The synthesis and characterization of nitrogen-containing ladder polymers and their model compounds

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The linear polymers obtained by reacting 2,6-diaminotoluene with benzaldehyde or formaldehyde were condensed in polyphosphoric acid or aqueous HCl. The ladder polymers obtained were characterized by ^{1}H n.m.r., *FT*i.r., u.v.-vis. and g.p.c.

(Keywords: synthesis; characterization; ladder polymers)

INTRODUCTION

Ladder polymers have received a lot of attention due to their thermal stability[1] originating from their ladder structures, their electrical conductivity[2–4] caused by π-electron delocalization in their planar structures, and their potential as precursors to organic ferromagnetic polymers[5].

In order to obtain a ladder polymer with periodic secondary amine moieties connecting benzene rings in the *meta* positions, the linear polymer was condensed in polyphosphoric acid or aqueous HCl.

EXPERIMENTAL

Synthesis of model compounds 1 and 2

The synthetic scheme for model compounds 1 and 2 is shown in *Figure 1*. A detailed synthetic procedure has been reported previously[6].

Synthesis of model compound 3

The synthetic procedure to produce model compound 3 has been reported by Snyder and Konecky[7]. 2,4-Diaminotoluene (9.7 g, 0.045 mol) and 2,4-diaminotoluene dihydrochloride (13.1 g, 0.045 mol), which was prepared by treating the free amine with concentrated HCl solution, were placed in a flask. To this was added 95% ethanol (85 ml), deionized water ($\sim$10 ml) and benzaldehyde (5.3 g, 0.045 mol). The solution was then heated under gentle reflux for 3 h. During the heating period, a white solid separated from the solution. After cooling to room temperature, the solid was collected by suction filtration, rinsed with ethanol and dried. The yield was 10.0 g (667.%) and t.l.c. analysis gave only one spot, which suggested that no further purification of the product was required. The synthetic scheme for model compound 3 is shown in *Figure 2*.

Synthesis of model compound 4

A mixture of the tetrahydrochloride of model compound 3 (4.76 g, 0.01 mol) and polyphosphoric acid (50 g) was warmed to 60°C in a flask to effect a suspension. At 60°C, hydrogen chloride was generated and caused the mixture to foam. The mixture was then further heated with mechanical stirring, and the rate of heating was controlled to prevent excessive foaming. Heat was applied steadily until the temperature reached 165°C. The temperature was maintained at 165–170°C for 3.5 h. Most of the mixture was poured slowly into cold water (100 ml). Immediately, a bright orange solid precipitated. The remainder of the viscous melt was transferred by rinsing with water. After cooling, the orange solid was removed by suction filtration. The damp solid, when treated with $\sim$100 ml of 2 N sodium hydroxide solution, changed from orange to yellow in colour. The mixture was digested on a hot plate at 60–70°C for 0.5 h. After cooling, the yellow solid was collected by suction filtration, washed with water, and dried in a vacuum oven at 40°C. The yield was 0.68 g (21.7%). The synthetic scheme for model compound 4 is shown in *Figure 3*.

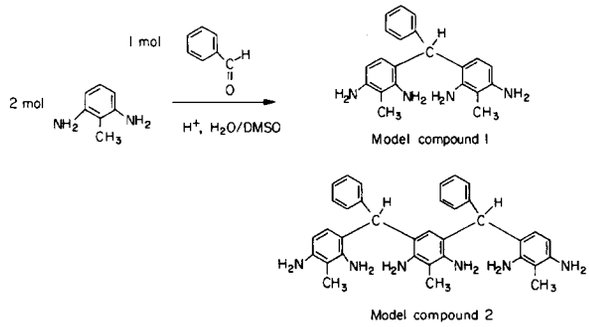

Figure 1 Synthetic scheme for model compounds 1 and 2

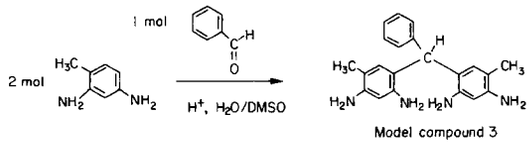

Figure 2 Synthetic scheme for model compound 3

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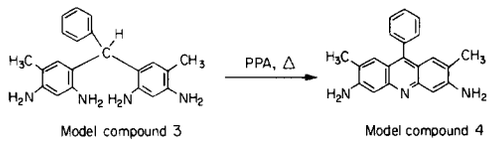


Figure 3 Synthetic scheme for model compound 4

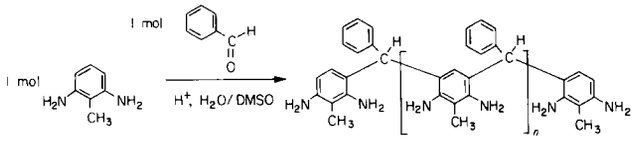


Figure 4 Synthetic scheme for polymer 1

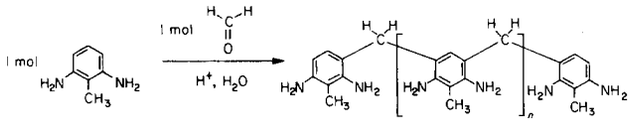


Figure 5 Synthetic scheme for polymer 2

Synthesis of polymer 1

The synthetic scheme for polymer 1 is shown in *Figure 4*. A detailed synthetic procedure has been reported previously.

Synthesis of polymer 2

The synthetic method to produce polymer 2 has been reported by Ruan and Litt[8]. Purified 2,6-diaminotoluene (3.06 g, 0.025 mol) was dissolved in deionized water (50 ml), and concentrated HCl (2.35 ml, 0.025 mol) was added at 60°C. The solution was cooled to 23°C. Formaldehyde solution (2.14 g, 0.026 mol) was added to the reaction mixture. The solution was then stirred at 25°C for 90 min under argon. The colourless solution changed to light yellow immediately after the formaldehyde was added, and eventually became orange. The solution was neutralized with an excess of sodium hydroxide in an aqueous solution. The light yellow precipitate was purified and dried by the same method as that for polymer 1. The yield was 2.6 g (39.0%). The synthetic scheme for polymer 2 is shown in *Figure 5*.

Condensation reaction of the polymers in polyphosphoric acid

A mixture of the polymer (1 g) and polyphosphoric acid (100 g) was heated and stirred under argon. The mixture was maintained at a certain temperature for 2 h. The mixture was then poured into cold water (100 ml). After cooling, the precipitate was collected by suction filtration and washed with excess sodium hydroxide solution and the mixture was stirred for 1 h. The solid was collected by suction filtration and dried in a vacuum desiccator over potassium hydroxide.

Condensation reaction of the polymers in aqueous HCl

The polymer (1 g) was dissolved in 3 N HCl solution (400 ml). The solution was maintained at a certain temperature for 18 h. After cooling, the solution was treated with excess sodium hydroxide solution. The resulting precipitate was collected by suction filtration, washed with water and dried in a vacuum desiccator over potassium hydroxide.

Characterization

The ^{1}H n.m.r. spectra were obtained using a 200 MHz Varian XL-200 NMR. $CDCl_3$ and DMSO-d_6 were used as the n.m.r. solvents. Tetramethylsilane (TMS, $\delta = 0.00$ ppm) was used as a reference. I.r. absorbance spectra were obtained using a Bomen Michelson 110 *FTi*.r. spectrometer. The KBr pellet method was used for sample preparation. A Cary 2300 spectrometer was used to obtain the solution u.v.-vis. absorbance spectra in the u.v.-vis. region. Spectrophotometric grade 1,4-dioxane was used as the solvent. The g.p.c. chromatograms were obtained using a Waters maxima 820 g.p.c./h.p.l.c. chromatograph.

RESULTS AND DISCUSSION

Condensation reaction of the polymers in polyphosphoric acid

Figure 6 shows g.p.c. chromatograms of polymer 1 condensed in polyphosphoric acid at different temperatures. As intramolecular condensation does not produce a large molecular weight change, the chromatograms do not show a change in the peak shape or the retention time up to 140°C. This also suggests that little or no decomposition (depolymerization) occurred up to this temperature. However, for the condensation reaction at 180°C, a sharp peak corresponding to a molecular weight of ~700 appeared next to the main peak indicating decomposition had occurred.

The ^{1}H n.m.r. spectra of polymer 1 condensed in polyphosphoric acid at different temperatures are shown in *Figure 7*. As the reaction temperature increases, new

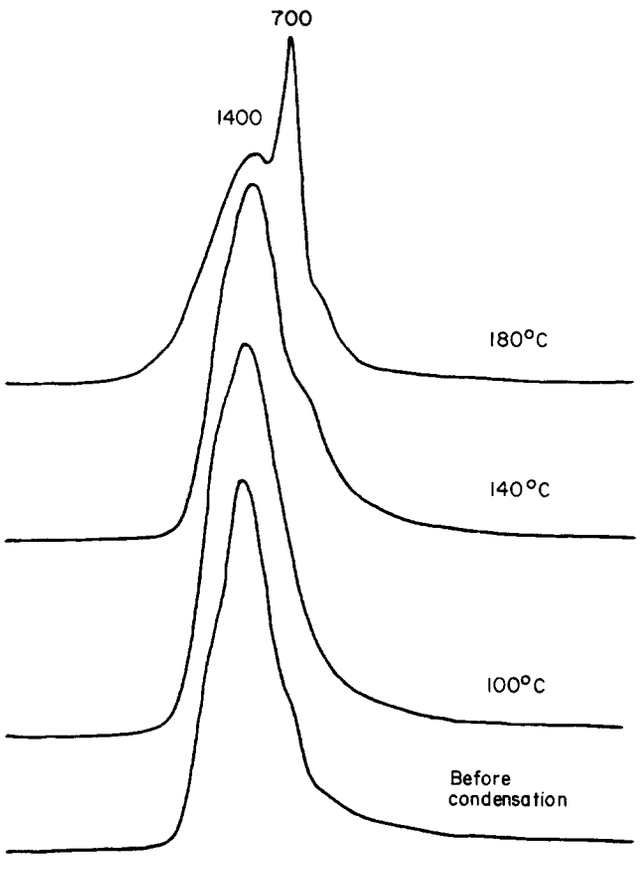


Figure 6 G.p.c. chromatograms of polymer 1 condensed in polyphosphoric acid at different temperatures

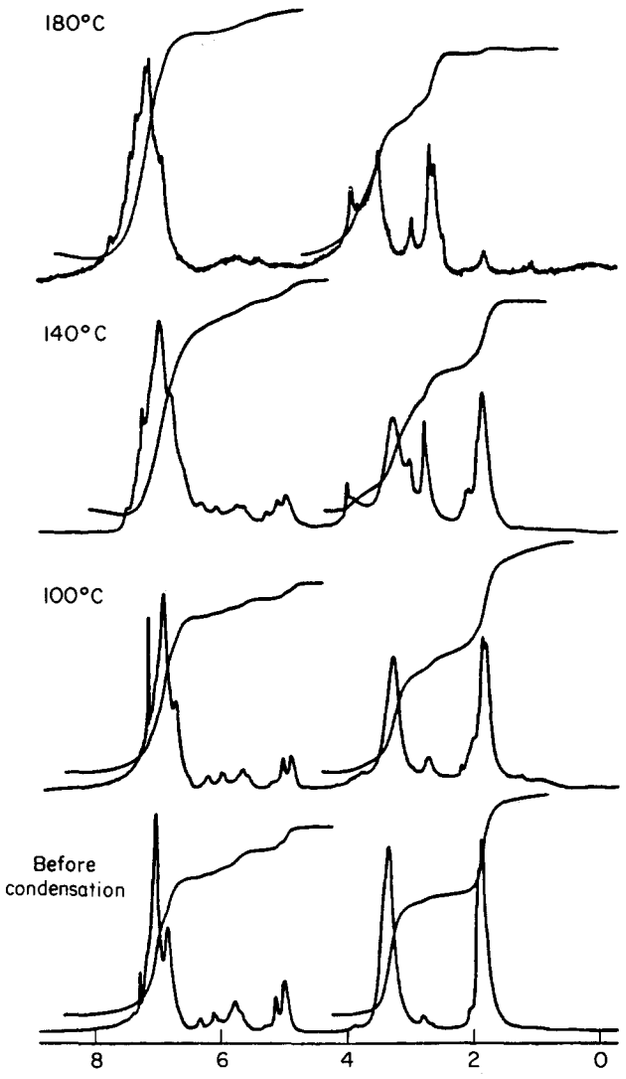


Figure 7 ^{1}H n.m.r. spectra of polymer 1 condensed in polyphosphoric acid at different temperatures. $CDCl_3$ was used as solvent except at 180°C where DMSO-d_6 was used

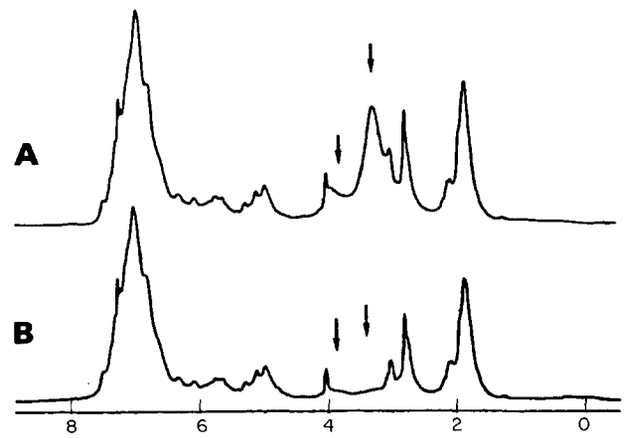


Figure 8 ^{1}H n.m.r. spectra of polymer 1 condensed in polyphosphoric acid (A) before and (B) after addition of D_2O.$CDCl_3$ was used as solvent. Arrows indicate active protons

peaks (4.0, 3.1, 2.8, 2.1 ppm) appear and become more intense. The existence of a new active proton besides NH_2 was confirmed by the proton exchange technique[9]. A few drops of deuterated water were added to the n.m.r. sample tube, which was then shaken. After phase separation (chloroform/water), the ^{1}H n.m.r. spectrum for the sample was obtained. The proton exchange with the deuterium of D_2O caused two peaks to disappear, as shown in *Figure 8*. The new active proton at 4.0 ppm was assigned to a secondary amine (NH). Any other new peaks (2.1, 2.8, 3.1 ppm) are thought to arise from CH_3 protons in different environments caused by the condensation reaction. *Figure 9* shows the g.p.c. chromatograms of polymer 2 condensed in polyphosphoric acid at different temperatures. As polymer 2 does not dissolve in tetrahydrofuran (the mobile phase of g.p.c.) completely, these chromatograms show only the soluble portions. However, some information about the decomposition of polymer 2 can still be obtained. The shape and the retention time of the chromatograms do not change up to 140°C. At higher temperatures, peaks become broadened and new peaks corresponding to low molecular weight species appear. The ^{1}H n.m.r. spectra at different temperatures (*Figure 10*) support this observation, showing that almost no decomposition occurred up to 140°C. At 200°C, several new peaks appeared indicating condensation or decomposition. It

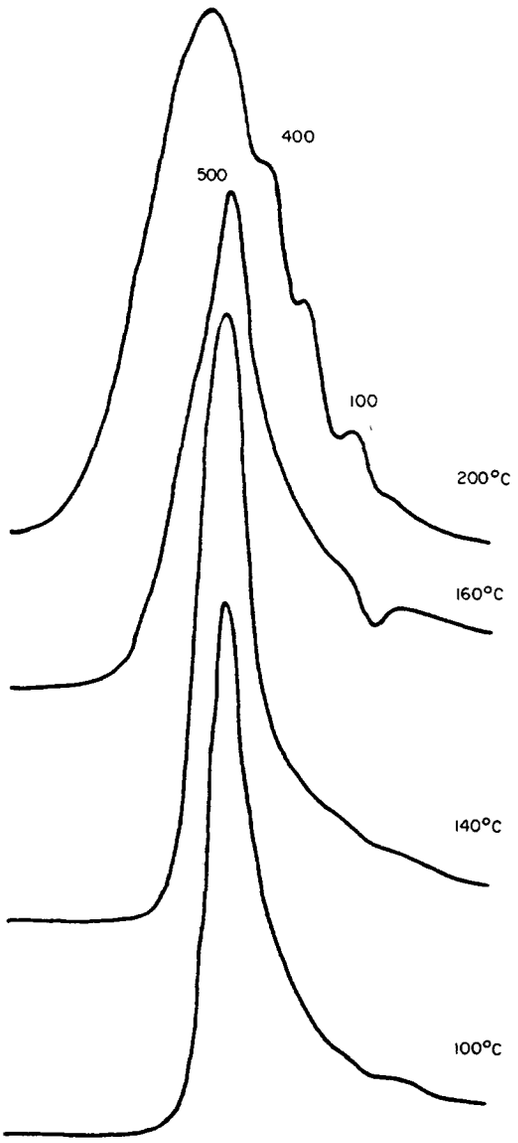


Figure 9 G.p.c. chromatograms of polymer 2 condensed in polyphosphoric acid at different temperatures

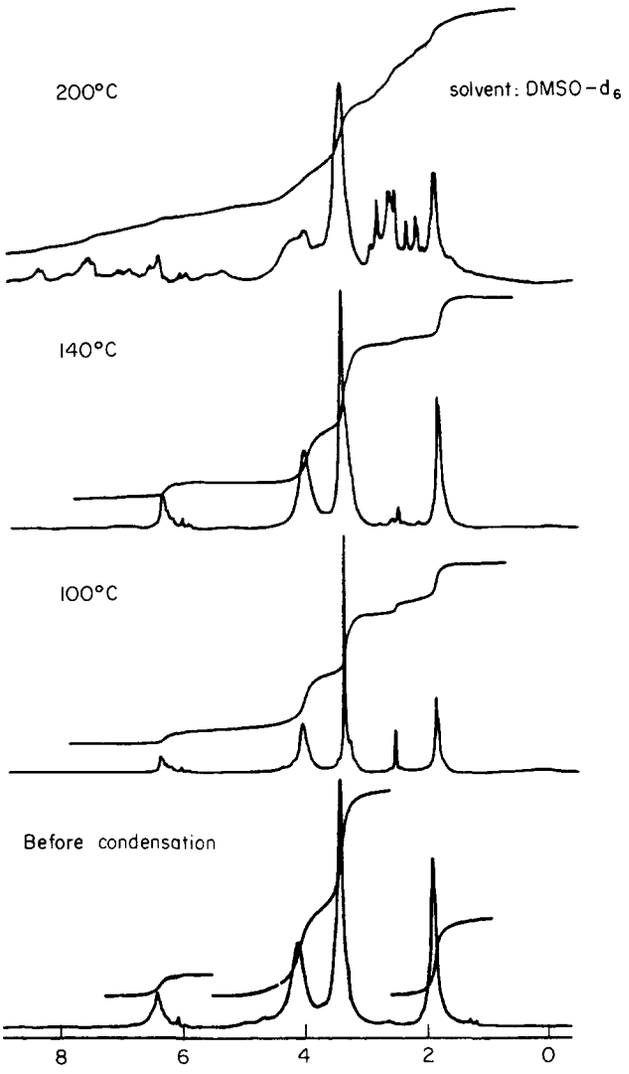


Figure 10 ^{1}H n.m.r. spectra of polymer 2 condensed in polyphosphoric acid at different temperatures

is obvious that polymer 1 is more reactive for condensation than polymer 2. Generally speaking, the conformation which favours condensation (two amino groups are close enough to condense) is not energetically stable due to the steric hindrance between NH_2 groups. However, polymer 1 has more steric hindrance due to the side chain benzene which is thought to hinder the rotation of the C–C bond linking the diaminotoluene unit to the phenyl methane unit. Instead of the side chain benzene, polymer 2 has a methylene proton which allows rotation of the C–C bond between diaminotoluene and the methylene unit leading to a more energetically stable conformation. In order to verify this hypothesis, model compound 1, which has a higher degree of free rotation than polymer 1, was treated with polyphosphoric acid at 140°C for 2 h. *Figure 11* shows the ^{1}H n.m.r. spectra of model compound 1 before and after condensation. It is obvious that model compound 1 did not condense. The bond rotation is more restricted for the higher molecular weight compound (polymer 1) than for the smaller molecular weight compound (model compound 1). Since the more rotation-restricted compound shows at least some degree of condensation as opposed to the smaller compound (more free rotation), it holds that the amount of rotation is important in the degree of condensation. *Figure 12* shows the ^{1}H n.m.r. spectra of model compound 2, and polymer 1 before and after the condensation reaction in the region of the methine protons. Polymer 1 has two types of methine protons (*Figure 13*): one is the end group (external) methine proton; and the other is the internal methine proton, which is more electrically shielded. It was found that the condensation occurred between the moieties of the internal methines since the relative intensity of the internal methine protons decreases after condensation

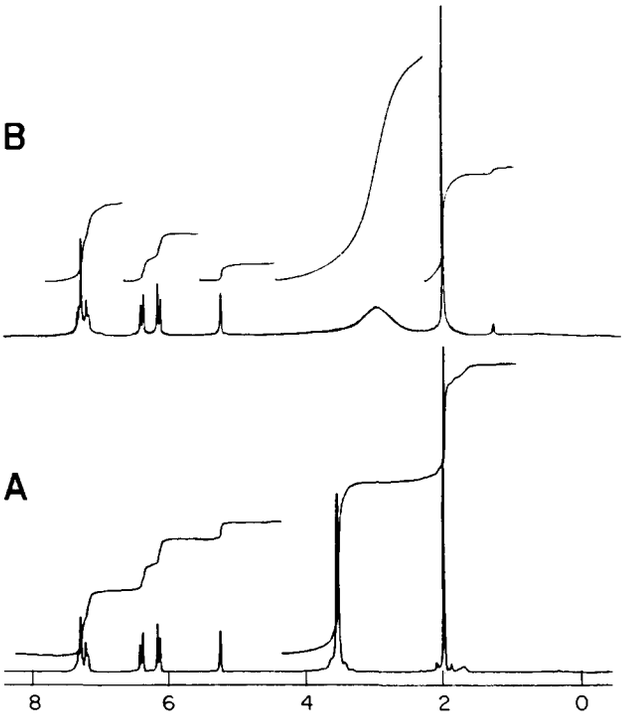


Figure 11 ^{1}H n.m.r. spectra of model compound 1 (A) before and (B) after condensation in polyphosphoric acid at 140°C. $CDCl_3$ was used as solvent

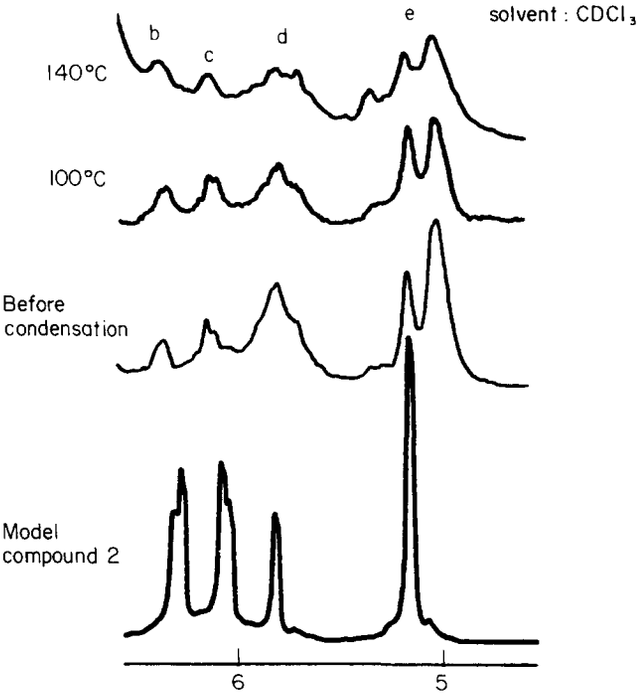


Figure 12 ^{1}H n.m.r. spectra of model compound 2 and polymer 1 before and after condensation in the region of the methine protons

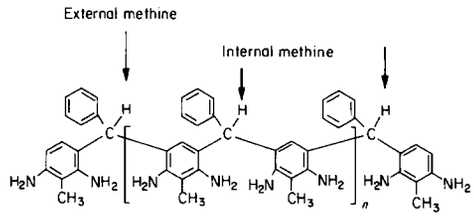


Figure 13 The two kinds of methine protons in polymer 1

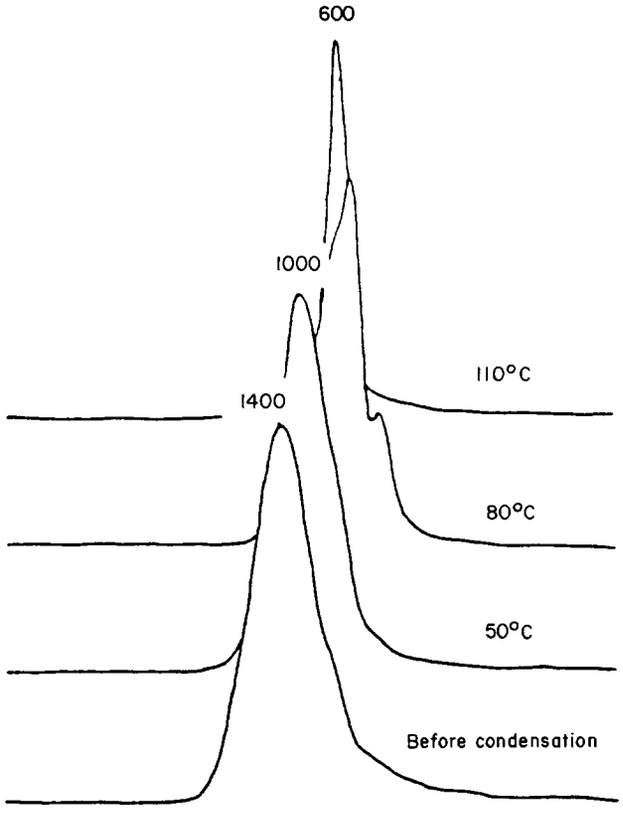


Figure 14 G.p.c. chromatograms of polymer 1 condensed in aqueous HCl at different temperatures

indicating the formation of the acridine moiety. This is due to the fact that the internal methine units have a more restricted rotation of the C–C bonds between the diaminotoluene and the phenyl methane as compared with the external methine units.

Condensation reaction of the polymers in aqueous HCl

The g.p.c. chromatograms of the polymer 1 condensed in aqueous HCl at different temperatures are shown in *Figure 14*. It was found that the molecular weight decreased as the temperature increased, indicating decomposition. The ^{1}H n.m.r. spectra (*Figure 15*) also show the decrease in the molecular weight by end group analysis.

Figure 16 shows the g.p.c. chromatograms of polymer 2 condensed in aqueous HCl at different temperatures. The chromatograms did not change in shape or in retention time up to 80°C, but at 110°C the chromatogram became broader and new peaks corresponding to low molecular weight portions appeared, indicating decomposition had occurred. *Figure 17* shows the ^{1}H n.m.r. spectra of polymer 2 condensed in aqueous HCl at different temperatures. As the reaction temperature increases, new peaks (8.1, 7.1, 5.2, 3.8, 2.7, 2.1 ppm) appear and become more intense. As the reaction temperature increases, the NH_2 intensity decreases while the new active proton (peak γ) and other new peaks (peak α, 8.1 ppm; peak β, 7.1 ppm) also increase, which means that condensation had occurred. Since the intensity ratio of peak α to peak β is $\sim$2 and the chemical shifts are typical of values for anthracene-like compounds[10], these new peaks were assigned to the protons in the acridine moiety (*Figure 18*). These intensities will be used for the calculation of the number of acridine moieties in polymer 2. Any other peaks (3.0, 2.7, 2.1 ppm) are thought to come from CH_3 protons in different environments caused by the condensation reaction. The existence of a new active proton besides NH_2 was confirmed by the proton exchange technique (*Figure 19*), as in polymer 1. However, in this case, the situation is more complicated than for polymer 1. Hydrogen bonding effects[11] should be taken into account because DMSO-d_6 was used as the n.m.r. solvent due the poor solubility of the polymer 2 in $CDCl_3$. Since the NH_2 in a different environment, formed by the

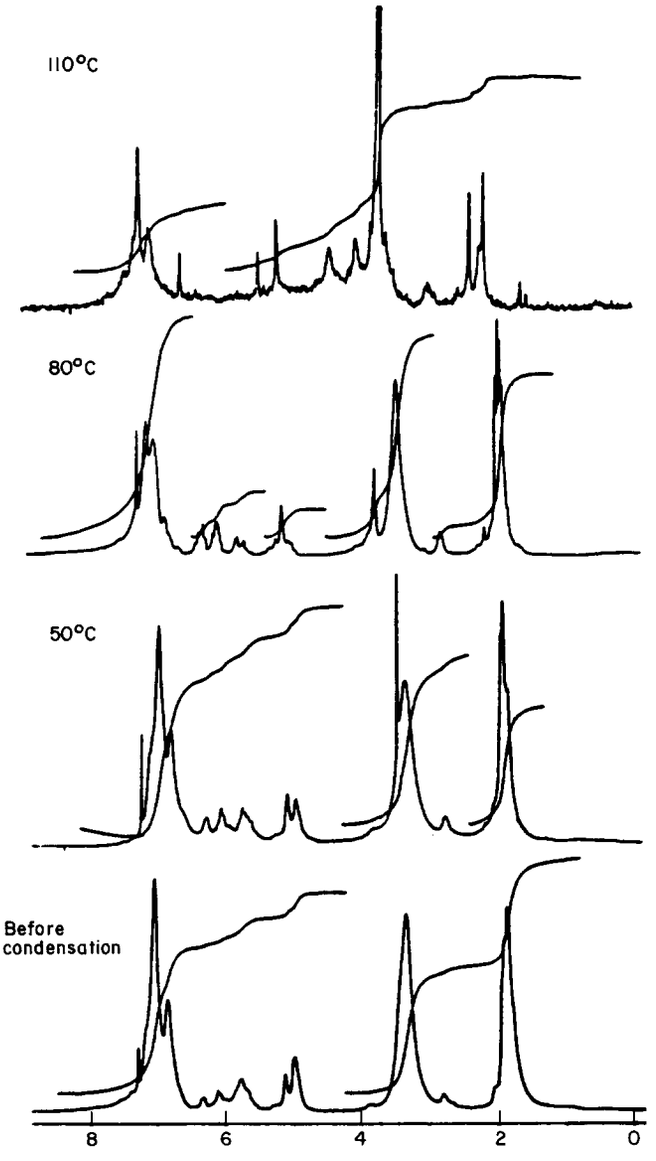


Figure 15 ^{1}H n.m.r. spectra of polymer 1 condensed in aqueous HCl at different temperatures. $CDCl_3$ was used as solvent except at 110°C where DMSO-d_6 was used

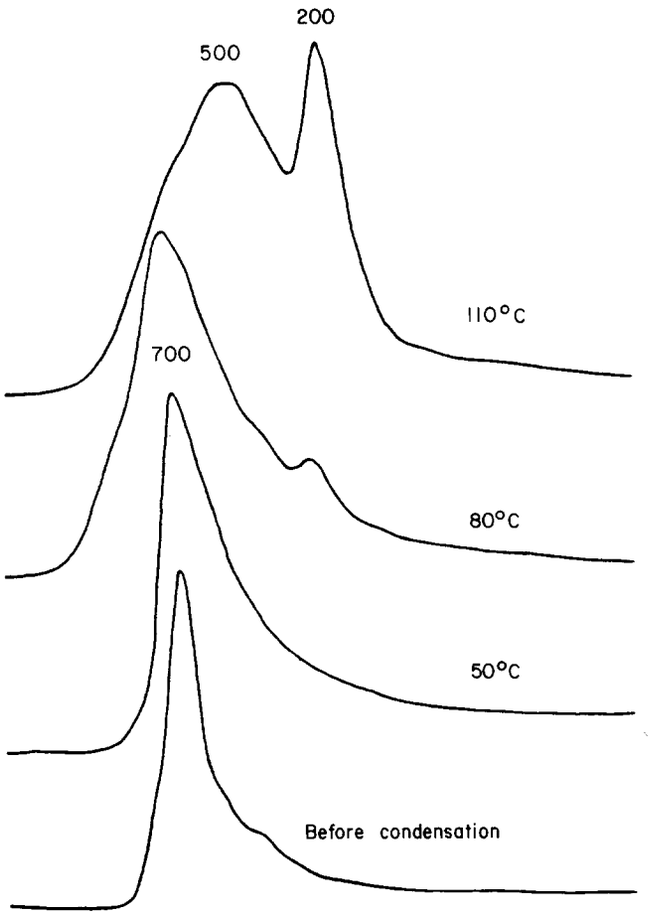


Figure 16 G.p.c. chromatograms of polymer 2 condensed in aqueous HCl at different temperatures

condensation, may be more accessible to hydrogen bonding, there is a possibility that the NH proton is overlapped with the NH_2 protons.

Further characterization of polymer 1 condensed in polyphosphoric acid and polymer 2 condensed in aqueous HCl

The ^1H n.m.r. spectra and g.p.c. analyses show that polymers 1 and 2 were best condensed in polyphosphoric acid and aqueous HCl, respectively. Further characterizations are now examined in order to clarify the condensation reactions involved.

U.v.-vis. spectra. Figure 20 shows the u.v.-vis. spectra of polymer 1 condensed in polyphosphoric acid at different temperatures. The new absorption peaks at $\lambda \simeq 285$ and 400 nm originate from the acridane and acridine moieties, respectively[12,13]. The absorption spectrum of the condensation at 180°C is more complex than the others due to decomposition. It also shows an absorption at longer wavelength ($\lambda \simeq 500$ nm) which is supposed to come from the more condensed ring structure. The u.v.-vis. spectra of polymer 2 condensed in aqueous HCl at different temperatures is shown in *Figure 21*. The absorption peak at $\lambda \simeq 400$ nm increases as the condensation temperature increases, although the absorption at 50°C is slightly higher than that at 80°C. This peak originates in the Π-Π* transition K band of the acridine moiety as in polymer 1. The Π-Π* transition K band of the acridane moiety can be seen as a shoulder ($\lambda \simeq 285$ nm) of the acridine K band ($\lambda \simeq 277$ nm). The Π-Π* transition B band of 2,6-diaminotoluene ($\lambda \simeq 301$ nm) is difficult to recognize as a peak due to the condensation. *Figure 22* shows the u.v.-vis. spectra of model compound 4 and the condensed polymers 1 and 2. Comparison of the spectra verifies the origin of the absorption at $\lambda \simeq 400$ nm as the acridine moiety. *Figures 23* and *24* show the relationship between absorptivity at $\lambda \simeq 400$ nm and the n.m.r. intensity of the acridine moiety in polymers 1 and 2. In both cases, there is a linear relationship showing that the u.v.-vis. spectra support the results suggested by the n.m.r. spectra. *Figure 25* shows that the NH_2 intensity has a linear relationship with the NH intensity with a negative slope ($\simeq -5.8$),

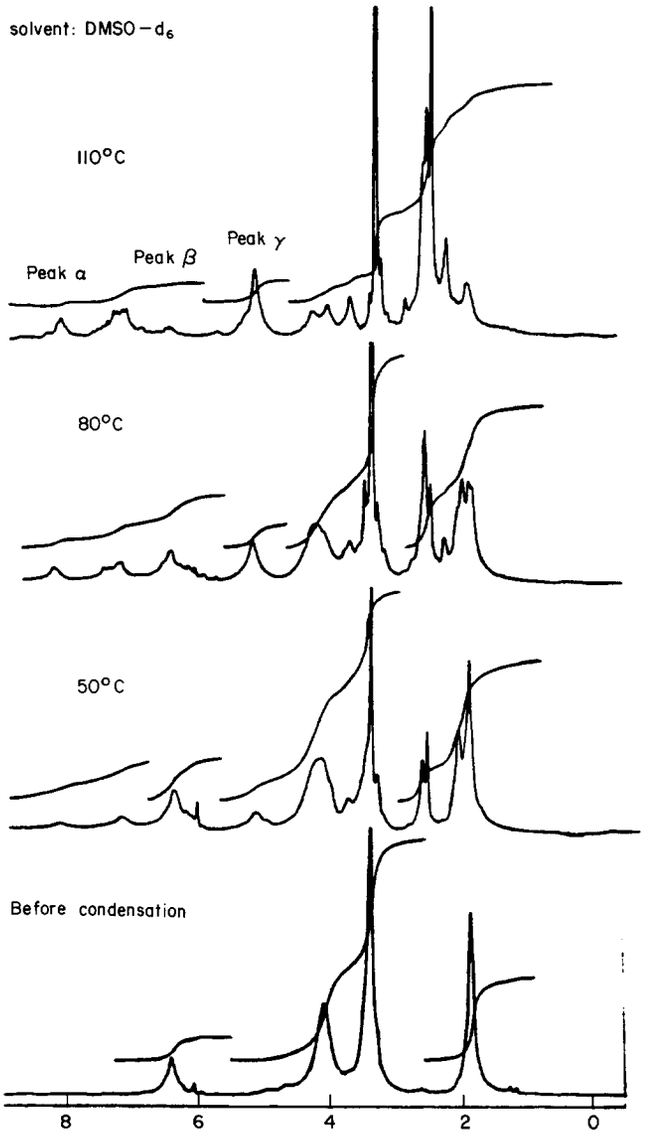


Figure 17 ^1H n.m.r. spectra of polymer 2 condensed in aqueous HCl at different temperatures

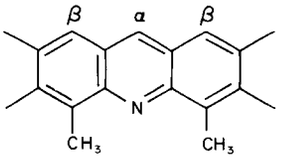


Figure 18 Acridine moiety of polymer 2

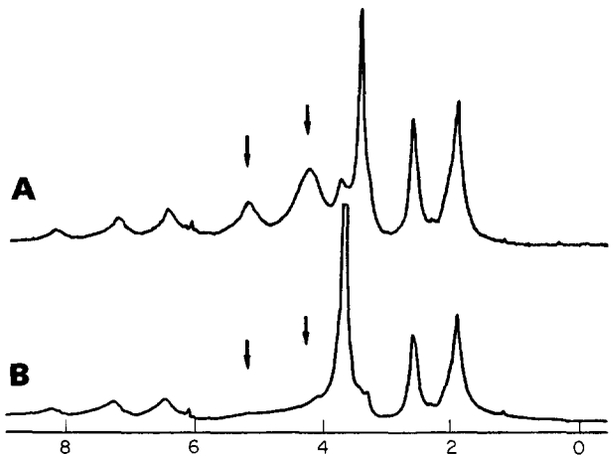


Figure 19 ^{1}H n.m.r. spectra of polymer 2 condensed in aqueous HCl (A) before and (B) after addition of D_2O. DMSO-d_6 was used as solvent. Arrows indicate active protons

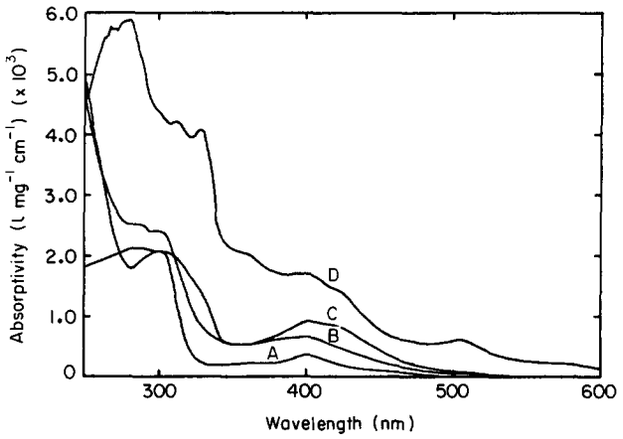
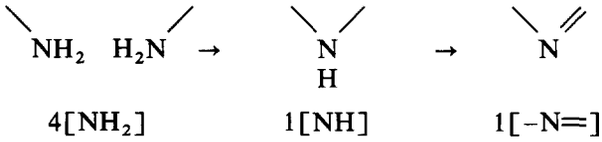


Figure 20 U.v.-vis. spectrum of polymer 1 condensed in polyphosphoric acid at different temperatures: (A) before condensation; (B) 100°C; (C) 140°C; (D) 180°C

which again indicates acridine formation. If the condensation reaction does not form the acridine moiety, the slope will be −4.0 according to the following scheme:



4[NH_2]	1[NH]	1[−N=]
Primary amine	Secondary amine (acridane)	Tertiary amine (acridine)

The n.m.r. intensity of the acridine moiety of polymer 1 was obtained by subtracting the acridane [NH] intensity from the initial NH_2 intensity. The n.m.r. intensity of the acridine moiety of polymer 2 was obtained from the normalized integrated intensity of peak β. The molar absorptivities of the acridine moiety of polymers 1 and 2 are estimated at 1.42×10^3 and 3.82×10^3 l mol^{-1} cm^{-1}, respectively, by the following equations:

$$[-N=] = \frac{a_{cp}}{a_{acm}} \quad (1)$$

$$\varepsilon_{acm} = \frac{a_{acm}}{M_{acm}} \quad (2)$$

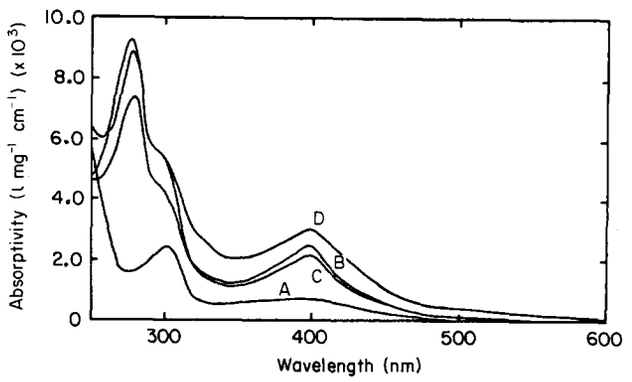


Figure 21 U.v.-vis. spectra of polymer 2 condensed in aqueous HCl at different temperatures: (A) before condensation; (B) 50°C; (C) 80°C; (D) 110°C

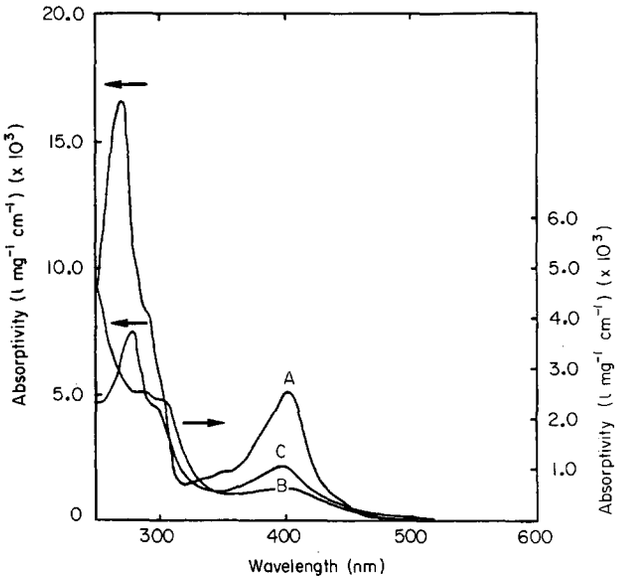


Figure 22 U.v.-vis. spectra of (A) model compound 4, (B) polymer 1 condensed in polyphosphoric acid at 100°C and (C) polymer 2 condensed in aqueous HCl at 80°C

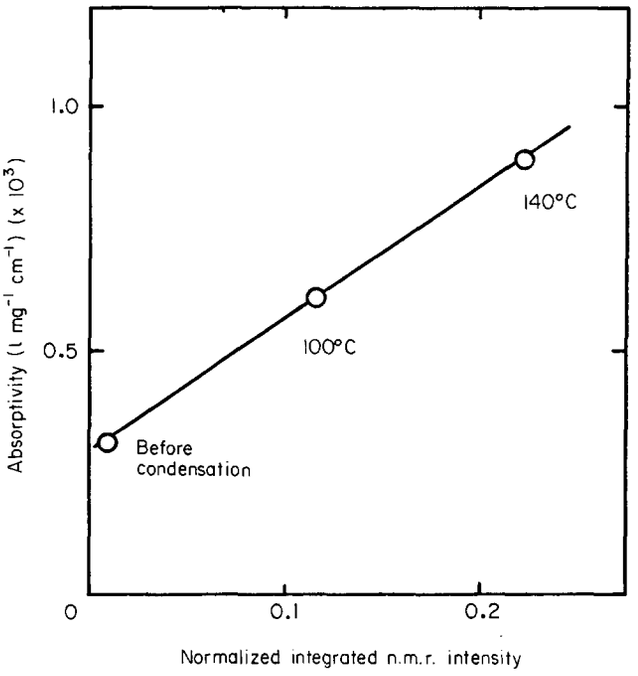


Figure 23 The relationship between the absorptivity at $\lambda_{max} \simeq 400$ nm and the n.m.r. intensity of the acridine moiety of polymer 1

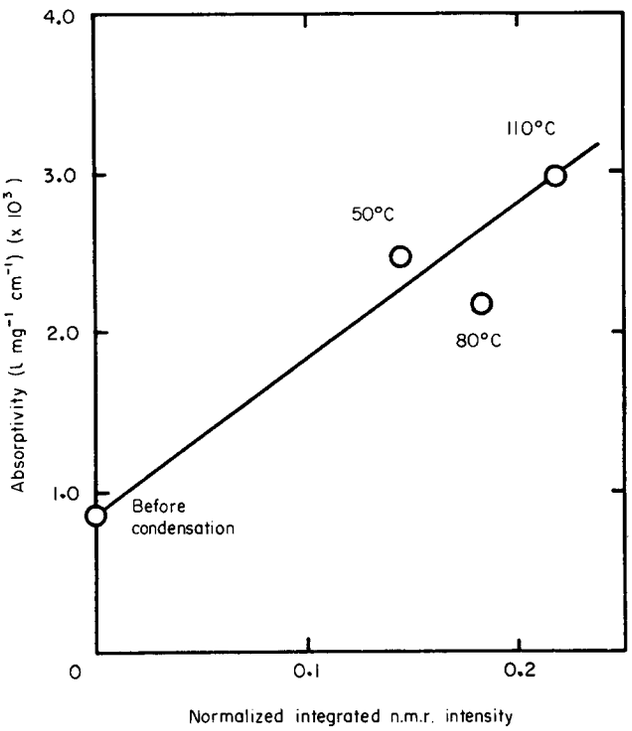


Figure 24 The relationship between the absorptivity at $\lambda_{max} \simeq 400$ nm and the n.m.r. intensity of the acridine moiety of polymer 2

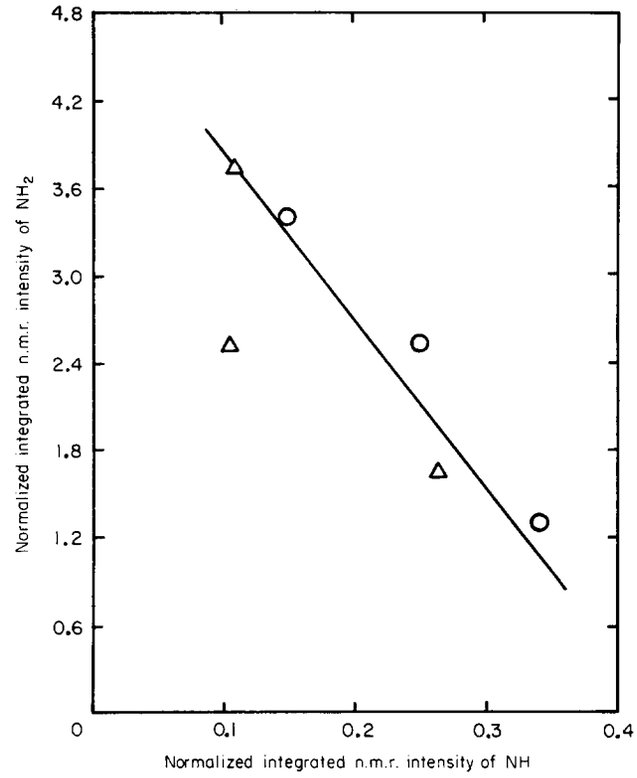


Figure 25 The relationship between NH_2 and NH n.m.r. intensities: (○) polymer 1; (△) polymer 2

where [–N=] is the acridine moiety content calculated from the ^{1}H n.m.r. spectra, a_{acm} and a_{cp} are the absorptivities of the acridine moieties and condensed polymers, ε_{acm} is the molar absorption coefficient of the acridine moieties, and M_{acm} is the molecular weight of the acridine moieties. M_{acm} = 313 for polymer 1 and 237 for polymer 2.

FT*i.r.* The *FT*i.r. spectra of polymer 1 condensed in polyphosphoric acid at different temperatures in the region of 1800–1000 cm^{-1} are shown in *Figure 26*. As the temperature increases, new bands, which can be assigned to aromatic C=C stretching, appear at 1540 and 1420 cm^{-1} and become more intense. These two peaks are located at 1600 and 1472 cm^{-1} before the condensation. The peak shifts to lower wavenumbers imply the formation of conjugation originating from ladder structures[14]. In the region of the CN stretching mode, the peak at 1267 cm^{-1} increases in intensity due to the structural change from a primary amine to an

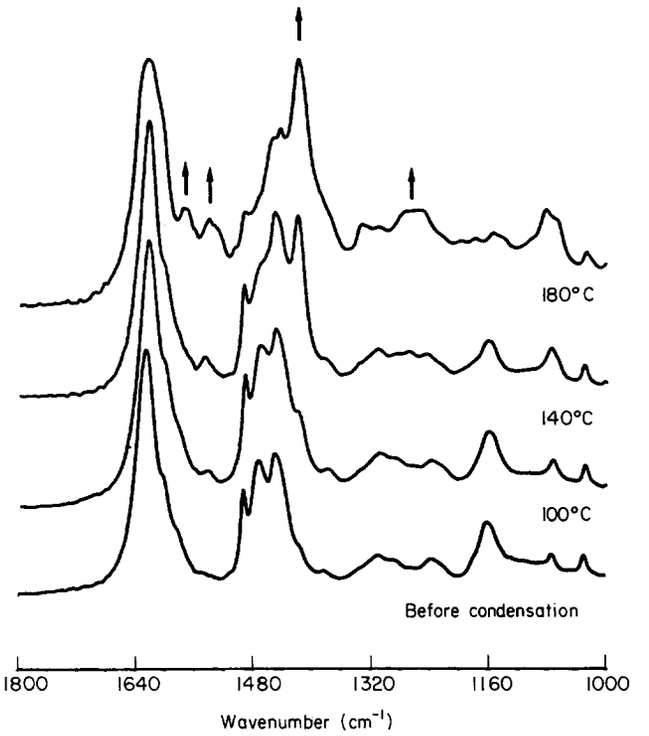


Figure 26 *FT*i.r. spectra of polymer 1 condensed in polyphosphoric acid at different temperatures in the region of 1800–1000 cm^{-1}

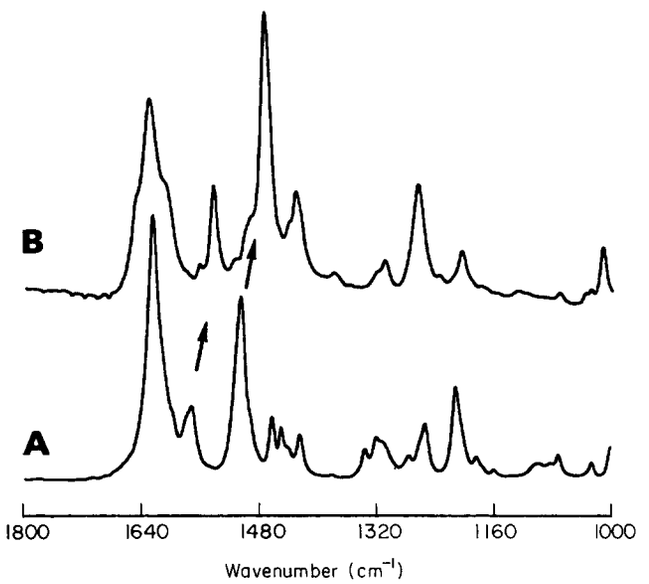


Figure 27 *FT*i.r. spectra of (A) model compound 3 and (B) model compound 4 in the region of 1800–1000 cm^{-1}

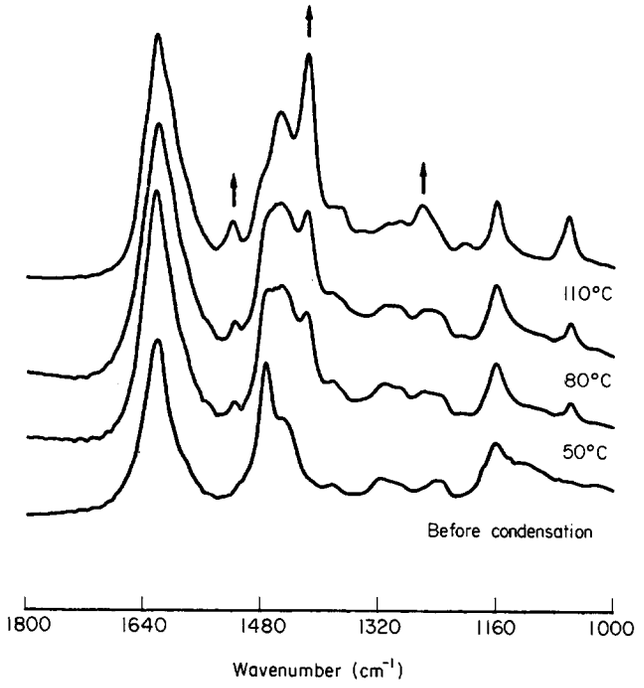


Figure 28 *FT*i.r. spectra of polymer 2 condensed in aqueous HCl at different temperatures in the region of 1800–1000 cm^{-1}

acridane or acridine moiety. The same result (peak shifts) was obtained for model compound 4 (*Figure 27*). *Figure 28* shows *FT*i.r. spectra of polymer 2 condensed in aqueous HCl at different temperatures in the region of 1800–1000 cm^{-1}. The same trend was obtained for polymer 2 except that the aromatic C=C stretching band arising from monosubstituted benzene (the peak at 1470 cm^{-1}) was not observed.

CONCLUSIONS

Polymers 1 and 2 were best condensed by polyphosphoric acid and aqueous HCl, respectively. For each case, ~60% of the NH_2 groups were consumed by the condensation reaction forming acridane (secondary amine) and acridine (tertiary amine) moieties in the ratio of 3:2. In spite of the mild reaction conditions, the acridine moiety was formed. The series of condensation reactions were confirmed by ^1H n.m.r., *FT*i.r., u.v.-vis. and g.p.c. The more rotation-restricted compound (polymer 1) showed some degree of condensation in polyphosphoric acid at 140°C. Under the same condition, the less rotation-restricted (more free rotation) compounds (model compound 1 and polymer 2) did not show any condensation.

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