Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Usanmaz, Ali and Çevik, N. Nurçin(2003) 'X-Ray and Mass Spectral Analysis of Poly Phenylisocyanate Obtained by Complex Base Catalyst', Journal of Macromolecular Science, Part A, 40: 3, 239 — 250
To link to this Article: DOI: 10.1081/MA-120018112
URL: http://dx.doi.org/10.1081/MA-120018112

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 3, pp. 239–250, 2003

X-Ray and Mass Spectral Analysis of Poly Phenylisocyanate Obtained by Complex Base Catalyst

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ABSTRACT

The polymerization of phenylisocyanate in bulk and in solution of THF by complex base (CB), $NaNH_2/(CH_3)_3CONa$ catalyst under vacuum was previously reported. The polymer obtained was fractionated by washing and extracted with different solvents. Polymer fractions were shown to be highly crystalline by X-ray analysis. Different fractions have similar crystalline structure with some modifications in cell parameters of primitive monoclinic unit cell. Mass spectral analysis gave valuable information for the chain structure and polymerization mechanism of polyphenylisocyanate. The evolution of NH_2^- and NH_3 at low temperature and early stage by pyrolysis showed the chain-ending with $-NH_2$. This is an indication of initiation by NH_2^- in complex base catalyst. The polymer does not contain large amounts of dimer and trimer when polymerized by this catalyst.

Key Words: Phenylisocyanade; DP-MS analysis; Crystal structure; Complex base; Polymerization mechanics.

INTRODUCTION

In our previous paper,[1] we reported the polymerization of phenylisocyanate (PIC) by complex base (CB) initiation. The kinetic of polymerization was explained and polymer

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DOI: 10.1081/MA-120018112
1060-1325 (Print); 1520-5738 (Online)

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was characterized by FT-IR, DSC, NMR, TGA, and X-ray methods. Thermal degradation by TGA gave some information about the nature of the polymer structure. Since the commercial application of poly(monoisocyanate) as liquid crystals[2] are closely related to the chain structure of polymers, a detailed investigation has to be done for better understanding of the subject. Thermal degradation of alkyl isocyanate polymers by direct pyrolysis mass spectroscopy has been reported,[3] but no reported work for aryl isocyanate polymers has come to our attention. The presence of an aromatic group in the polymer chain makes the polymer properties quite different from those of alkyl isocyanate polymer.[4–7]

Most initiators generally give insoluble polyisocyanates in common solvents.[8–11] High molecular weight poly (alkyl monoisocyanate) with alkyl group 3 or less carbon atoms are not soluble in common solvents but dissolve in concentrated H_2SO_4 or F_3CCOOH with partial degradation. When the alkyl group is butyl or longer, the polymer is soluble in a variety of aromatic or chlorinated solvents to a limited extent.[10]

Poly(phenylisocyanate) (PPIC), is not soluble in any solvent except dissolution by degradation to trimer in concentrated sulfuric acid. However, we have already shown that[1] polymer of PIC obtained by the complex base catalyst is a heterogenous material and partially soluble in different common solvents when polymerized in solution. The polymer is fractioned with respect to solubility and each fraction was characterized by different techniques. The results of FT-IR, NMR, DSC, TGA, and partly X-Ray are given in a previous paper.[1]

The polyisocyanates degrade to trimer or monomer when they are kept at an ambient temperature in a solution containing the active catalyst used for the polymerization. Around their melting points, polyisocyanate also degrades to a trimer or monomer.[12,13]

It was shown before that most of the spectroscopic methods cannot differentiate different products such as dimer, trimer, and polymer[10] from each other. We hope the X-Ray and Mass investigation will give much better results in term of identification. In the Direct Pyrolysis Mass Spectra Technique (DP-MS), pyrolysis is achieved inside the mass spectrometer under high vacuum conditions of the MS.[14] In addition to low molecular weight products, relatively high molecular weight fragments can be detected as condensation is prevented. The data obtained by DP technique is reliable because of high vacuum conditions and rapid detection system. Hence, the possibility of a secondary reaction is prevented and primary thermal degradation products can be analyzed. The temperature is increased gradually and the degradation products as a function of temperature can be detected continuously during the process.

EXPERIMENT

Chemical and Instruments

The materials and procedure of polymerization are given in a previous paper.[1] The X-ray powder pattern of samples obtained by fractionation of bulk and solution polymerization products were taken on a Huber–Guinier G600 powder diffractometer camera. The generator was a Enraf–Nonius 551-Model Generator equipped with CuKα X-ray tube (15 mA and 35 kV). DP-MS of samples were obtained by using Balzers QMS

311 quadruple mass spectrometer via a personal computer for the control of the MS data acquisition and analysis. For molecular weights greater than 300, Fisons Instrument VG Platform II Mass Spectrometer (electron energy = 70 eV; source temperature = 180°C; probe temperature = 300°C; source vacuum = 1.2×10^{-5} mbar; analyzer vacuum = 3.0×10^{-6} mbar) was used.

Polymer Fractionation

The procedure of polymerization in bulk and solution has been previously reported.[1] All the polymerization reactions were carried out at −20°C and 0°C under vacuum. After desired polymerization time the reaction tubes were broken open and reaction terminated with a methanol/acetic acid (4/1) mixture. The insoluble polymer fraction was separated by filtration. The polymer obtained by bulk-polymerization is insoluble in common solvents. The filtrate was evaporated to dryness, but no residue could be found. The polymer sample was labeled as A. It was washed with, each of THF at room temperature (B), boiling THF (C), boiling acetone (D), and boiling methanol (E). The samples, after treatment, were labeled with letters in parenthesis.

In solution polymerization, the filtered polymer was partially soluble in acetone. The acetone insoluble sample was labeled as F and soluble one as G. In this case, there was a residue from the filtrate after evaporation. The residue was washed with acetic acid and the insoluble sample was washed further with methanol. The insoluble part was labeled as H and the soluble one as K. The methanol insoluble fraction was fractionated further with acetone. The insoluble part was labeled as L and the soluble one as M.

The X-ray and DP-MS spectra of each fraction were investigated.

RESULTS AND DISCUSSIONS

X-Ray Investigation

The X-ray powder diffraction spectra of almost all fractions were taken to study the possible structural differences. The X-ray powder diffractogram of sample A (unfractioned polymer) showed that the material was heterogeneous and contained a high amount of amorphous fraction. Therefore, the spectrum data could not be indexed.

The X-ray powder pattern of fraction B obtained from the bulk polymerization of PIC by CB at each of −20°C and 0°C were identical. The percent crystallinity is relatively low and a strong peak was observed at a Bragg angle of 8°. The indexed result for cell parameters is given in Table 1. The X-ray powder patterns of fraction C, D, and E were also similar to that of B. The percent crystallinity was increased from B to E in series. The X-ray powder pattern of acetic acid insoluble fraction was given in a previous paper.[1] The X-ray patterns of other fractions were very similar with some changes in peak positions and peak intensities. The results of cell parameters after indexing are given in Table 1. All fractions are crystallized in a primitive monoclinic unit cell with some modifications in cell parameters. The results are much different from the structure of

Table 1. The results of cell parameters for poly(phenylisocyanate) fractions.

Sample	a (Å)	b (Å)	c (Å)	β (°)	Space group
B	15.328	19.445	13.737	104.59	Pm
F	12.570	17.696	11.556	97.87	Pm
G	13.880	12.440	15.986	94.22	Pm
H	10.169	14.408	16.908	99.91	Pc
K	10.481	14.516	12.454	90.67	Pm
L	13.411	14.449	17.367	97.33	$P2_1$
M	10.065	12.513	16.557	118.55	Pc

trimer.[10] Therefore, all of the fractions are polymer with none or a small amount of trimer.

Mass Spectral Investigation

Thermal analysis of monomer, trimer, and PPIC (F, G, H, and K fractions) were carried out by a DP-MS technique. The mass spectrum of monomer (PIC) is given in Fig. 1. The monomer gave intense peaks at 28 (CO^+), 12 (C^+) 15 (NH^+), 16 (O^+), 42 (NCO^+), 77 ($C_6H_5{}^+$), 91 amu ($C_6H_5N^+$), 119 amu (base peak, monomer ion, $C_6H_5NCO^+$), 68 amu ($N_2C_2O^+$), and 52 ($N_2C_2{}^+$). Some of the peaks cannot be explained by simple fragmentation of monomer molecule (C_6H_5—N=C=O). Most likely, monomer dimerize and/or trimerize to a limited extent before further pyrolysis.

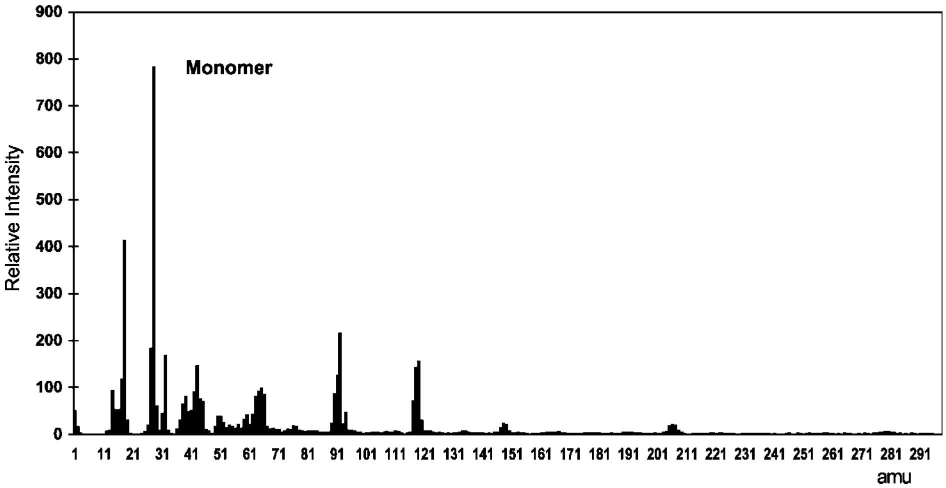


Figure 1. Mass spectra of PIC.

The mass spectrum of fraction F recorded at 215°C, using 70 eV electrons, is given in Fig. 2(a). The base is observed at m/z = 119 amu (monomer ion). The other intense and/or characteristic ions are 16 (NH_2^+), 17 (NH_3^+) 28 (CO^+), 43 ($NHCO^+$), 44 (NH_2CO^+), 52 ($N_2C_2O^+$), 77 ($C_6H_5^+$), 91 ($C_6H_5N^+$) and 92 ($C_6H_5HN^+$). The relative intensities of peaks with molecular weight greater than that of monomer are very low. For example the intensities of cyclic dimer and cyclic trimer were only about 0.2–0.6%, respectively to that of the monomer. In order to determine the thermal stability and thermal decomposition range, ion–temperature profiles, variation of intensity as a function of temperature of most intense and/or characteristic peaks were plotted in Fig. 2(b). The thermal decomposition started around 204°C and the maximum ion yield was observed at 215°C. A second maximum at 221°C was also present, pointing out that decomposition of F occurred in two regions or two different fragmentation pathways.

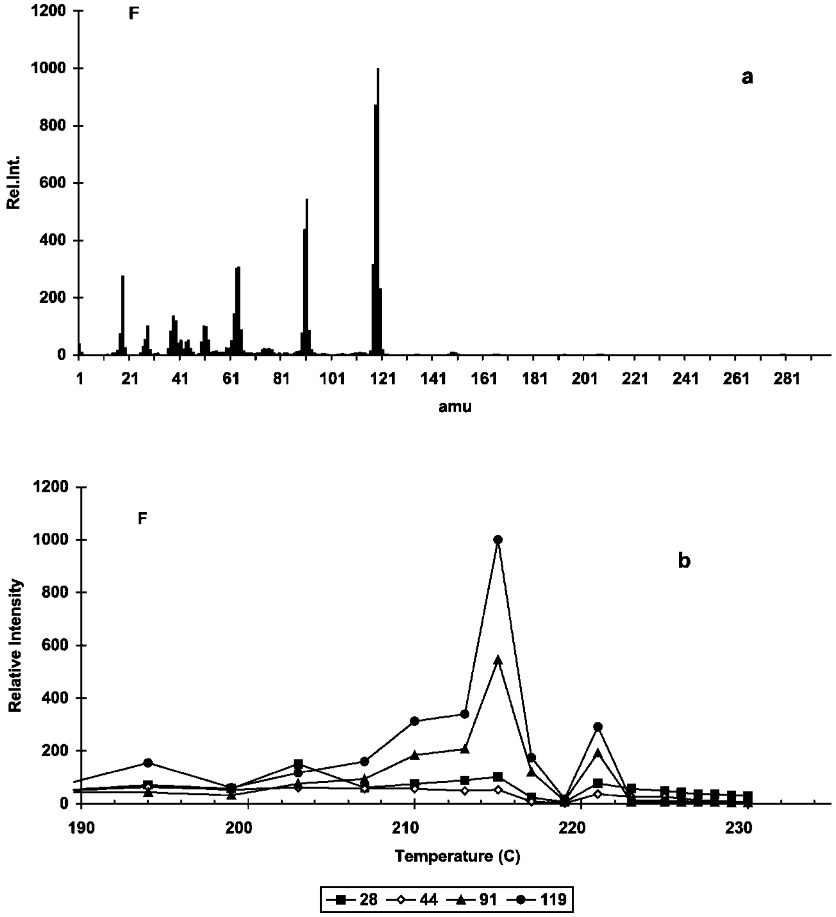


Figure 2. (a) DP-MS of fraction F recorded at 215°C, using 70 eV electrons; (b) The ion–temperature profiles of some characteristic ions.

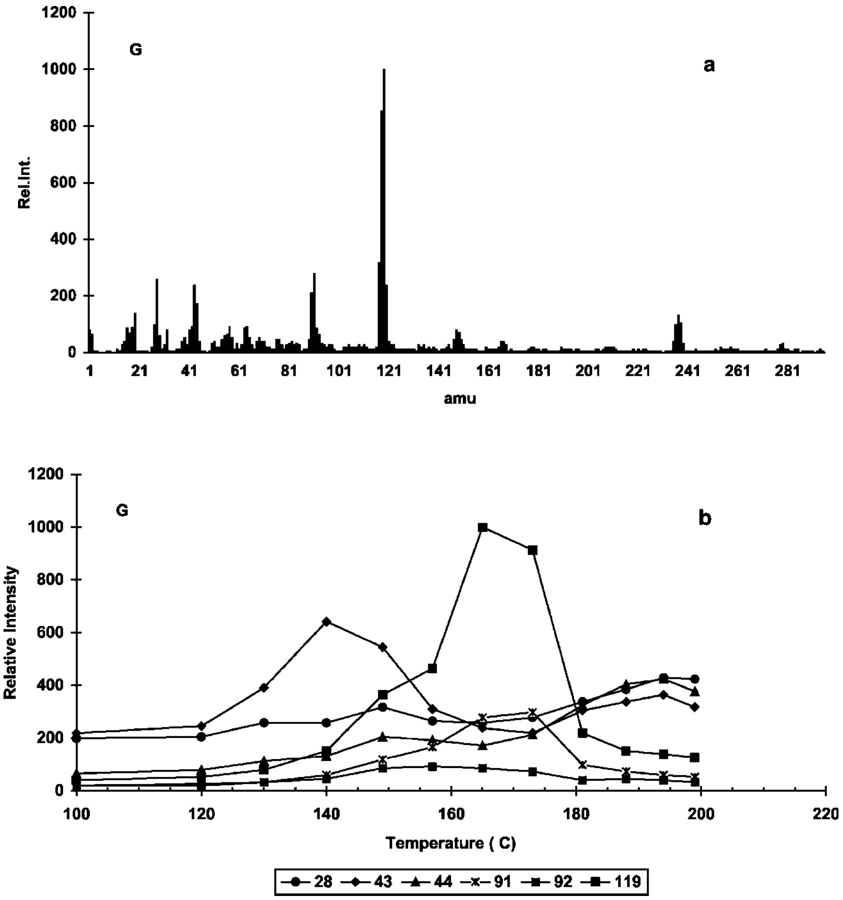
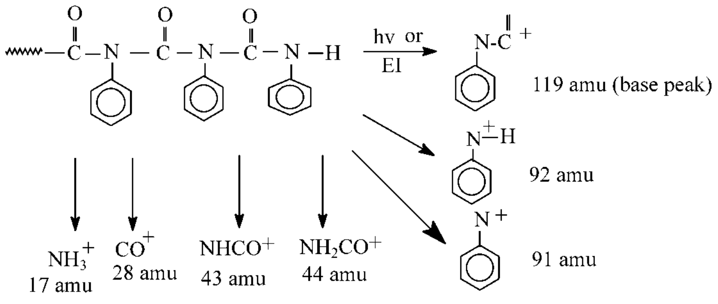


Figure 3. (a) DP-MS of fraction G recorded at 165°C, using 70 eV electrons; (b) The ion–temperature profiles of some characteristic ions.

The possible fragmentation of chain is shown as follows:



DP-MS of fraction G recorded at 165°C, using 70 eV electrons, is given in Fig. 3(a). The base peak is observed at 119 amu (monomer ion). The other intense and characteristic ions are at 16, 17, 28, 43, 44, 52, 77, 91, 92, 237 ($C_{14}H_{10}N_2O_2{}^+$, cyclic dimer) and 238. The ion–temperature profiles of some characteristic ions are given in Fig. 3(b). The thermal decomposition started at 140°C, and the ion yield reached the maximum at 165°C. There was no second maximum for all ions as for F fraction, but the relative intensity of peak 43 ($NHCO^+$) is much higher than that of F fraction. The intensity of cyclic dimer was about 11% that of the monomer intensity.

DP-MS of fraction H recorded at 157°C, using 70 eV electrons, is given in Fig. 4(a). The base peak is observed at 119 amu (monomer ion). The other intense and characteristic ions are at 16, 17, 28, 43, 44, 52, 77 ($C_6H_5{}^+$), 91, 92, 205 ($C_9H_6N_3O_3{}^+$), 237 and 238. The minor peaks with m/z = 128 ($C_3H_2N_3O_3{}^+$), 204 amu ($C_9H_6N_3O_3{}^+$) 280 amu

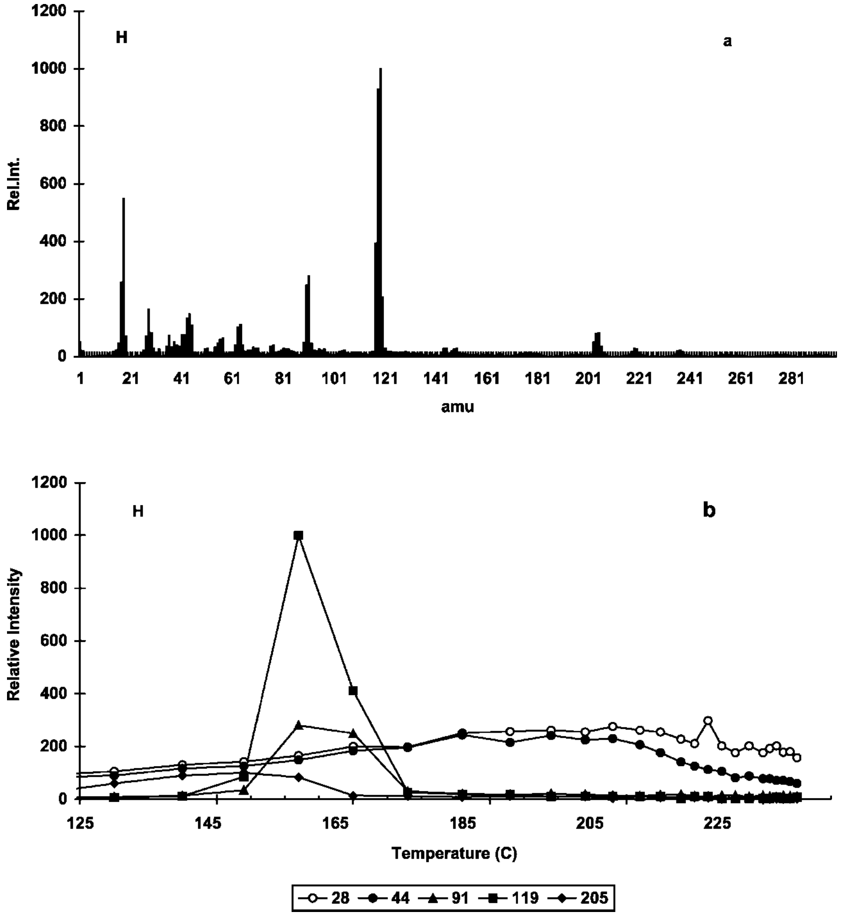


Figure 4. (a) DP-MS of fraction H recorded at 157°C, using 70 eV electrons; (b) The ion–temperature profiles of some characteristic ions.

($C_{15}H_{10}N_3O_3{}^+$) are fragmentations from trimer. These peaks were not observed from fraction F, but observed in fraction G. It can be due to small amounts of trimer in the original sample or formation of some trimer in the early stage of degradation. The ion–temperature profiles of some characteristic ions are given in Fig. 4b. The thermal decomposition started at 150°C and the ion yield reached the maximum at 157°C. The maximum ion yield for the peak at 204 amu was observed at 149°C as 12% of the base peak (monomer ion). The peak observed at 77 ($C_6H_5{}^+$) can probably be attributed to an electron impact (E1) fragment originating from the isocyanurate (trimer) ring.

DP-MS of fraction K recorded at 157°C, using 70 eV electrons, is given in Fig. 5(a). The base peak is observed at 119 amu (monomer ion). The other intense and characteristic ions are at 16, 17, 28, 43, 44, 56, 77 ($C_6H_5{}^+$), 91, 92, 128, 204, 278, 279, 280. No cyclic dimer was formed during decomposition. The intensity of characteristic ions against

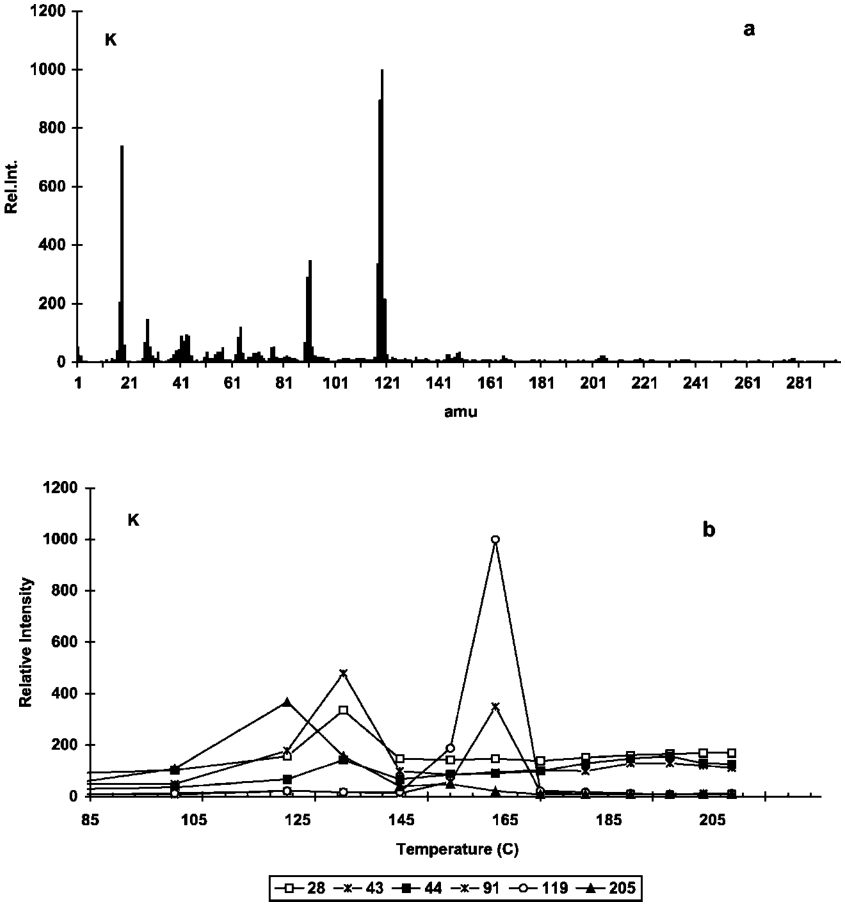


Figure 5. (a) DP-MS of fraction K recorded at 157°C, using 70 eV electrons; (b) The ion–temperature profiles of some characteristic ions.

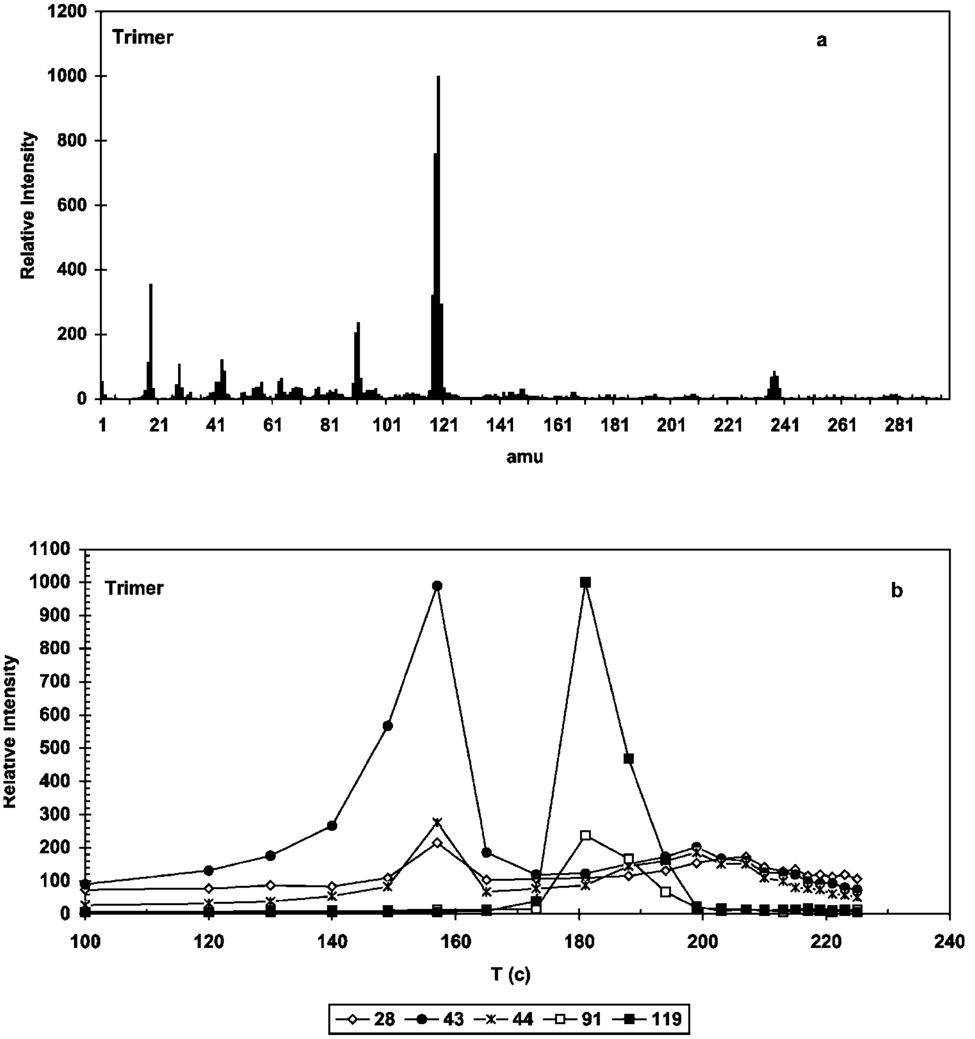
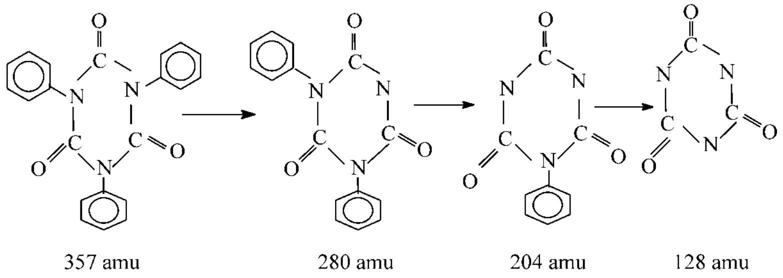


Figure 6. (a) DP-MS of trimer recorded at 181°C, using 70 eV electron; (b) The ion–temperature profiles of some characteristic ions.

temperature is plotted in Fig. 5(b). The thermal decomposition started at 150°C and the ion yield reached the maximum at 157°C. The maximum ion-yield for the peak at 204 amu was observed at 120°C as 40% of the base peak. The minor peaks appearing at 205, 278, 279, and 280 are assigned to E1 fragments obtained from trimer.

DP-MS of trimer recorded at 181°C, using 70 eV electrons, is given in Fig. 6(a). The base peak is observed at 119 amu (monomer ion). The other peaks are at m/z = 16, 17, 28, 43, 44, 77, 91, 92, 119, 237, 238, 278, 280. The ion–temperature profiles of some characteristic ions are given in Fig. 6b. There are two maxima at 160°C and 181°C.

The simple fragmentation of PIC trimer will be as follows:

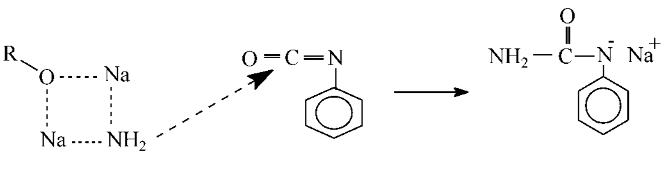


Mass spectra of F, G, H, K, and trimer were also taken on Fison Instrument VG Platform II Mass Spectrometer. They all gave fragments with m/z larger than 300, which could not be obtained on Balzers QMS 311 quadrupole Mass Spectometer. All the spectrum looks similar and a relatively weak trimer peak at m/z = 357.1 amu.

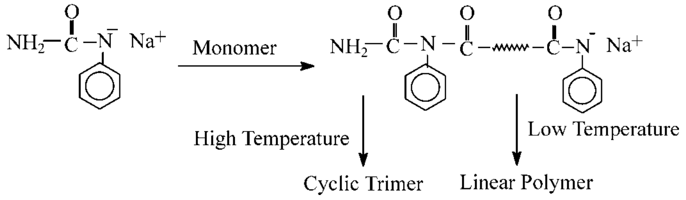
CONCLUSION

Phenyl isocyanate is polymerized by complex base to give linear polymer. From the X-ray analysis of different polymer samples, it was shown that a highly crystalline polymer could be obtained. The polymer is not sufficiently soluble in common solvent to measure the molecular weight. However, the product is mainly polymer, not dimer or trimer. This suggestion is also supported by thermal analysis. The detailed mass spectral analysis showed that the amount of trimer and dimer in the product is quite limited. They are relatively more in extract from polymer. Therefore, dimer and trimer free polymers (e.g. fraction F) can be obtained by proper washing. The fragments of pyrolysis also showed the polymer is basically linear and NH_2 groups are present at the end of most polymer chains. Therefore, initiation of the complex base starts with an amide group addition. This is given in the mechanism of polymerization below. The DP-MS results for all samples gave 119 amu as a base peak and 91 amu as one of the intense peak. Thus, the decomposition takes place by depolymerization. However, there are some differences in detail. For example, fraction F gave a second maxima at 215°C, which indicates that this fraction is not composed of one fraction and decomposition of F fraction occurred in two regions or two different fragmentation pathways. The proposed mechanism of polymerization is as follows:

Initiation:

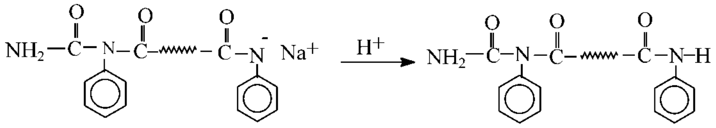


Propagation:

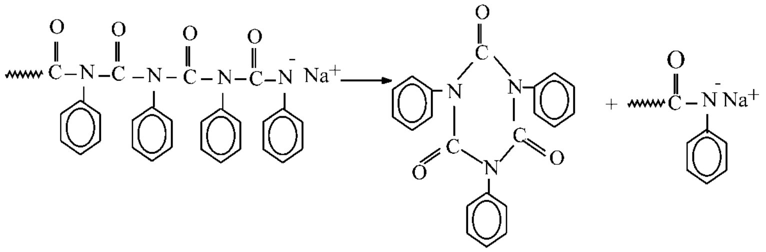


Termination:

i. Termination by neutralization



ii. Trimer formation by backbiting of the active end



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Received September 2002