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Ionic liquid mediated synthesis of 4, 4'diamino azo benzene substituted aliphatic polyamides and thermal studies

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Ionic liquids act as green solvents, which can replace the usual traditional solvents which pose both environmental and biological hazard. In the present work 4,4'diamino azobenzene has been condensed with various aliphatic diacids such as succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and Pimelic acid using imidazolium based ionic liquids in the presence of triphenylphosphite(TPP). The resulting azopolyamides have been obtained in high yield with intrinsic viscosity ranging from 0.56 - 0.81 dlg^{-1}. This method is compared with modified Higashi's method. The thermodynamic parameters like ΔG, ΔH and ΔS are calculated by approximate methods such as Freeman & Carroll, Coats & Red fern, Doyle and Murray and White. The resulting polyamides prepared using green condition show increased thermal stability when compared to polyamides prepared by modified Higashi's method.

Keywords: Ionic liquid, Polyamides, Thermal studies, Green conditions, Viscosity

The introduction of greener technologies has become a major concern in the search for alternatives to the eco system. Therefore, it has become utmost priority for the research scientist to explore the area of green chemistry. Various policies for protecting the environment paved the way for the progression of green chemistry[1].

For the replacement of ceramic and metals in the field of aerospace and automotive Industries, thermally stable polyamides have received much attention. Thermal stability of polyamides can be increased by changing the approach of synthesis. In this percept synthesis of polyamides using ionic liquids provides green and safe medium and has catalytic effect on polymerisation reaction.

Room-temperature ionic liquids are currently being extensively studied for a variety of applications. Use of ionic liquid has overtaken the difficulties such as prolonged reaction times, unsatisfactory yields, and difficult workup procedures in conventional methods. A convenient and simple method for polymerization reaction of diamines with diacids proceeded well in imidazolium based ionic liquids without any catalyst and polyamides were obtained in high yields and high inherent viscosities. The advantages of choosing ionic liquids are for more sophisticated processing and ecofriendly media.

In connection with our research on usage of imidazolium based ionic liquids in polymer synthesis and their importance as novel reaction media we here in report an efficient poly condensation of 4,4' diamino azo benzene with various di acids such as succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and pimelic acid.

A comparative study between conventional polymerization and green conditioning using ionic liquids has been carried for synthesized azo polyamides. Thermo gravimetric properties of all the prepared polymers were investigated with DSC and TGA and DTA methods.

Experimental Section

Method I

Synthesis of Polyamides Using Ionic Liquids

Azo polyamides were prepared by condensation of 4,4' diamino azo benzene with different aliphatic diacids such as succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and pimelic acid in different imidazolium based Ionic Liquids having different number of alkyl group. High inherent viscosity and yield was obtained when 1,3 diisopropylimidazolium bromide was used for one pot polymerisation reactions.

Into a porcelain dish (4.88×10^{-4} mol) of dicarbxylic acid, (4.88×10^{-4} mol) of 4,4' diamino azo benzene was dissolved in 0.30 g of 1,3 diisopropylimdazolium bromide and heated. To this mixture 0.26 mL (9.76×10^{-4} mol) of TPP was added and was refluxed at 110°C for 2.5 h. At the end of reaction the azo polyamide was poured into methanol. The colour varied from grey to dark brown and the polymer was obtained in high yield. It was again washed with CH_3OH and hot H_2O dried at 100°C under reduced pressure.(yield 92%) (Fig.1 and Table 1).

The reaction was performed under different imidazolium based Ionic Liquids bearing different alkyl group. The yield and visocity was determined for the azopolyamides. The ionic liquid which gave high yield and viscosity was noted. Further all the azopolyamides was prepared using this ionic liquid. In our case 1,3 diisopropylimidazoliumbromide showed high yield and viscosity (Table 2).

It was also found that the azopolyamides were not obtained in absence of either TPP or Ionic Liquids. So the presence of both the components are necessary for polymerisation reaction. In this polycondensation polymerisation reactions ionic liquid play the role of solvent as well as catalyst. The amount of Ionic Liquids used for the above reaction is very low. So recycling of Ionic Liquids was avoided[2-6].

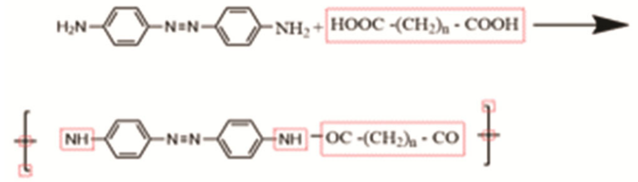

Fig. 1 — Synthesis of Azopolyamides

Table 1 — Different types of ionic liquids used.

Ionic liquid	Yield(%)	Viscosity
1,3 Diethylimidazolium bromide	81	0.48
1,3 Diisopropylimidazolium bromide	92	0.56
1,3 Diisobutylimidazolium bromide	73	0.43
1,3 Dimethyylimidazolium bromide	66	0.41
1,3 Dipenylimidazolium bromide	75	0.36

Table 2 — Different types of diacids used.

R	Acid Name	Polymer Code
$(-CH_2-)$	Malonic Acid	AZ- PA1
$(-CH_2-)2$	Succinic Acid	AZ- PA2
$(-CH_2-)4$	Adipic Acid	AZ- PA4
$(-CH_2-)5$	Pimelic Acid	AZ- PA5
$(-CH_2-)6$	Suberic Acid	AZ- PA6
$(-CH_2-)7$	Azealic Acid	AZ- PA7
$(-CH_2-)8$	Sebaac Acid	AZ- PA8
CLSU	Chloro Succinic Acid	AZ-PA9
CLAD	Chloro Adipic Acid	AZ-PA10

Synthesis of azo polyamides using modified higashi's method

The azopolyamide was prepared by modified phosphorylation method employing Higashi's condition. A solution of NMP(65 mL), pyridine (10mL), LiCl (1g) and $CaCl_2$ (3 g) was added to a mixture of 4,4'diaminoazobenzene (0.005 mol), diacid (0.005 mol) tri phenyl phosphite (0.01 mole) mixture was stirred for 4 h at 110°C. Adark coloured viscous solution was obtained. The resulting mixture was poured into hot aqueous methanol. The precipitated azopolyamide was filtered and washed with dil. HCl and aqueous solution of Na_2CO_3, water and methanol. The azopolyamide obtained was dried in vaccum at 100°C over P_2O_5 for 24 h. The azopolyamide was obtained in moderate yield (80-84%)[7].

Characterisation

Viscosity

The polyamides synthesized were characterized by viscosity measurements in 98% (AR) sulphuric acid. The inherent viscosity was calculated using the formula,

$$\eta_{inh} = \frac{2.303}{C} \log \frac{t1}{t2} \qquad ...(1)$$

where, C is the concentration of the azopolyamide solution in g dl^{-1}. t_1 and t_2 are the flow times of the polymer solution and solvent respectively. For both the polymers 0.5g dl^{-1} concentration was used. An ubbeldobe viscometer provided with guard tubes with only $CaCl_2$ to prevent absorption of moisture was used to determine the flow time.

FT-IR spectra

FT-IR spectra of the azopolyamide were recorded with a Perkin-Elmer. 257. For most of the polymers KBr pellet technique was adopted.

Thermal studies

The thermal studies (TG , DTA and DSC) were carried out for all the polymers in nitrogen atmosphere.TG analysis were carried out on the thermal analysis Stanton– Redcoft Simultaneous TG, DTA apparatus.

Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Platinumpan was cleaned, driedand accurately weighed powder was taken and heated at a programmed rate of 5°C/min and 10°C/min in the temperature range from 50° to 760°C under nitrogen gas flow.

Evaluation of kinetic parameters of the synthesized azopolyamides was studied using various approximation methods such as Murray and white, Coats and Redferm, Doyle's and Freeman-Carroll methods. From this frequency factor, free energy change, entropy change was calculated.

T_{max} corresponds to the maximum decomposition temperature and DSC was used for recording DSC thermograms of azopolyamides.

Calculation of kinetic parameters

Activation energy from TGA

From the charteristic thermograms for the azopolyamides, which was obtained by plotting the percentage of weight loss against temperature, activation energy was calculated. The temperature at which maximum decomposition occurred was taken as the initial decomposition temperature. The order and energy of activation were calculated by various methods.

The results obtained by,

- Murray and White
- Coats and Redfern
- Doyles
- Freeman and Carroll's Methods

For any given applications, it is likely that one (or) a few physical and chemical properties will be important. A few which were often encountered are structural integrity, thermal behaviour, weight loss and susceptibility to oxidation.

Activation energy was calculated using the following approximation methods. The Arrhenius equation can be given as,

$$\frac{dc}{dt} = Ae^{-E/Rt}(1-C)^n \qquad \ldots(2)$$

Integration of L.H.S gives,

$$\int_{C_0}^{C} \frac{dc}{(1-C)n} = \frac{(1-C)^{(1-n)}-1}{1-n} \qquad \ldots(3)$$

For 'n' not equal to = ln (1-C)

For the R.H.S of equation the most complete integral are so numbers that various author's have sought and formed approximate integrals that permitted convenient and reasonably accurate evaluation of kinetic parameters. Some of these will be discussed below,

1) Murray and white[8] :

$$\int_{T_0}^{T} e^{-E^*/RT} \approx \left(\frac{RT^2}{E}\right) e^{-E^*/RT} \qquad \ldots(4)$$

Plots, ln[ln(1-C)]-2lnT Vs 1/T for (n=1) …(5)

2) Coats and Redfern[9] :

$$\int_{T_0}^{T} e^{\frac{-E^*}{RT}} dt \approx (RT^2)\left[1-2\frac{RT}{E}\right] e^{\frac{-E^*}{RT}} \qquad \ldots(6)$$

Plots, $\log \frac{[\ln(1-C)]}{T^2} Vs 1/T$ for (n=1) ...(7)

3) Doyle[10] :

$$Log R/E \int_{T_0}^{T} e^{-E^*/RT} dT \approx -2.315 - 0.4567(E/RT) \qquad \ldots(8)$$

$$Log R/E \int_{T_0}^{T} e^{-E^*/RT} dT \approx -2.315 - 0.4567(E/RT) \qquad \ldots(9)$$

$$Log R/E \int_{T_0}^{T} e^{-E^*/RT} dT \approx -2.315 - 0.4567(E/RT) \ldots(10)$$

For 20≥E/RT ≥60

Plots, log[ln(1-C)] Vs 1/T for n=1 ...(11)

The activation energies were calculated graphically from the above equations and correct order of the reaction was determined by Freeman and Caroll's method.

4) Freeman and caroll's method[11] :

Freeman and carroll's method is plots of,

$$A = \frac{\Delta \log(dw/dt)}{\Delta \log Wr}\ Vs\ B = \frac{\Delta 1/T}{\Delta \log Wr} \qquad \ldots(12)$$

For the purpose of this plot dW and dW_r can be determined directly from the thermogram in term of the no. of division. The activation energy calculation from TG curves of the polyamides[5,12-13].

To calculate the kinetic parameters of synthesised azopolyamides, we derived the TG curves by using an analytical method given by Freeman-Carroll. Free energy change (ΔG)

$$\Delta G = \Delta H - T\Delta S, \qquad \ldots(13)$$

Where, ΔH= change in enthalpy

T = Temperature in K, ΔS = change in entropy

Calculation of change in entropy

Intercept=log(KR/hE)+ΔS/2.303R ...(14)

For all decomposition reaction by plotting the L.H.S of equation as a function of 1/T, E was calculated from the slope and A was calculated from the intercept. Therefore, ΔS=change in entropy

h = Planck's constant 6.625×10^{-27} erg/sec

E = activation energy

Free energy change is calculated from the relation $\Delta G = \Delta H - T\Delta S$

$$\Delta S = 2.303 R \log Ah/KT \qquad ...(15)$$

$K = 1.3806\text{x}10^{-16}$ erg/deg/mole,

R=1.987 cal/deg/mol or 8.314 J/K/Mol

Results and Discussion

With a view to increase the thermal stability of the polyamides a different method green synthesis using imidazolium based ionic liquid was adopted. These polyamide have already been synthesised and reported in our laboratory using phosphorylation method, low temperature solution method and modified phosphorylation method under Higashi's condition was also adopted. As an extension of our research work on the application of ionic liquids in the synthesis of polyamides we report a very simple, facile and efficient method for the polymerisation of 4,4' diamino azo benzene with various aliphatic diacids such as malonic acids, succinic acid, glutaric acids, adipic acid, pimelic acids, suberic acid, chloro succinic acid and chloro adipic acid. The polymerisation proceeded efficiently with the combination of ionic liquid and an activating agent as TPP, enabling a direct route to the polycondensation reaction between diamines and diacids without using NMP, $CaCl_2$ or LiCl or Py which were necessary for our previous method. Here in this polymerisation reaction the ionic liquids play a dual role both as a solvent and as a catalyst. Since only a minimum of ionic liquid was used for polycondensation reaction, recycling was not required.

On comparing our present study and previous work which we synthesised using modified Higash's condition- direct phosphorylation method employing ($NMP/TPP/CaCl_2/LiCl/Py$) system, the polyamides prepared using ionic liquid and TPP required lower reaction time and gave azopolyamides with high inherent viscosity and high thermal stability (Table 3). Further the use of ionic liquids/TPP reduced the overall cost of synthesis, imparted a green condition by avoiding chemicals such as NMP or TPP which were necessary for conventional heating.

The following polyamides were synthesised using ionic liquids from 4,4'diamino azo benzene condensed with different aliphatic di acids.

Table 3 — Comparision of viscosities of azopolyamides employing traditional method and ionic liquids.

S.No.	Polyamide Code	Viscosity dlg^{-1}	
		Traditional method	IL's with TPP
1	AZ-PA1	0.24	0.31
2	AZ- PA2	0.26	0.34
3	AZ- PA3	0.38	0.43
4	AZ- PA4	0.78	0.83
5	AZ- PA5	0.49	0.56
6	AZ- PA6	0.62	0.81
7	AZ- PA7	0.45	0.52
8	AZ- PA8	0.20	0.39
9	AZ- PA9	0.22	0.38
10	AZ- PA10	0.36	0.42

As the number of alkyl substituent increases the viscosity of the polyamides also increases. Moreover the viscosity of these polyamides reported using traditional methods is given (Table 1). The viscosities of the polyamides AZ-PA1 and AZ-PA2 is very low in phosphorylation method but is greatly enhance when Ionic Liquids with TPP is employed. This may be due to the increase solubility of the diacids in ionic liquids. The polyamides obtained from substituted diacids such as AZ-ClSU(AZ-PA9) and AZ-ClAD(AZ-PA10) showed enhanced inherent viscosity than their unsubstituted counter parts. This may be due to rigidity leading to a cross -linking rigid polymer with a long chain formation.

The resulting polyamides were characterised using FTIR. In IR spectra, the azopolyamides are usually characterised by amide band at 3300 cm^{-1} as broad peaks with medium intensity and C=O of the amide group at 1720-1820 $cm^{-1}$with high intensity (Table 4) (Fig. 2 and Fig. 3)[14,15].

Thermal analysis of the polyamides was carried out using TGA and DSC techniques in nitrogen atmosphere[16-19]. Samples were heated upto 500°C at the rate of 10°C and N_2. In general all the polyamide synthesis in our present study shows 3 stages of weight loss. In the first stage a weight loss of 5% occurs which is accompanied by a small endotherm in the temperature range 130-160°C in DTA curve. This is attributed to the removal of H_2O molecule. The second stage corresponds to steep fall in TG curves corresponding to 20% corresponding to major decomposition. In the 3rd stage the weight loss in the curve is steady which corresponds to different reactions such as bond scissions and decomposition etc. The T_{max} value corresponds to 20% weight loss (Tables 5 and 6) (Figs 4, 5 and 6).

Table 4 — IR spectra of azopolyamides (frequency in cm^{-1}).

Polymer	Amide A band N-H stretching	Amide I band C=O stretching	Amide II band coupling of NH in-plane de formation CN stretching	Amide III band N-H bending + CN in-plane stretching		AmideV band Out-of-plane NH Deformation	C=C stretching of aromatic rings	CH_2 group in phase and out of phase vibrations of hydrogen atoms		C-H aromatic stretching
AZ- PA1	3410	1670	1520	1290	1250	680	1580	3010	2845	3030
AZ- PA2	3400	1660	1520	1290	1250	680	1585	2010	2840	3030
AZ- PA3	3405	1660	1520	1290	1260	680	1580	3020	2840	3030
AZ- PA4	3400	1660	1520	1290	1260	680	1580	3010	2840	3030
AZ- PA5	3405	1665	1520	1290	1260	680	1580	3010	2840	3030
AZ- PA6	3400	1670	1520	1290	1260	680	1585	3010	2840	3030
AZ- PA9	3410	1670	1520	1290	1260	680	1580	3010	2840	3030

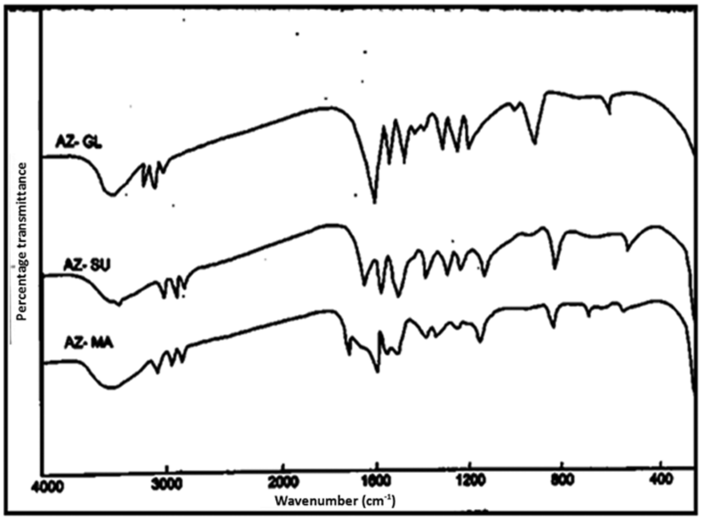

Fig. 2 — IR sepctra of azopolyamides - AZPA1, AZPA2, AZPA3

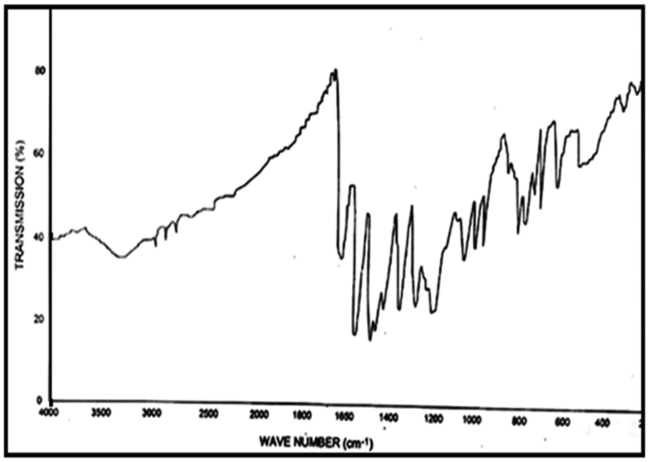

Fig. 3 — IR spectra of azopolyamides-AZPA4

From the equation of the approximate method a graph was plotted. From the slope and intercept, activation energy was calculated.

Comparison of activation energy (Kcal/mole) of polymers using different approximate methods

Charyield was applied as external for estimation of limiting Oxygen Index of the polyamide in accordance with Van Krevlen and Hoftzer equation,

$$LOI = 175.5 + 0.4CR. \text{ (CR – Char yield)} \qquad ...(16)$$

Table 5 — Thermal properties of azopolyamides in nitrogen.

Polymer	η_{inh} (dlg^{-1})	Temperature(°C)at which the following % weight loss occur						T_{max} (°C)	Number of Phases	
		10	20	30	40	50	60			
AZ-PA1	0.26	285	425	465	495	575	-	290	2	290
AZ-PA2	0.29	270	405	440	475	545	-	275	3	235,275
AZ-PA3	0.39	330	365	400	475	555	-	290	3	290,435
AZ-PA4	0.47	345	385	445	480	565	-	395	3	390,460
AZ-PA5	0.45	335	375	435	490	540	-	360	2	365,455
AZ-PA6	0.24	260	380	410	480	505	-	290	2	305,505,335

Table 6 — Thermal studies.

S.No	Polyamide code	Viscosity(dlg^{-1}) η_{inh}	UV-Visible λ_{max}(nm)		TGA		DTA Exotherm(°C)
					20%(°C) Decomposition	T_{max}(°C)	
1	AZ-PA1	0.31	257	485	310	295	290
2	AZ-PA2	0.34	255	475	305	310	320
3	AZ-PA3	0.43	238.4	432.9	345	370	-
5	AZ-PA7	0.83	-	-	-	-	-
6	AZ-PA8	0.56	242	455	-	-	-
7	AZ-PA5	0.81	246	456	369	289	-
8	AZ-PA9	0.52	246	453	369	336	-
9	AZ-PA10	0.39	237	474	265	260	27-
10	AZ–PA6	0.38	-	-	-	-	-

Table 7 — Calculation of activation energy using different methods

S.No	Polyamide	Activation Energy			
		Murray and White	Coats and Redfern	Doyles	Freemann & Caroll
1	AZ-PA1	9.412	10.321	9.963	16.34
2	AZ-PA2	9.944	9.210	8.314	5.541
3	AZ-PA3	8.635	8.748	7.377	19.083
4	AZ- PA4	9.643	9.7007	8.662	22.109
5	AZ- PA5	10.760	10.84	9.997	11.054

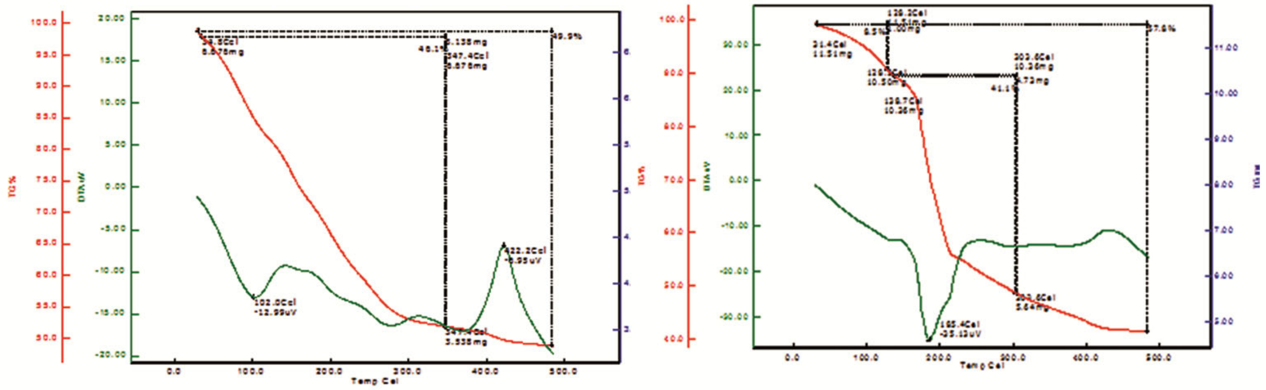

Fig. 4 — TGA of AZPA3, AZPA4, AZPA5, AZPA6

None of the polyamides showed self-extinguishing property. According to above equation the DTG curve also indicate that the transition centres about 280°C due to pyrolysis of the sample.ΔG values are found to be and hence the dissociation process is non spontaneous. For all the azopolyamides synthesised the value of ΔS was found to be negative indicates the formation of highly ordered activated complex. It can be concluded that the synthesised azo polyamides showed good thermal properties which can be seen from their half decomposition temperature (Tables 7 and 8).

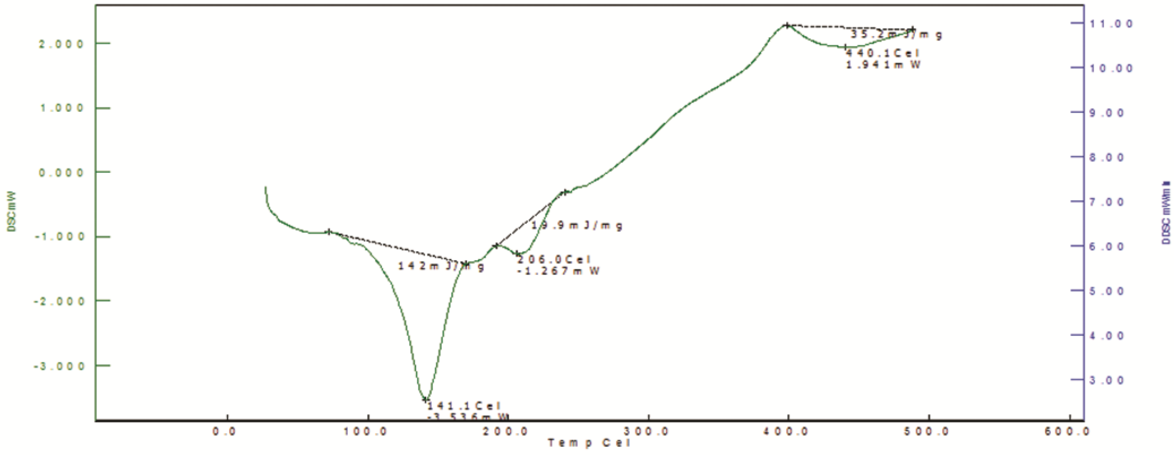

Fig. 5 — DSC of AZPA3

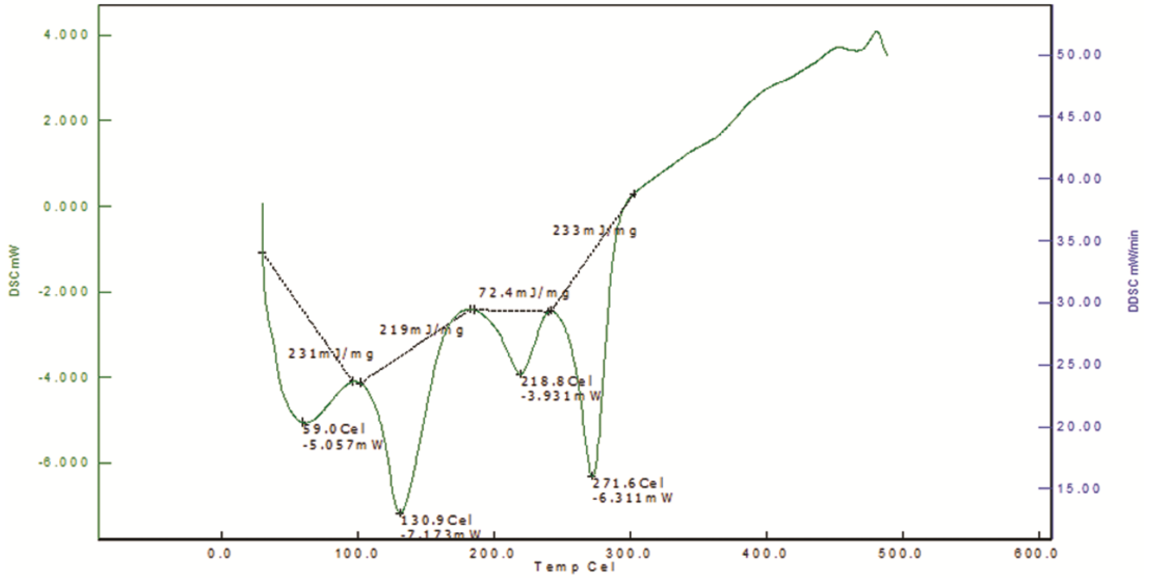

Fig. 6 — DSC of AZPA4

Table 8 — Calculation of kinetic parameters

Polyamides	ΔE(KJ)	ΔH(KJ)	ΔS(KJ)	ΔG(KJ)
AZ-PA1	24.09	23.8	-1.763	1485
AZ- PA2	15.32	15.02	-1.942	1532
AZ- PA3	21.38	20.97	-2.174	1630
AZ- PA4	26.74	25.38	-2.843	1741
AZ- PA5	29.38	28.97	-3.001	1862

Conclusion

This paper presents the preparation of 4,4' diamino azo benzene with various aliphatic diacids using Ionic Liquids. Thus providing green conditions, the polyamides synthesised showed enhanced viscosity when compared to modify phosphorylation method employing Higashi condition. The thermal stability increased in Ionic Liquid method. By applying the different approximation methods E_a was calculated. From this kinetic parameter were calculated. △G value was found to be positive. Therefore, dissociation process is nonspontaneous. None of the polyamides showed self-extinguishing property. Since all the PAs showed viscosity less than 0.6dl/g fibre forming capacity could not be studied. Hence the method of preparation should be modified further to enhance the viscosity and hence the fibre forming capacity of polyamides.

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