SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOME POLY(2-VINYL PYRIDINE) COMPLEXES

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Poly(2-vinyl pyridine) complexes were prepared via quaternization of the ring nitrogen with different reagents (I_2, Br_2, Cl_2, CrO_3, picric acid and $HgCl_2$). The thermal behaviour of these polymer complexes, such as ΔE and the order of decomposition, were studied by using the modified Freeman and Carroll procedure. Generally, it was found that the presence of a substituent on the nitrogen in the polymer lowers the activation energy and the thermal stability.

Keywords: polymer complexes

Introduction

The radical polymerization of 2-vinylpyridine is very comparable to that of styrene [1]. Unlike polystyrene, which is very susceptible to modification by electrophilic aromatic substitution, poly(vinylpyridine)* is very resistant to electrophilic aromatic substitution but has a high chemical reactivity which is due to its nucleophilic and weakly basic ring nitrogens. Typical reactions of poly(2-vinylpyridine) include its quaternization by nucleophilic attack on alkyl halides or by protonation:

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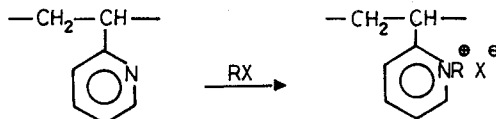
*   Poly(vinylpyridine) contains both poly(2-vinylpyridine) and poly(4-vinylpyridine).

In addition, while polystyrene is non-polar, poly(vinylpyridine) is quite polar and thus can be expected to interact strongly with other polar molecules, or to act as a good ligand for a variety of metal ions. It is this special reactivity of poly(2-vinylpyridine) which makes it so attractive material for a number of special applications [2-5].

In the present work linear poly(2-vinylpyridine) was subjected to quaternization reactions induced by nitrogen. The thermal degradation of quaternized poly(2-vinylpyridine) complexes were studied by using the modified Freeman and Carroll procedure [9] to evaluate the rate parameters for the thermal decomposition. Furthermore, the activation energy and the order of reaction may be evaluated from a single experimental curve.

Experimental

Materials and spectra

Commercial monomer and reagents including the solvent were used. Molecular weight of polymer was determined using Ostwald viscometer with benzene as a solvent at 25°C.
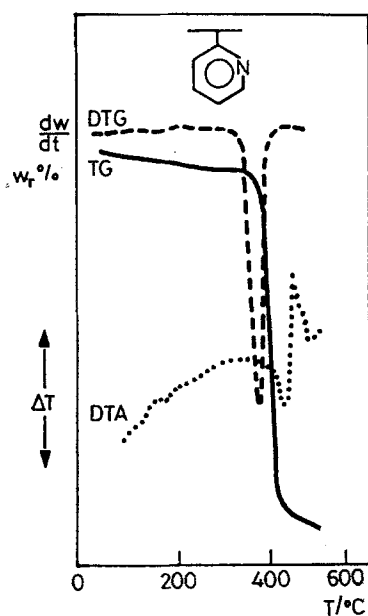

Fig. 1

Infrared spectra were recorded on an infrared spectrophotometer (Sp$_3$ – 300 s) in KBr discs. Atomic absorption analyses for mercury and chromium were carried out with an atomic absorption spectrophotometer (Sp$_3$ – 9). The degree of quaternization (DQ) is the percentage of aromatic residue which undergoes quaternization.

TG, DTG and DTA analyses were carried out on a Stanton-Redcroft apparatus (STA-780 Series) with a thermobalance equipped with a 4-pen strip chart recorder under nitrogen gas flowing at a rate of 50 ml·min^{-1}. 3–7 mg polymer samples were heated in a platinum pan at a rate of 20 deg·min^{-1}.

All polymer samples were dried in the oven overnight at 60°C and ground well before analysis.

Preparation of poly(2-vinylpyridine)

80 mg of 2,2'-azo-bis-isobutyronitrile (AIBN) as initiator was added to 16 g of 2-vinylpyridine in 30 ml of benzene, and the mixture was heated at 70°C under
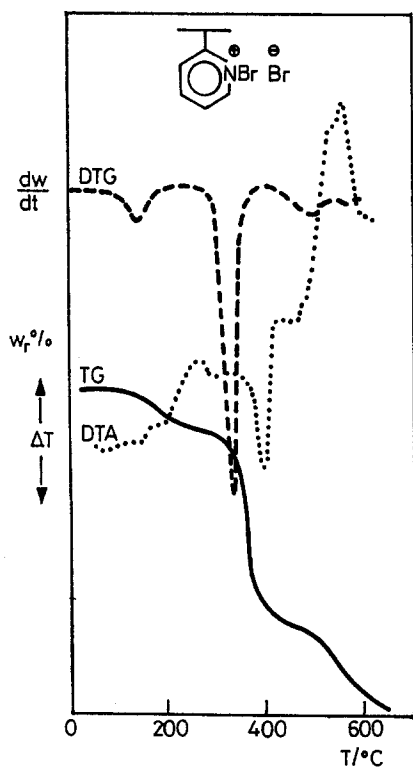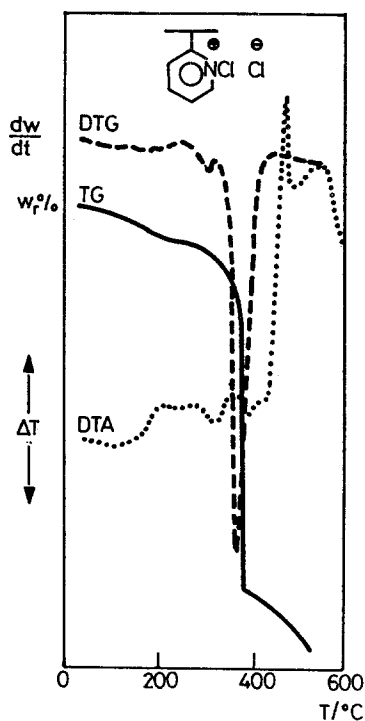

Fig. 2

Fig. 3

reflux after the exclusion of oxygen with a nitrogen current. Then, after cooling, the mixture was added dropwise to 400 ml of petroleum spirit (b.p. 60°–80°C).
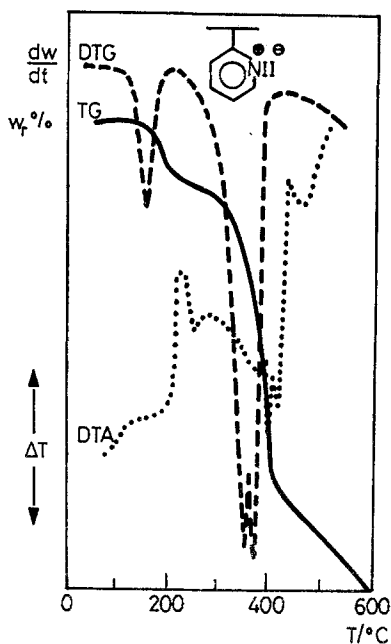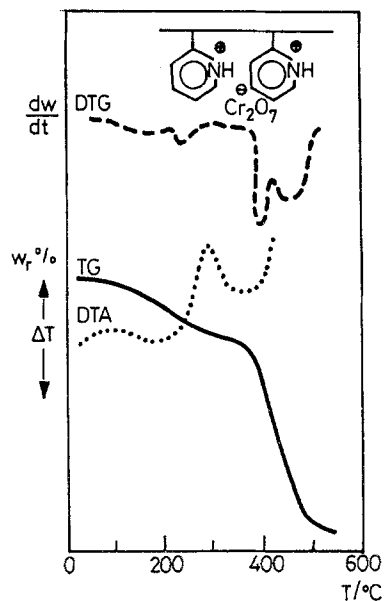

Fig. 4   Fig. 5

The faint brown precipitate was collected, stirred with fresh petroleum ether, then was filtered and dried.

Weight recovered = 10.5 g. Percentage yield = 65%. $\overline{M}v$= 51.000. The IR spectrum showed the disappearance of the band at 1630 cm^{-1} (C=C str.) which relates to the monomer.

Quaternization reactions of poly(2-vinylpyridine)

Reaction with mercuric chloride

To a solution of 0.3 g (0.003 mole of repeating unit) of polymer in 10 ml of tetrahydrofuran in a 100 ml round-bottomed flask containing a magnetic bar and fitted with a separating funnel, a solution of 0.8 g, (0.003 moles) of mercuric chloride in 20 ml of distilled water was added dropwise through a separating funnel. A sudden precipitation occurred. Stirring was continued for 30 min at room temperature, after which the mixture was left to stand overnight, then filtered and washed extensively with hot distilled water until the washings did not give a positive test for mercuric ions (with NaOH solution). The polymer was then washed

with methanol. Weight recovered after drying = 0.66 g. Analysis: Hg = 33.6%. DQ* = 33%, DQ by weight increase = 42%.

The mercury analysis was carried out as follows: Two samples (each containing 60 mg of the polymeric mercury complex) were treated with conc. HCl (6 ml) at 70°C with stirring for 20 h. A third sample (60 mg) was treated with distilled water (6 ml) as above. The three samples were then filtered, diluted and analysed by using two standard solutions.

Reaction with bromine

To a solution of 1 g (0.009 mole) of polymer dissolved in 20 ml of dichloromethane, 1 ml of bromine (0.019 mole) was added dropwise with stirring. The yellow precipitate of brominated polymer salt formed immediately. The mixture was stirred for 30 min, and the precipitate was then filtered off and washed extensively with dichloromethane and water.

The weight recovered after drying was 1.86 g.

Reaction with iodine

1 g (0.009 mole) of polymer dissolved in 20 ml of dichloromethane was reacted with 2.5 g (0.009 mole) of iodine dissolved in 20 ml of dichloromethane, using the same procedure as described in the previous paragraph (reaction with bromine). The dark-red polymer weighed 2.36 g after drying.

Reaction with chlorine

A solution of 1 g (0.009 mole) of polymer dissolved in 20 ml of dichloromethane was reacted with chlorine gas (prepared by adding concentrated HCl to solid potassium permanganate), the gas being passed through an air bubbler into the brown polymer solution for about 2 min, with stirring. The solution turned a faint yellow. The mixture was left to stand overnight at room temperature, after which the partially solidified product was filtered off and washed with water several times. The solid obtained was dried, the weight recovered was 1.37 g.

Reaction with picric acid

To a solution of 0.3 g (0.003 mole) of polymer in 10 ml of tetrahydrofuran, a solution of picric acid (prepared by dissolving 0.7 g (0.003 mole) of picric acid in 10 ml of THF) was added dropwise. A yellow precipitate formed immediately. The mixture was stirred for 3 h at room temperature, after which the precipitate was filtered off and washed extensively with methanol until a colourless filtrate was obtained. After drying, the weight recovered was 0.65 g.

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*   Calculated by assuming 100 repeating units, of which only X = DQ undergoes quaternization

Reaction with chromium trioxide/water

To a solution of 0.3 g (0.003 mole) of polymer in 10 ml of tetrahydrofuran, a solution of dichromic acid $H_2Cr_2O_7$ (prepared by dissolving 0.3 g (0.003 mole) of chromium trioxide in 10 ml of distilled water) was added dropwise with stirring. A brown precipitate was formed. The mixture was left to stand overnight at room temperature, and the product was then filtered off on a harsh funnel, and washed extensively with methanol and water. The weight recovered after drying was 0.55 g. Analysis: Cr = 22.63% (determined by atomic absorption analysis as in the case of mercury). DQ = 51%, DQ by weight increase = 42%.
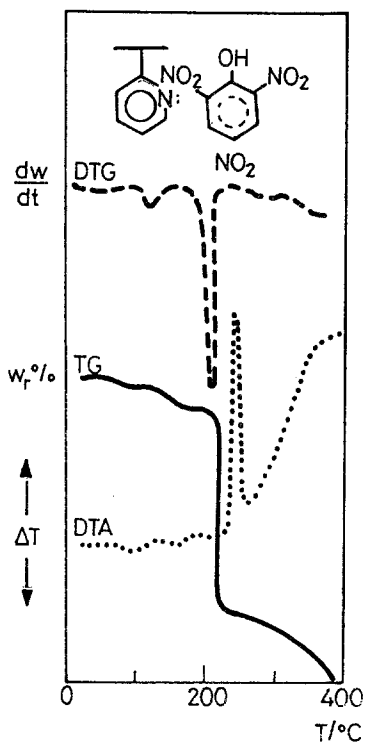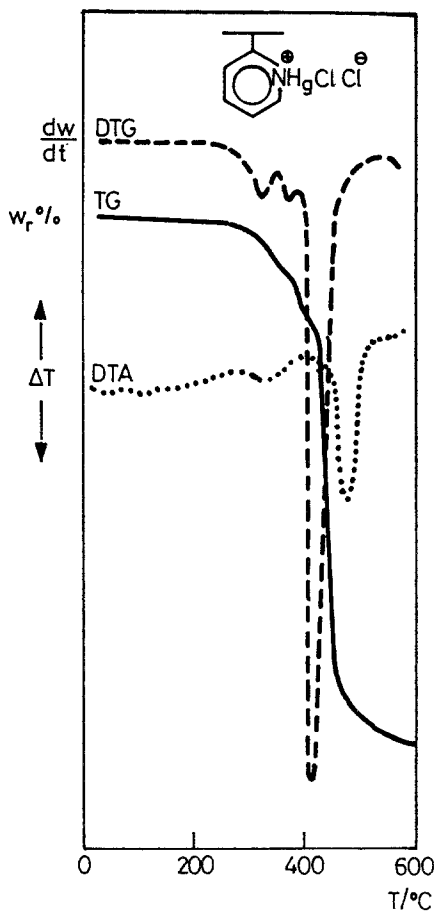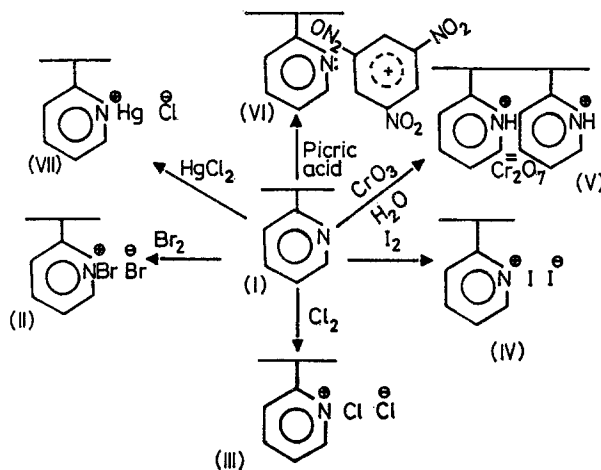

Fig. 6

Fig. 7

Results and discussion

Preparation of polymer complexes

The polymer complexes were prepared by using the simple procedures indicated in the experimental section. Schematic presentation of the preparation of these complexes is shown is Scheme 1.

Scheme 1

The structures of the above polymer complexes were confirmed via the IR spectra, and the characteristic absorptions are given in Table 1. A detectable weight increase on complexation was observed in all experiments.

Table 1 Assignment of characteristic frequencies in IR spectra

Polymer	Wave number /cm^{-1}	Intensity	Assignment
I	1350	w, b	C–H bending (aliphatic str.)
II	410	w, sh	N–Br[6]
III	530	m, b	N–Cl[6]
IV	not clear	–	N–I
V	960	s, b	Cr=O[7]
VI	1550; 1330	s, b; s, b	–NO$_2$
VII	350	w, b	–HgCl
	460	w, b	–Hg–N[8]

sh=sharp, b=broad, s=strong, w=weak, m=medium

Thermal behaviour

The TG, DTA and DTG curves of compounds I–VII are shown in Figs 1–7. The main decomposition steps characterized the thermal behaviour of these polymer complexes.

The initial decomposition temperature and the peak maximum depend on the type of group on the nitrogen. The TG and DTG curves contain the information necessary to evaluate the kinetics of degradation by the modified method of Freeman [9], which is based on the expression:

$$\Delta\log\frac{dw}{dt} = X\Delta\log W_r - (\Delta E/2.3R)\Delta\frac{1}{T}$$

where dw/dt is the rate of reaction, X is the order of reaction, ΔE is the energy of activation, R is the gas constant, T is the absolute temperature and $\Delta W_r = \Delta W_c - \Delta W$ (proportional to the amount of reactant), ΔW being the total weight loss at the point where dw/dt is taken, and ΔW_c being the total weight loss associated with the given reaction.

Table 2 Kinetic parameters for the decomposition of pure poly(2-vinyl pyridine) and poly(2-vinyl pyridine) complexes

Polymer complex	E_a / kJ·mol^{-1}	Reaction order, X
I	147.1	0.773
II	98.2	2.65
III	114.5	3.52
IV	93.6	2.72
V	164.3	3.36
VI	91.9	1.62
VII	123.3	2.32

The equation above gives a straight line with average slope X and negative intercept for the calculation of ΔE. The resulting activation energies (Table 2) indicate the decrease in thermal stability of the free polymer (except polymer V) in the following sequence:

V > I > VII > III > II > IV > VI

The order of degradation (mean slope) varies in the range 1–3. This is probably due to the degraded species attached to the nitrogen, which may act in various roles to destabilize the poly(2-vinylpyridine), with the exception of the dichroma-

te groups, where the product exhibited some thermal stability compared with the free polymer.

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Zusammenfassung — Durch Quaternierung von Ring-Stickstoffatomen mit verschiedenen Reagenzien (I$_2$, Br$_2$, Cl$_2$, CrO$_3$, Pikrinsäure, HgCl$_2$). wurden Poly(2-vinylpyridin)komplexe hergestellt. Unter Anwendung der modifizierten Freeman and Carroll Methode wurde das thermische Verhalten dieser Polymerkomplexe untersucht, wie z.B. ΔE und Reaktionsordnung der Zersetzungsreaktion. Allgemein wurde festgestellt, daß die Anwesenheit einer Gruppe am Stickstoff im Polymer die Aktivierungsenergie senkt und seine thermische Stabilität verringert.