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STUDIES ON AMIDATION AND IMIDIZATION PROCESSES OF AMINE SALTS OF AROMATIC TETRACARBOXYLIC ACIDS AND DIAMINE

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ABSTRACT

The amidation (A) and imidization (I) processes of several amine salts prepared from aromatic tetracarboxylic acids and diamine have been studied by means of thermal analysis (TG, DTA and DSC) and IR spectroscopy. The degrees of imidization (cyclization) of these salts, as estimated via thermal analysis under programmed heating, are 87–93%. The activation energies of these A–I processes, as determined from DSC curves, are 125 and 250 kJ mole^{-1}. From the thermal analysis curves and infrared absorption spectra, it appears that the amidation and imidization processes are superimposed, and the imidization process occurs before the completion of the amidation.

INTRODUCTION

Polyimides are a class of thermally stable polymers, but the extent of imidization (cyclization) affects their stability. The study of imidization reactions of the polyamic acids is usually carried out by the infrared spectroscopic method [1] or the weight change method [2]. In the infrared method, a sample heated at high temperature (e.g. ~ 300°C) for a given time is taken as a standard of completely imidized specimen. However, the standard thus obtained is not completely cyclized.

Because the synthesis of the polyamic acid is often carried out in a polar aprotic solvent such as *N*,*N*-dimethylacetamide or *N*,*N*-dimethylformamide with boiling points near the A–I process temperature, it is impossible to distinguish the dehydracyclization from the evolution of the solvent during thermal analysis. Furthermore, some side reactions of polyamic acid with the polar solvent accompany the main cyclization process [3,4].

The present work reports the results of an investigation of the A–I process of amine salts prepared in methyl alcohol by means of thermal analysis techniques and IR.

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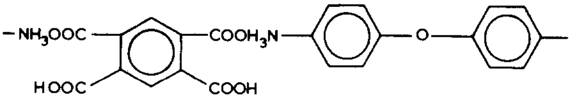
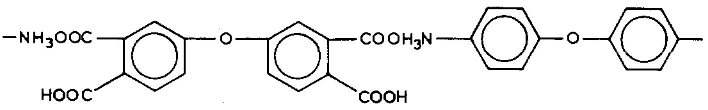
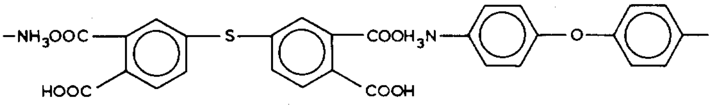
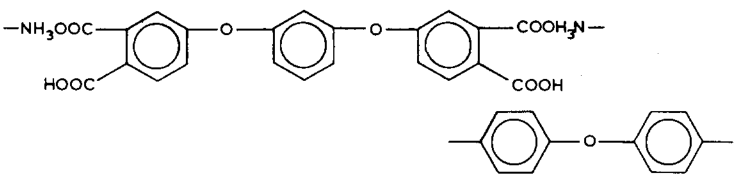
TABLE 1

Peak temperatures and reaction temperature ranges on DTA and DSC curves of several amine salts and their calculated and experimental weight losses due to dehydracyclization

Abbreviated symbol of salt	Structural formula
Bm	
Mm	
Lm	
M_2m	

EXPERIMENTAL

Preparation of samples

4,4-Diaminodiphenyl ether solution (3% in methanol) was added dropwise to an equimolar amount of an aromatic tetracarboxylic acid solution (10% in methanol) at room temperature. The amine salt precipitate was filtered off, washed with methanol and dried under reduced pressure to remove any residual solvent. The salt, which was in the form of a white powder, was used for the study of the A–I process. The chemical structures of the salts thus prepared are listed in Table 1.

Apparatus and experimental conditions

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed on a Thermoflex thermal analyzer (Rigaku Co., Japan). A sample

Peak temperature and reaction temperature range (°C)						Wt. loss (H_2O) (%)		Extent of cyclization (mole %)
Thermoflex		4.1		CDR-1		Calcd.	Exptl.	
I	II	I	II	I	II			
186	213		212	189 (peak) 168–228 (range)	212 15	15.86	14.8	87
208	225	204	225	209 120–260	228	13.19	12.7	93
185	207	187		185 124–244	203	12.81	12.3	92
181	203	184	202	163,182 124–263	203, 228	11.29	10.7	90

of 5 mg was used at a heating rate of 10°C min^{-1}. A stream of air was passed over the sample at a controlled rate of 50 ml min^{-1}. The TG scale was 10 mg and the DTA scale ± 100 μV. A 4.1 differential thermobalance (Peking optical instrument factory) was also employed. The experimental conditions were: 10 mg sample; heating rate, 5°C min^{-1}; atmosphere, static air; TG scale, 25 mg; DTA scale, ±25 μV. Differential scanning calorimetry (DSC) was performed on a CDR-1 differential scanning calorimeter (Shanghai Tienping instrument factory) using an air atmosphere and 7 mg of specimen. The specimen was heated at a rate of 5°C min^{-1}. The scale was ±5 mcal sec^{-1}. Infrared spectra were recorded on a Perkin–Elmer 599B spectrophotometer using KBr pellet.

RESULTS AND DISCUSSION

The A–I processes of these amine salts give obvious responses on the thermal analysis curves, as shown in Figs. 1 and 2. The endothermal peaks at

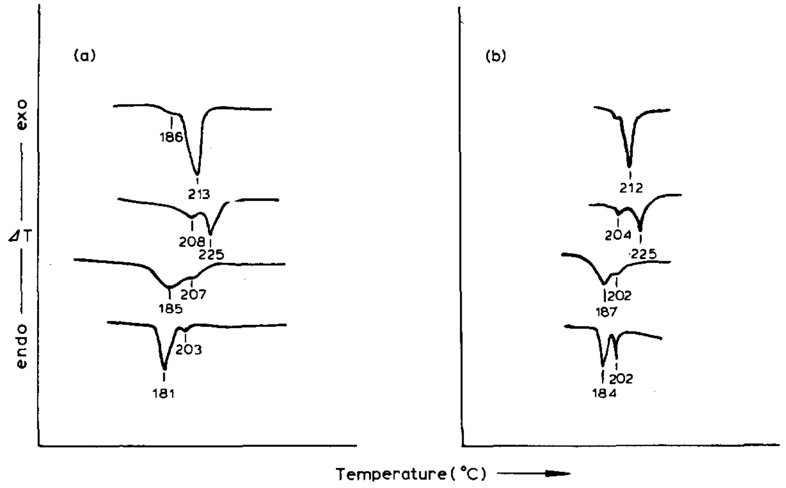


Fig. 1. DTA curves of amine salts using (a) Thermoflex thermal analyzer; (b) 4.1 differential thermobalance.

~ 200°C correspond to a dehydracyclization process. This can be verified from the IR spectra and theoretical calculations based on the TG curves. From the DSC curves, it can be seen that the reaction temperature range of

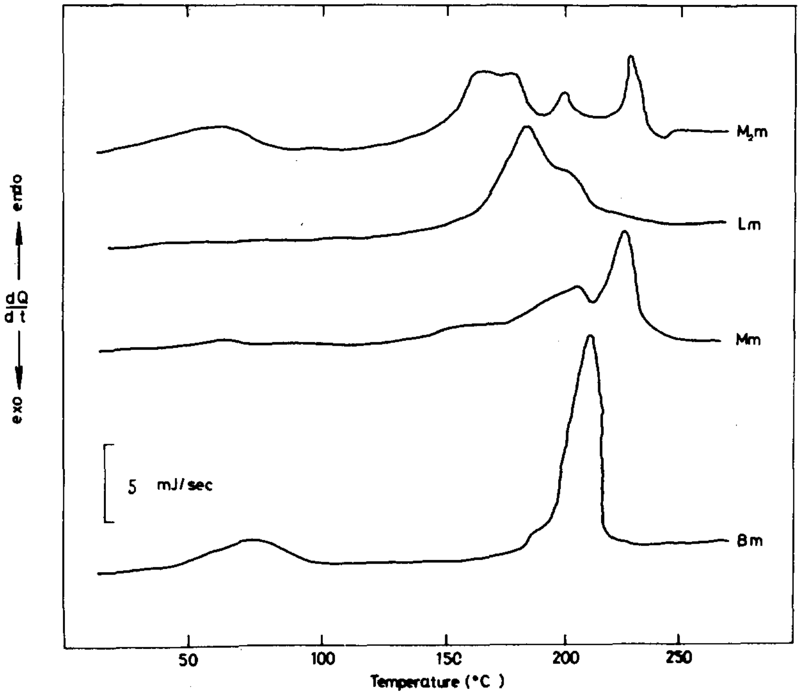


Fig. 2. DSC curves of amine salts.

Bm is about 60°C which is narrower than those of other salts (about 130°C). In addition, it seems that the peak temperature increases slightly with the increase in the chain rigidity in connection with the structure of the tetracarboxylic acid. The results are given in Table 1.

Investigation of the A–I processes of the amine salts prepared in methanol should be free from interference from the residual solvent. Figure 3 shows the TG and DTA curves of M_2m, which was prepared in DMAc as well as in CH_3OH. In the case of CH_3OH, although the amine salt still contains a small amount of included CH_3OH, it is evolved completely below 70°C where a broad endothermal peak is noticed on the DTA curve, while the A–I process takes place at much higher temperatures (140–216°C). In this case, these two processes are completely separated. When DMAc is used as solvent, the evolution of the solvent and the A–I process take place in the same temperature range. The residual DMAc content in the sample after evacuation at lower temperatures is as much as 9%, as determined from the first weight loss step (see Fig. 3), leading to a widening of the DTA peak. If higher temperatures were employed to remove the polar solvent, the A–I process would take place simultaneously, and as a result it is impossible to investigate the latter process.

Since the amine salts were synthesized in CH_3OH in the present work, interference due to the solvent was avoided, making it possible to study clearly the extent of completion and the characteristics of the A–I process.

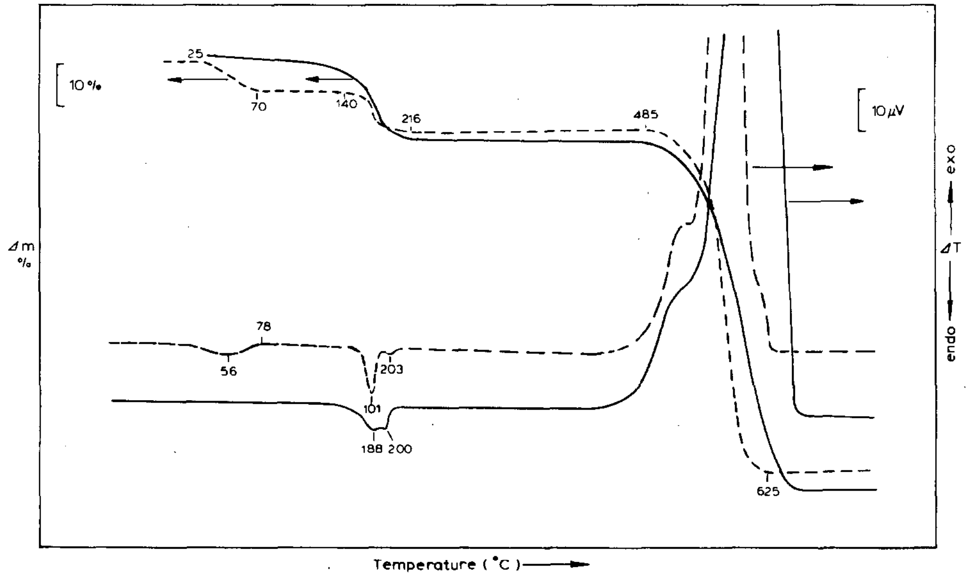
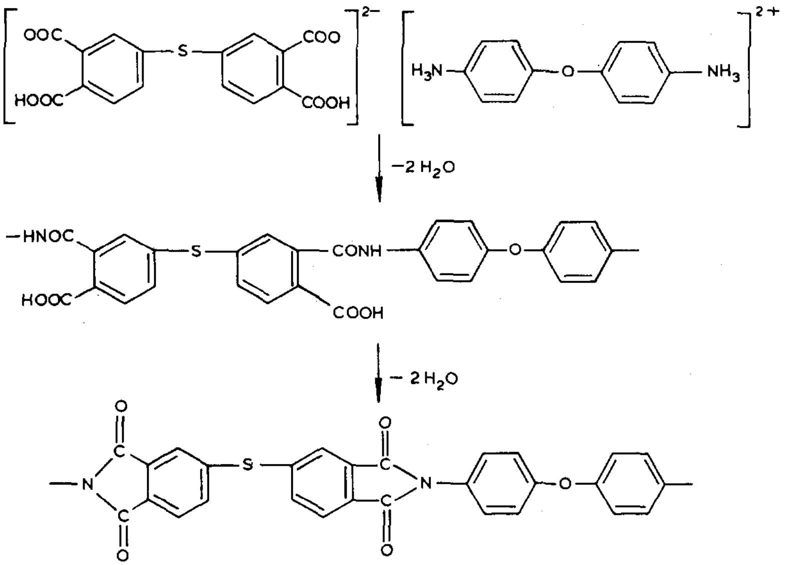


Fig. 3. TG and DTA curves of M_2m prepared in: - - - - - -, CH_3OH; ————, DMAc. (Curves obtained on a Thermoflex thermal analyzer.)

Quantitative estimation of the degree of imidization

The amine salt Lm is taken as an example. Figure 4 illustrates the TG and DTA results obtained with Lm. From the obvious weight loss processes on the TG curve, it can be seen that in the temperature range 149–245°C water loss occurs due to the A–I process and thermo-oxidative decomposition occurs at 514–645°C. The endothermal peaks at 185 and 207°C on the DTA curve represent the A–I process. The reaction process may be described as follows:



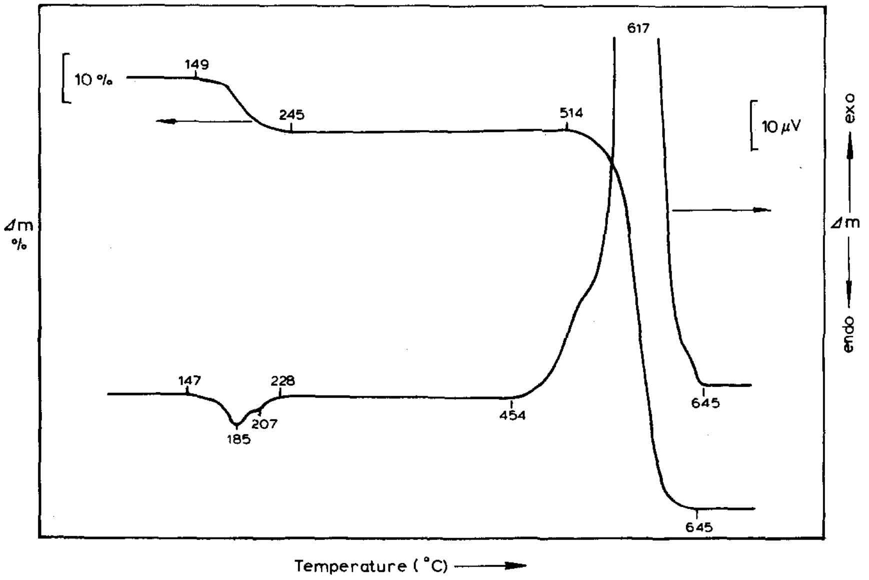


Fig. 4. TG and DTA curves of Lm.

In this reaction four water molecules are evolved from each repeating unit. The weight of the repeating unit of this polyimide is 490.11, therefore the theoretical amount of water loss must be $[18.02 \times 4/(490.11 + 18.02 \times 4)] \times 100\% = 12.82\%$, compared to an actual weight loss of 12.3% determined from Fig. 4. The difference is −0.5%. If the first step of the foregoing reaction (amidation) is assumed to be complete, then this difference corresponds to 8% incompletion of cyclization in the second step. In other words, the extent of imidization is 92%: similar calculations for the other salts give 87–93% imidization (see Table 1).

Determination of the rate of the A–I process

The amine salt samples were treated at given temperatures for 2 h. Thereafter, their DSC curves were obtained and the peak area determined. Change in peak area denotes the occurrence of the A–I process during the thermal treatment at different temperatures, as shown in Fig. 5. From these DSC curves it is seen that the peak areas of the A–I processes decrease with increasing temperature of heat treatment, because more and more of the amine salts would have undergone the A–I process during the thermal treatment. Let S_0 and S represent the peak areas before and after heat treatment, respectively; the extent of cyclization can then be described by $1 - S/S_0$. Figure 6 shows how the extent of imidization changes during the thermal treatment of the salts at different temperatures. Most of the A–I processes are completed below 195°C. For example, the reaction of Lm takes place primarily at 130–170°C. Figure 6 also shows that the temperature range for the formation of imide rings depends on the structure of the amine salts. The reaction temperature range of Bm is narrower (~ 20°C) than those of other amine salts Mm, Lm, M_2m (~ 40–60°C). This is in agreement with the data mentioned previously (see Fig. 2, Table 1).

The apparent activation energies of the A–I processes and of the evolution of residual CH_3OH are calculated from the dependence of peak temperatures upon heating rates to be 125 and 250 kJ mole^{-1} and 84 kJ mole^{-1}, respectively, for Lm (see Fig. 7).

Some characteristics of A–I processes

The structural changes of amine salts during thermal treatment at programmed heating rates and constant temperature were examined by means of IR spectra. Figure 8 shows the spectra of the original samples (curve 1), and those at certain stages of programmed heating in the thermal analyzer: between peaks I and II (curve 2), and after peak II (curve 3). In these experiments the programmed heating rate was 5°C min^{-1}. When the temperature was raised to an interval between peaks I and II or after peak II, the specimen was rapidly removed from the thermal analyzer for IR measure-

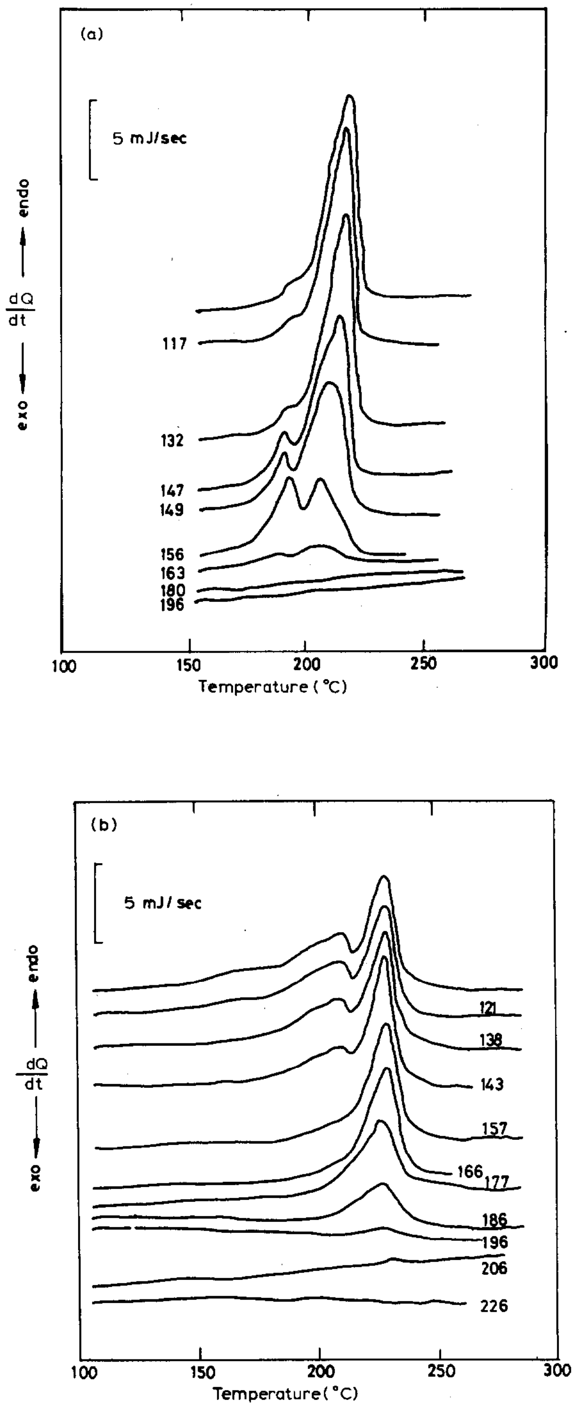
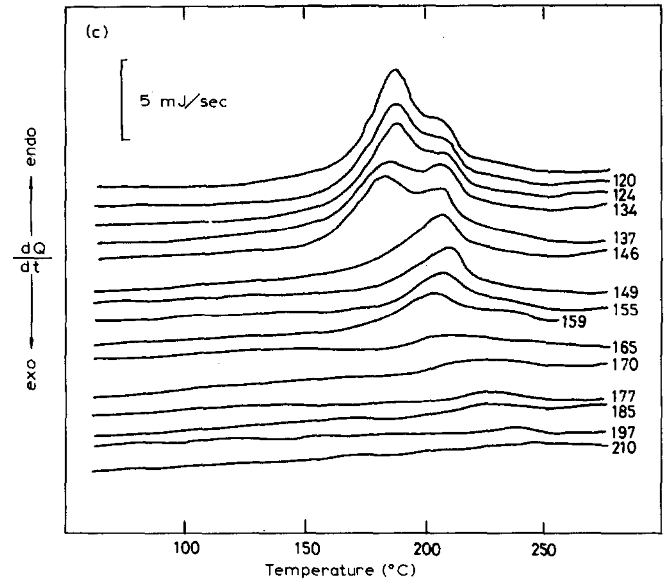
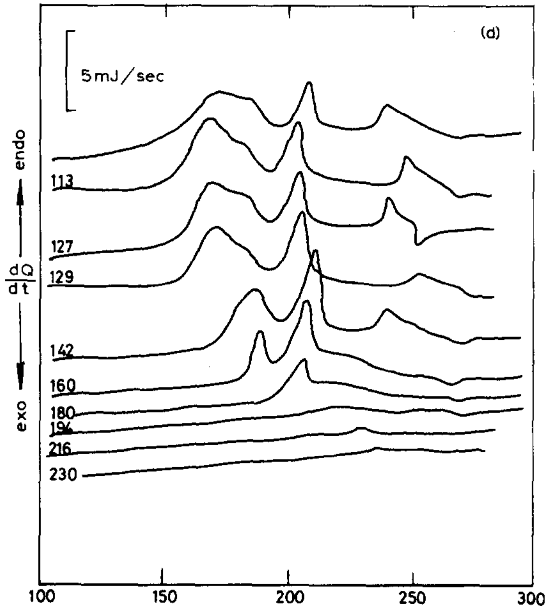


Fig. 5. The change in DSC curves for the amine salts after heat treatment for 2 h at different temperatures. (a) Bm; (b) Mm; (c) Lm; (d) M_2m.


(c)
5 mJ/sec
endo
exo
dQ/dt
120
124
134
137
146
149
155
159
165
170
177
185
197
210
100
150
200
250
Temperature (°C)


(d)
5mJ/sec
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113
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160
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196
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230
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250
300
Temperature(°C)

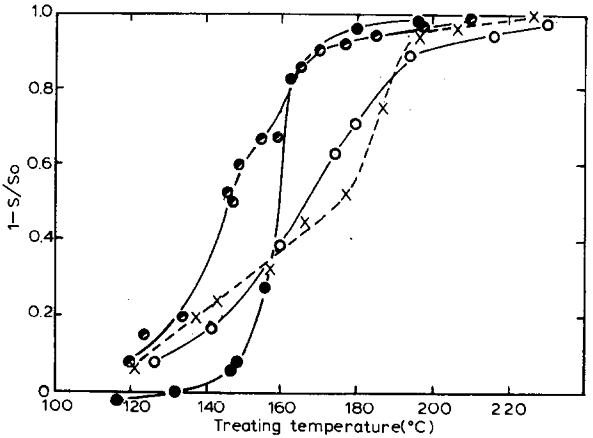

Fig. 6. The temperature dependence of the extent of cyclization of amine salts. (Samples were treated at corresponding temperatures for 2 h.) ●, Bm; ×, Mm; ◐, Lm; ○, M_2m.

ment. For example, curves 2 and 3 in Fig. 8(a) are the IR spectra of specimens (Lm) taken from the thermal analyzer at 187 and 216°C, respectively. The course of this reaction is represented by the changes of the absorption bands characteristic of the NH_3^+ salt, i.e. 2590 cm^{-1}, and the carbonyl group in the imide group, i.e. 1780 cm^{-1}. It follows from curve 2 that the characteristic absorption band for the imide ring appears before the absorption band for NH_3^+ disappears completely. Similar results were obtained with the other two amine salts [see Fig. 8(b) and (c)].

The IR spectra of Lm obtained after heat treatment at certain given temperatures indicate that the A–I process takes place at temperatures as low as 124°C (see Fig. 9). This can be seen from the appearance of a small

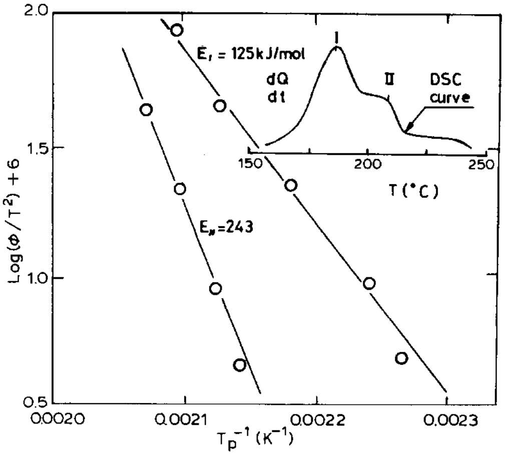

Fig. 7. Kissinger plot of DSC data for the dehydracyclization of Lm.

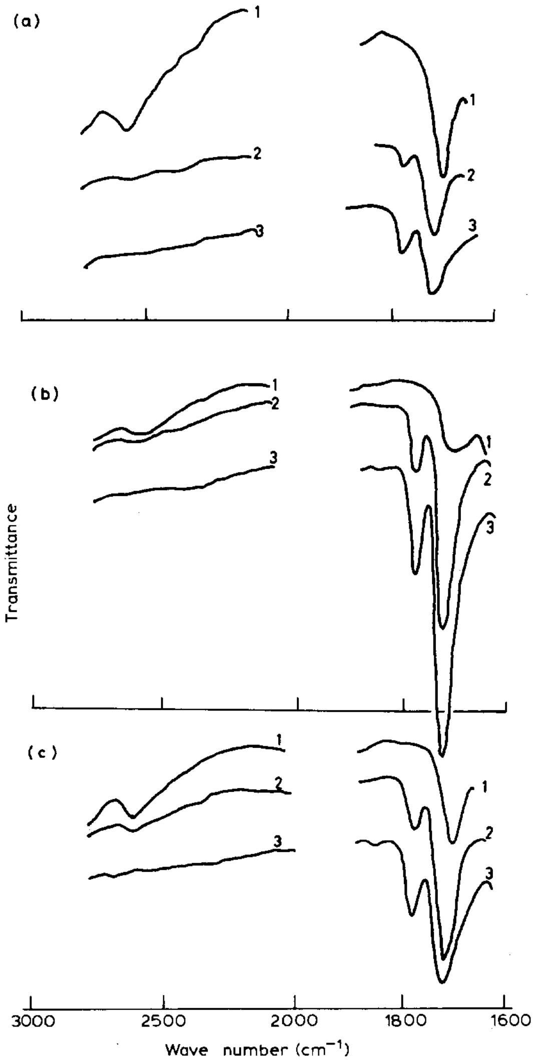

Fig. 8. The IR spectra of amine salts at different stages of programmed heating. (a) Lm; (b) M_2m; (c) Mm. 1, Original sample; 2, between peaks I and II; 3, after peak II.

absorption band at 1780 cm^{-1}. This band gradually strengthens with increasing temperature of heat treatment, and at the same time the absorption band at 2590 cm^{-1} diminishes, which means that the course of the A–I process gradually deepens. Similar results were obtained for other amine salts.

In the temperature range of the A–I process, a single weight loss step appears on the TG curve and a peak with a shoulder appears on the DTA and DSC curves. It is our conclusion that A–I processes are obviously not separated and the imidization process closely follows the amidation reaction.

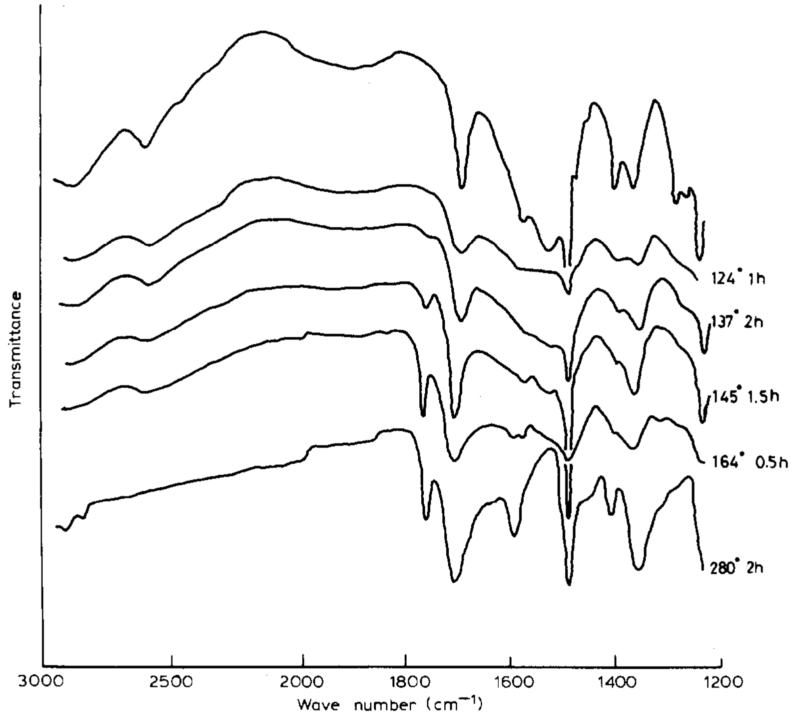

Fig. 9. The IR spectra of Lm samples after heat treatment at different temperatures.

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