 4 h at 110°C until a viscous solution was obtained<sup>7,8</sup>. The resulting mixture was poured into hot aqueous methanol. The precipitated polymer was filtered and washed with dil. HCl, aqueous solution of Na<sub>2</sub>CO<sub>3</sub>, water and methanol. The polymer obtained was dried in vacuum at 100°C over P<sub>2</sub>O<sub>5</sub> for 24 h.

#### Characterisation:

The polyamides synthesized were characterized by viscosity measurements, UV-Visible spectra and FT-IR spectra. The thermal studies (TG, DTA and DSC) were carried out for the polymer in nitrogen atmosphere. Thermogravimetry analysis of synthesized unsaturated polymer has been carried out in the temperature range of 40–500°C. The thermogravimetric data was analysed by Murray and White, Coats and Redfern, Doyles and Freeman and Carroll's for each polymer to calculate energy of activation. Different kinetic parameters were determined from Freeman and Carroll's method<sup>9,10</sup>.

### Results and discussion

The viscosity of the polyamide was reported to be 0.29. IR and UV spectral details are already discussed in the previous paper.

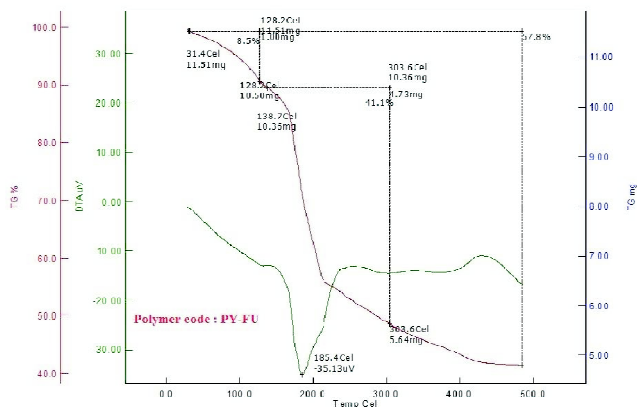


Fig. 1. TG and DTA curve of polymer: PY-FU.

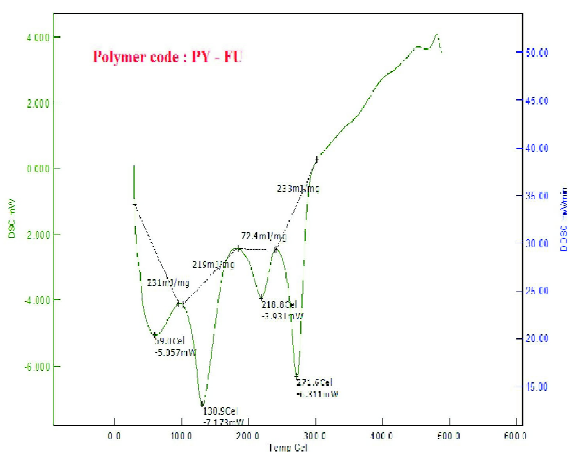


Fig. 2. DSC curve of polymer: PY-FU.

Thermogravimetry analysis of unsaturated polyamide PY-FU depicts two stage decomposition reaction. In the first stage there is a loss of one crystalline water molecule entrapped in the polyamide molecule. The next step of decomposition reaction starts from 128°C to 303°C corresponding to gradual mass loss (41.05% found and 44% calculated). This is due to breaking of amide bond. The residue left behind is the heterocyclic moiety (57.83% found and 56.68% calculated). The thermal degradation by increasing temperature may be due to increasing strain on stability and cross linking of molecule. Increasing thermal vibration decreases the strain and to maintain the stability the unsaturated polyamide undergoes degradation. From the equations of the approximation methods discussed in earlier paper graph was plotted and slope-intercept calculated and the activation energy was calculated. The activation energy of PY-FU by Murray and White

Table 1. Thermal properties of unsaturated polyamides in nitrogen

Sr. No.	Polymer code	$\eta_{inh}$	Temperature (°C) at which the following % weight loss occur				
			10	20	30	40	50
1.	PY-FU	0.29	128	205	210	230	303

was 21.57 KJ, Coats and Redfern was 25.19 KJ, Doyles 1.34 KJ and Freeman and Carroll's was 26.69 KJ. From the intercept calculated by Freeman and Carroll's method the entropy was found to be  $-4.10 \times 10^2$  J and the free energy was reported  $200.1 \times 10^2$  KJ.

Char yield was applied as criteria for estimation (LOI) of the polyamide in accordance with Van Krevelen and Hoftzer equation.

$$LOI = 17.5 + 0.4 CR;$$

$$CR - \text{char yield}; \quad \text{PY-FU: } 40.3$$

The polyamide had LOI value calculated from their char yield was higher than 37. On the basis of LOI value such polymers can be classified as self extinguishing polymers.

PY-FU is a self extinguishing polymer. According to above equation the DTG curve also indicates that the transition centered about 180°C due to pyrolysis of the sample.  $\Delta G$  values for the dissociation constants are positive thus the dissociation process is not spontaneous. A positive value  $\Delta S$  indicates a malleable activated compound that leads to a large number of degrees of freedom of rotation and vibration. On the otherhand, a negative value of  $\Delta S$  is an indication of a highly ordered activated complex and the degrees of freedom of rotation as well as vibration are less than they are in the non activated complex. It can be concluded that the synthesized unsaturated polyamides had good thermal stability as evident from their half decomposition temperature.

### Conclusions

The viscosity of the polymer PY-FU 0.29 was reported to be higher than that of PY-MA 0.24. The LOI of PY-MA was reported to be 37.1 and that of PY-FU was reported 40.3. So the self extinguishing property of PY-FU is higher than that of PY-MA. Also the thermal stability is higher for PY-FU than PY-MA. The comparison is given in the table. Hence PY-FU has better thermal stability than PY-MA due to its *trans* structure.

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