

Thermal studies of unsaturated aliphatic-heterocyclic polyamides

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Thermal analysis provides important information on the temperature dependent properties of materials and on thermally induced process (phase transition, decomposition etc.). Thermal analysis is advantageous as it gives a general view of the thermal behavior of material under various conditions and requires a small amount of sample. Thermogravimetry analysis of synthesized unsaturated polymer using 2,6-diamminopyridine and maleic acid 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 method to calculate energy of activation. Different kinetic parameters were determined from Freeman and Carroll's method and reported.

Keywords: 2,6-Diamminopyridine, maleic acid, energy of activation, entropy, free energy.

Introduction

Aromatic polyamides are a class of high performance polymers that have excellent thermal and electrical properties. They are currently applied in many areas such as aerospace, micro electronic, automotive and gas separation industries as high temperature coating material, structural adhesives, matrix resins, films, interlayer dielectrics, wire insulation and semi permeable membranes^{1,2}. Unsaturated polyamides were among the first polymer prepared by Carothers³. These early polymers were easily gelled by heat and seemingly had little practical value. However the concept of having a polyamide with latent cross linking capability and the development of low temperature polycondensation by interfacial techniques encouraged more recent investigators to explore further the preparation and properties of large numbers of unsaturated polyamides^{4,5}.

Synthesis of polymer: Higashi's method of phosphorylation:

The polymer was prepared by modified phosphorylation method employing Higashi's conditions⁶. A solution of NMP (65 ml), pyridine (10 ml), LiCl (1 g) and CaCl₂ (3 g) was added to a mixture of 2,6-diaminopyridine (0.005 ml), maleic acid (0.005 ml) and triphenyl phosphate (0.01 mol). Mixture was stirred for 4 h at 110°C until a viscous solution was obtained.

The resulting mixture was poured into hot aqueous methanol. The precipitated polymer was filtered and washed with dil. HCl, aqueous solution of Na₂CO₃, water and methanol. The polymer obtained was dried in vacuum at 100°C over P₂O₅ for 24 h.

Results and discussion

In our present investigation the bands in the visible region are due to n- π transition, 253 λ for C=N pyridine ring, 267 λ for C=C pyridine ring, where as those in UV region are associated with n- π^* transition. C=O amide bonds at 284 λ .

Polyamides are generally characterised by the amide band at 3300 cm⁻¹ characteristic of N-H stretching. The presence of characteristic bands for the amide linkage and the absence of characteristic bands due to diamine (NH stretching two bands in the region (3300–3500 cm⁻¹) and diacids (CO stretching, 1680–1715 cm⁻¹) and CH stretching (2500–2700 cm⁻¹) confirm the formation of amide linkages and hence of the polyamides. Amide functional group combines the features of amines and ketone because it has both the N-H bond and C=O bond therefore show a very strong broad band at the left end of the spectrum generally in the range between 3100 and 3500 cm⁻¹ for the N-H stretch. At the same time they also show the staple shaped band in the middle of the spectrum 1630 cm⁻¹. The >C=O stretch is the

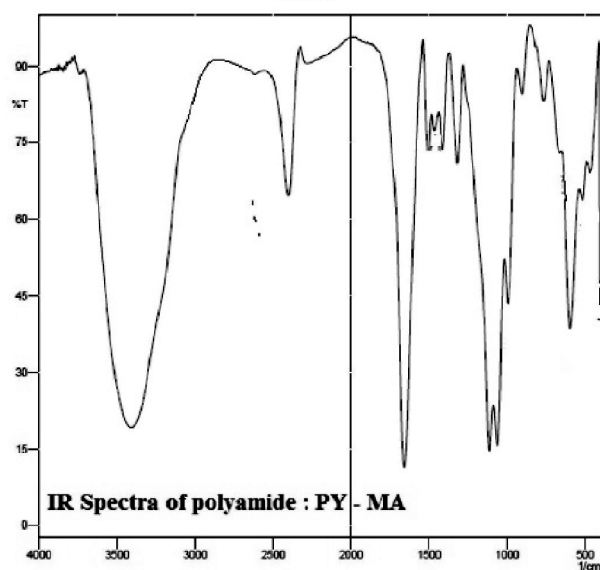
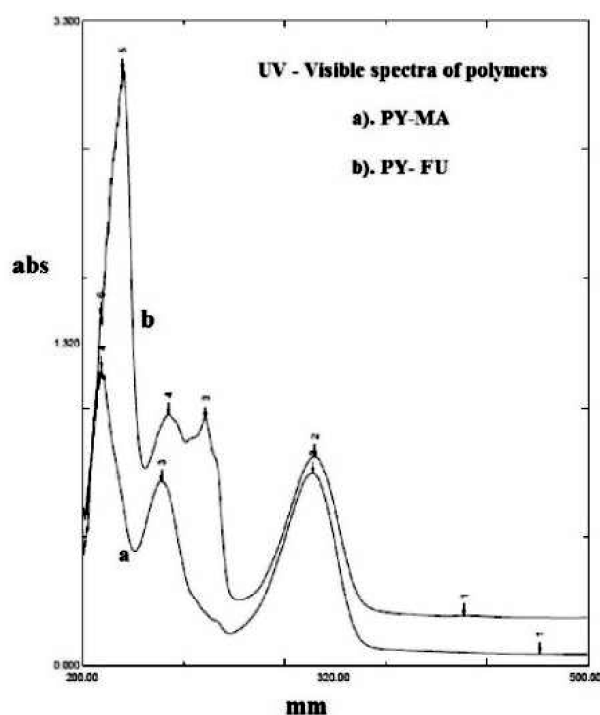


Fig. 1.

most intense peak in IR spectrum. The bond is a fairly polar bonds, and when it stretches the bond dipole changes resolving in intense peak. However, the alkene peak C=C is not a polar bond unless it is asymmetrically substituted, therefore the peak resulting from C=C stretch has weak to medium intensity and sometimes cannot be clearly visible. The band display at 1651 cm^{-1} was assigned to C=C in pyridine ring. The absorption at 1427 cm^{-1} was attributed to C=N stretch in pyridine ring. The band at 1114, 1112, 783, 731 cm^{-1} is due to 2,6-di-substituted pyridine ring 2339, 2360,

2418 cm^{-1} are overtone bands in polymers derived from maleic acid and 2,6-diaminopyridine. The two (O=C-N-H) groups can be close enough to interact internally producing intramolecular (H)-bonding. The *cis* olefinic C-H out of plane stretching is around 820 cm^{-1} strong and sharp in nature due to conjugation with >C=O group as compared to its *trans* counterpart.

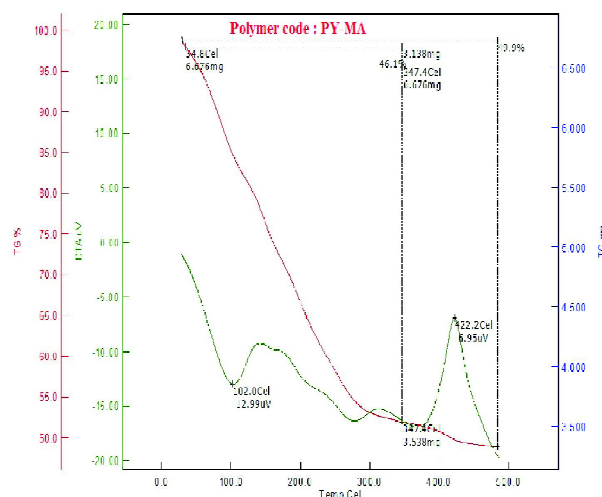


Fig. 2. TGA and DTA curve.

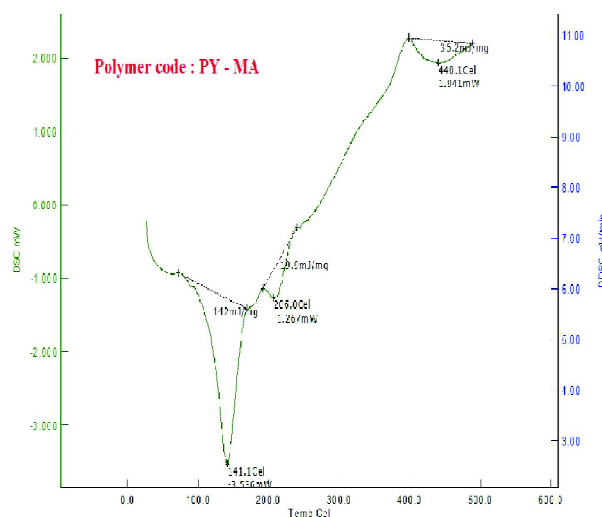


Fig. 3. DSC curve.

Thermal analysis:

Thermogravimetry analysis of unsaturated polyamide containing maleic acid depicts two stages in 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 110°C to 350°C corresponding to gradual mass loss of (46.05% found and 44% calculated). This is due to breaking of amide linked bond. The residue left behind is the heterocyclic moiety (50% found and 56% calculated). From the primary thermograms obtained for the unsaturated polyamides, by plotting the percent weight loss against temperature activation energy can be calculated. The temperature at which major decomposition started was noted as the initial decomposition temperature. The temperature at which the rate of decomposition was maximum T_{max} was obtained from the derivative of weight change with respect to time (DTG). The glass transition temperature T_g in all the cases was observed and taken as the extra plotted onset of the base line departure and was determined from the DTA endothermic peak. In the case of melting temperature the peak temperature were taken. Graph was plotted for all the approximation methods and slope-intercept calculated. The activation energies were calculated graphically from equation after introducing the appropriate approximations assuming the correct order of the reaction which is determined by Freeman and Carroll's method. The activation energy of polymers was reported to be 21.01 KJ for Murray and white, 23.94 KJ for Coats and Redfern, 1.02 KJ for Doyle's and 25.19 KJ for Freeman and Carroll. The activation energies obtained from Murray and White, Coats and Redfern are in fairly good agreement with each other. But there is a little difference in Freeman and Carrolls method. This may be due to the different differential functions over a short interval of time. One of these involved is the tangent dw/dt . Therefore any inaccuracy in determining a single value for dw/dt affects the position of the two points in the plot, which are needed to determine the activation energy. The approximation of Freeman and Carroll's is the one that leads to the smallest errors in the determination of the activation energy. Hence, from the graph E was calculated from the slope and A was calculated from the intercept entropy and free energy was calculated.

Table 1. Thermal properties of unsaturated polyamides in nitrogen

Sr. No.	Polymer code	η_{inh}	Temperature (°C) at which the following % weight loss occur				
			10	20	30	40	50
1.	PY-MA	0.24	98	160	197	250	420

$$\text{Intercept} = \log (KR/h E) + \Delta S/2.303 R$$

The kinetic parameters for the thermal decomposition of the polyamides are reported.

$$E = 25.31(\text{KJ}), \quad \Delta S = -5.09 \times 10^2 \text{ J}, \\ \Delta G = = 177.5 \times 10^2 (\text{KJ})$$

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

$$\text{LOI} = 17.5 + 0.4 \text{ CR}$$

$$\text{PY-MA: } 37.1$$

The polyamide had LOI value calculated from their char yield. If the value goes above 37 such polymers can be classified as self extinguishing polymers.

It is very difficult to draw any unique conclusion from the magnitude of thermal activation energy as decomposition mechanism is expected to be complicated. Positive values of activation energy is due to oxidation-reduction of the unsaturated polymer. Fairly straight line plots are obtained using the three methods. However using the Freeman and Carroll method some abnormal points were ignored to get a clear picture about most of the points. Some points at the beginning or the end did not fall on the straight line. This is expected, since the decomposition of polymers is not obeying first order kinetics perfectly.

ΔG values for the dissociation constants are positive thus the dissociation process is not spontaneous. A positive value ΔS indicates a malleable activated compound that leads to a large number of degrees of freedom of rotation and vibration. On the other hand, a negative value of ΔS 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 moderate thermal stability as evident from their half decomposition temperature.

Conclusions

The polyamide synthesized using Higashi's phosphorylation method had higher viscosities as reported from the earlier literature using low temperature solution and interfacial polycondensation technique. Since the viscosities were fairly high solubility also increases. Increase in viscosity also

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increases the thermal stability of the polymers. The viscosity of the polyamide was reported 0.24. Based on the LOI value the polymer is a self-extinguishing polymer. ΔG values for the dissociation constants are positive thus the dissociation process is not spontaneous. A negative value of ΔS 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 polyamide had moderate thermal stability.

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