

Thermal Degradation of Polymers. Part XVIII. The Synthesis and Characterization of Quinazolone Pre-Polymers

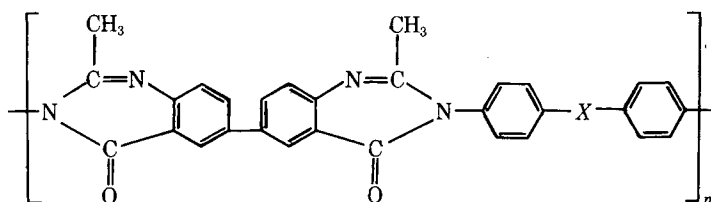
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Synopsis

A series of quinazolone pre-polymers have been prepared from 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid and aromatic diacetamido compounds by melt polycondensation. The pre-polymers have been characterized by combustion analysis, viscometry, vapor pressure osmometry, and thermal analytical methods (TG, DTA, and DSC). Structures have been elucidated by spectroscopic methods (IR and NMR). The thermal cyclization of these pre-polymers to the partial ladder polyquinazolone has been studied and optimized using IR, DSC/DTA, TG, and evolved gas analysis. The cyclization behavior of these systems has been resolved in terms of concurrent dehydration and decarboxylation.

INTRODUCTION

In previous papers^{1,2} the preparation of some polyquinazolones of generalized repeating structure



where X was CH_2 , $-\text{O}-$, SO_2 , and S_2 was discussed. Their thermal characterization and tribological evaluation was also investigated. We now report the preparation and characterization of precursor pre-polymer systems, their detailed structural analysis, and thermal characterization to optimize conditions for the preparation of the partial ladder poly(quinazolone) systems.

MATERIALS

BDC (4,4'-diaminodiphenyl-3,3'-dicarboxylic acid) was prepared as the dihydrochloride from *o*-nitrobenzoic acid by the method of Kurihara and Yoda.³ The hydrochloride was converted to the free base by suspending it in excess of distilled water and the bright yellow free base was obtained by filtration under nitrogen. It was washed free from chloride ion and finally washed with methanol. The material so obtained was dried at 60°C at 1 Torr. It had a melting point

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(m.p.) 302°C (DSC), literature,³ 300°C and combustion analysis gave the following data. Analysis calculated for $C_{14}H_{12}N_2O_4$: C, 61.8%; H, 4.4%; N, 10.3%; O, 23.5%; found: C, 61.2%; H, 4.9%; N, 10.5%.

The following diacetamido compounds were obtained by acetylation of the corresponding diamine: *o*-diacetamidophenylene (*o*-DAP), m.p. 185°C (DSC), literature,⁴ m.p. 185–186°C; *m*-Diacetamidophenylene (*m*-DAP), m.p. 190°C (DSC), literature,⁴ m.p. 191°C; *p*-Diacetamidophenylene (*p*-DAP), m.p. 305°C (DSC), literature,⁴ m.p. 303°C; 4,4'-diacetamidodiphenyl methane (DADM), m.p. 227°C, literature² m.p. 227°–228°C; 4,4'-diacetamidodiphenyl disulphide (DADDS), m.p. 209°C, literature,⁴ m.p. 205–206°C; 2,6-diacetamidopyridine (DAPY), m.p. 201°C, literature,⁴ m.p. 204°C; 1,5-diacetamido naphthalene (DAN), m.p. 360°C, literature,⁴ m.p. 360°C; 4,4'-diacetamidodiphenyl sulphone (*p*-DADS), m.p. 285°C, literature,⁴ m.p. 285°C; 4,4'-diacetamidodiphenyl ether (DADE), m.p. 227°C, literature,⁴ m.p. 228–229°C.

3,3'-diacetamido diphenylsulphone (*m*-DADS) was obtained from the corresponding diamine by acetylation in glacial acetic acid with acetic anhydride. *m*-DADS so obtained was recrystallized from ethanol and had a m.p. 219°C (DSC), 221°C (HSPM).

Analysis calculated for $C_{16}H_{16}N_2O_4S$: C, 57.8%; H, 4.8%; N, 8.4%; O, 19.6%; S, 9.6%; found: C, 57.8%; H, 4.7%; N, 8.2%; S, 9.7%.

PRE-POLYMER PREPARATION

Pre-polymers were prepared from equimolar amounts of BDC and the diacetamido compound in the melt phase under nitrogen at a pressure of 0.1 Torr. Conditions were optimized for each system studied in terms of the reaction temperature and time to yield a product of maximum molecular weight as assessed by viscometry. The pre-polymers prepared are as follows and the combustion analysis data are for samples after purification by Soxhlet extraction with water followed by drying to constant weight at 30°C and 1 Torr.

Melt polycondensation of BDC and *o*-DAP at 200°C for 1 hr yielded pre-polymer *o*-DP_p as a pale yellow glass in 61% yield. Analysis calculated for *o*-DP_p ($C_{24}H_{20}N_4O_4$)_n: C, 67.3%; H, 4.7%; N, 13.1%; O, 14.9%; found: C, 68.3%; H, 5.2%; N, 12.7%.

Pre-polymer *m*-DP_p was obtained in 80% yield as a yellow glass from BDC and *m*-DAP after 3 hr at 243°C; found: C, 68.3%; H, 5.2%; N, 12.7%.

Pre-polymer *p*-DP_p was obtained in 87% yield as a green glass from BDC and *p*-DAP after 2 hr at 255°C; found: C, 67.9%; H, 5.2%; N, 12.9%.

Pre-polymer *p*-DS_p was obtained in 85% yield as a lime green glass from BDC and *p*-DADS after 2 hr at 243°C. Analysis calculated for *p*-DS_p ($C_{30}H_{24}N_4O_6S$)_n: C, 63.4%; H, 4.3%; N, 9.9%; S, 5.6%; O, 16.9%; found: C, 64.0%; H, 4.9%; N, 10.2%; S, 5.9%.

Pre-polymer *m*-DS_p was obtained from BDC and *m*-DADS after 2 hr at 231°C as a dark green glass in 83% yield. Analysis calculated for ($C_{30}H_{24}N_4O_6S$)_n: C, 63.4%; H, 4.3%; N, 9.9%; S, 5.6%; O, 16.9%; found: C, 64.2%; H, 4.9%; N, 10.2%; S, 5.8%.

Pre-polymer DE_p was obtained from BDC and DADE after 2 hr at 243°C as a grey glass in 73% yield. Analysis calculated for ($C_{30}H_{24}N_4O_5$)_n: C, 69.2%; H, 4.7%; N, 10.8%; O, 15.3%; found: C, 69.9%; H, 5.2%; N, 11.0%.

Pre-polymer DM_p was obtained from BDC and DADM after 2 hr at 243°C as a yellow glass in 84% yield. Analysis calculated for $(C_{31}H_{26}N_4O_4)_n$: C, 71.8%; H, 5.1%; N, 10.8%; O, 12.3%; found: C, 71.0%; H, 5.5%; N, 10.6%.

Pre-polymer DDS_p was obtained from BDC and DADDS after 2 hr at 231°C as a brown glass in 81% yield. Analysis calculated for $(C_{30}H_{24}N_4O_4S_2)_n$: C, 63.4%; H, 4.3%; N, 9.9%; S, 11.3%; O, 11.3%; found: C, 64.1%; H, 5.0%; N, 10.3%; S, 11.0%.

Pre-polymer DPY_p was obtained from BDC and DAPY after 2 hr at 243°C as an orange glass in 84% yield. Analysis calculated for $(C_{23}H_{19}N_3O_4)_n$: C, 64.3%; H, 4.5%; N, 16.3%; O, 14.9%; found: C, 65.2%; H, 4.9%; N, 15.9%.

PRE-POLYMER CHARACTERIZATION

A Sofica automatic Ubbelohde suspended-level viscometer (bore diameter 0.4 mm) was used to determine intrinsic viscosity in distilled DMF at 25° ± 0.03°C. Number average molecular weights were obtained using a Mechrolab Model 301A vapor pressure osmometer with a chamber temperature of 65°C. DMF was used as a solvent and benzil was used as the calibration standard. The prepolymers had the molecular weights and intrinsic viscosities shown in Table I.

SPECTROSCOPIC STUDIES

Infrared spectra were recorded using a Unicam SP200 spectrophotometer. The sample (2 mg) was ground with dry potassium bromide (200 mg) and the suspension converted to a disk under vacuum using a hydraulic press.

Nuclear-magnetic-resonance spectra were run on saturated solutions of the pre-polymers in deuterated dimethyl sulphoxide using a Perkin-Elmer NMR spectrophotometer Model R10.

THERMAL ANALYSIS

Studies were made using a Du Pont 900 thermal analyzer equipped with DTA and DSC cells. DTA studies were made on finely divided samples in glass macro tubes (filled to 4 mm depth) using glass beads as the reference material. DSC

TABLE I
Pre-Polymer Number Average Molecular Weights and Intrinsic Viscosities

Prepolymer	$\overline{Mn} \times 10^{-3}$	DP	$[\eta]$ dl/g ^a	$[\eta]$ dl/g ^b
<i>o</i> -DP _p	3.31	7	0.053	0.061
<i>m</i> -DP _p	4.26	10	0.071	0.078
<i>p</i> -DP _p	5.49	13	0.070	0.076
<i>p</i> -DS _p	7.63	13	0.073	0.079
<i>m</i> -DS _p	5.64	10	0.064	0.067
DE _p	6.67	12	0.072	0.079
DM _p	6.12	12	0.073	0.078
DDS _p	6.12	11	0.069	0.074
DPY _p	4.86	11	0.071	0.077

^a Normal extrapolation, i.e., $[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c$.

^b From equation derived by Fuoss⁵ for polyelectrolytes.

studies were made on samples (5 mg) contained in crimped aluminum pans using an empty crimped pan as the inert reference material. DTA and DSC experiments were performed at a heating rate of 20°C/min in a "static air" atmosphere unless otherwise stated.

HOT-STAGE POLARIZING MICROSCOPE (HSPM)

Studies were made using a Kofler hot-stage polarizing microscope from ambient to 320°C at a similar heating rate to that used in the DTA/DSC experiments.

THERMOGRAVIMETRIC ANALYSIS (TG)

TG was performed on a Stanton thermobalance model TR02. All temperatures are furnace wall temperatures and in dynamic studies the heating rate was 3.0°C/min (nominal). The sample (10 mg) was pulverized and spread as a thin layer at the bottom of a platinum crucible (rim diameter 1.125 cm, base diameter 1.00 cm, height 0.8 cm).

White spot nitrogen or compressed air was used as the test atmosphere at a flow rate of 450 ml/min. Results are corrected for buoyancy effects. Isothermal studies were made by heating the furnace and sheath to the required temperature without the crucible in place on the rise rod and the balance in the arrested position. The furnace was then raised, the sample was placed in position, the furnace was lowered immediately followed by releasing of the balance mechanism and the weight loss was recorded.

THERMAL CYCLIZATION STUDIES

Thermal cyclization studies were made by spreading the pre-polymer powder as a thin layer on a microscope slide which was then heated in a nitrogen atmosphere for different periods of time at the chosen cyclization temperature. The resulting materials were subjected to DSC/DTA analysis, and IR spectra were recorded on the polymers dispersed in potassium bromide. The area associated with the peak at 3300 cm^{-1} and that at 1600 cm^{-1} for both the pre-polymer and cyclized polymer was determined.

Isothermal weight loss studies in nitrogen were also used to evaluate weight losses from the pre-polymers under similar conditions to those used in the cyclization experiments.

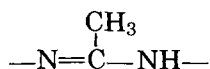
DISCUSSION

Pre-polymers were prepared from high-purity BDC and diacetamido compounds by melt polycondensation since previous studies had shown solution polymerization at high temperatures in polyphosphoric acid and at lower temperatures in dimethyl acetamide or *N*-methyl pyrrolidone failed to give open chain polymers.⁶

Attempts to prepare prepolymer DN_p from BDC and DAN failed because the high melting point of DAN (360°C) prevented polymerization. Polymerization at temperatures in excess of 280°C resulted in decomposition of BDC and benzidine could be isolated from the reaction medium. Solution polymerization in quinoline also failed to yield polymeric products.

Prepolymers obtained from *o*-DAP and BDC at temperatures above 200°C were only partially soluble in DMF. DTA and TG showed unexpectedly high thermal stability as compared with pre-polymer *p*-DP_p and a DMF soluble *o*-DP_p polymer (Fig. 1). Further to this, the combustion analysis data indicated a higher carbon and nitrogen content than that required by the assumed pre-polymer structure, suggesting that cyclization had occurred.

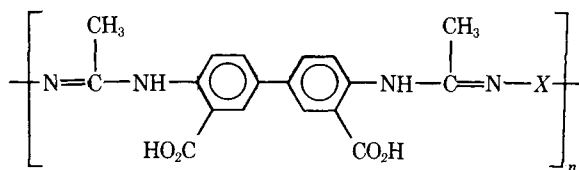
Phillips⁷ has reported that 2-methylbenzimidazole may be prepared by thermal cyclization of *o*-DAP, and 2-methylbenzimidazole was found to be formed when *o*-DAP was heated alone under the polymerization conditions. A 12% yield of 2-methylbenzimidazole was obtained from prepolymer *o*-DP_p on extraction with water, indicating that concurrent polymerization and cyclodehydration occurred together with the thermal cyclization of *o*-DAP. The abnormal behavior of the *o*-DAP/BDC system may be attributed to the proximity of the acetamido groupings in *o*-diacetamido phenylene, leading to cyclization. Further, the proximity of the carboxyl and the



function in the pre-polymer favors cyclization to the quinazolone at relatively low temperatures.

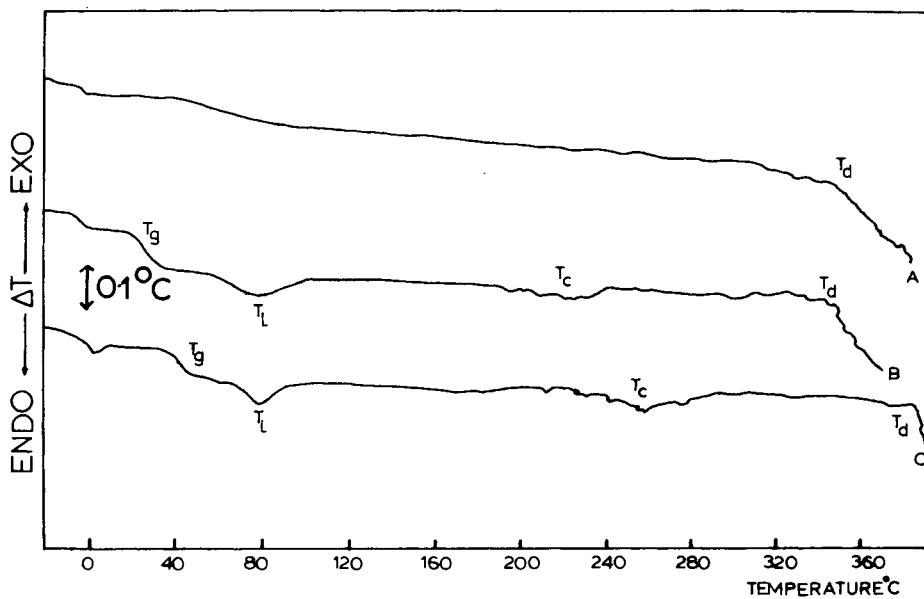
PRE-POLYMER CHARACTERIZATION

The structure of the prepolymers has been suggested^{1,2,6} to be of the form (I)

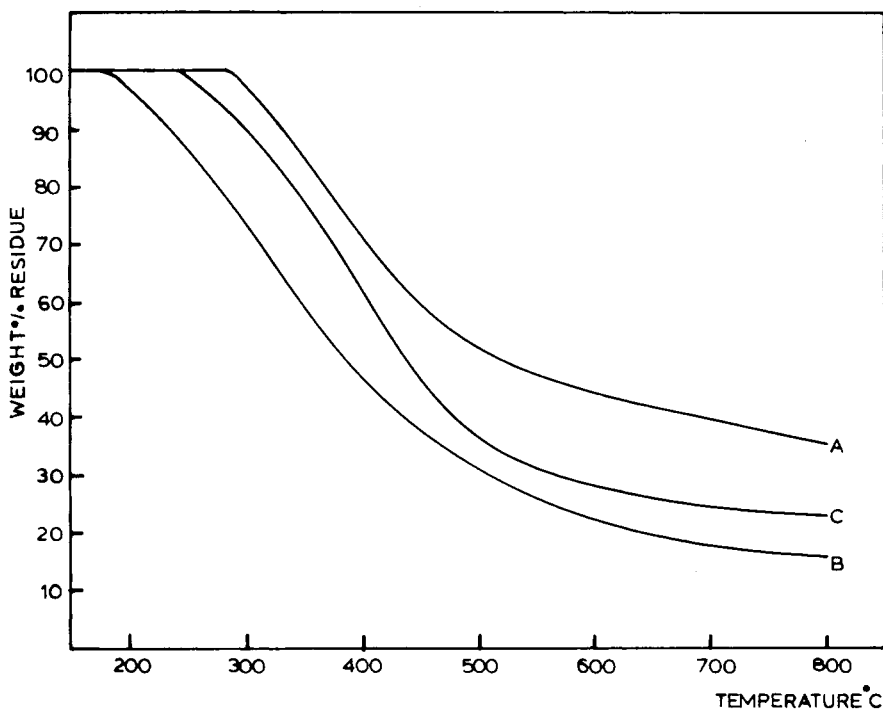


(I)

However, a possible alternative mode of reaction could lead to the formation of



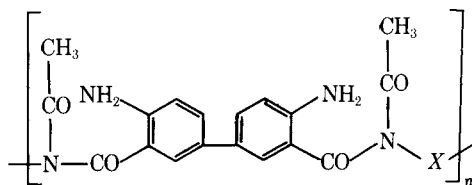
A



B

Fig. 1. DSC and TG curves for *p*-DP_p and *o*-DP_p in nitrogen. A) *o*-DP_p insoluble polymer; B) *o*-DP_p soluble polymer; C) *p*-DP_p soluble polymer; T_g = glass transition; T_c = cyclization endotherm; T_d = onset temperature for degradation; T_L = liquefaction temperature range.

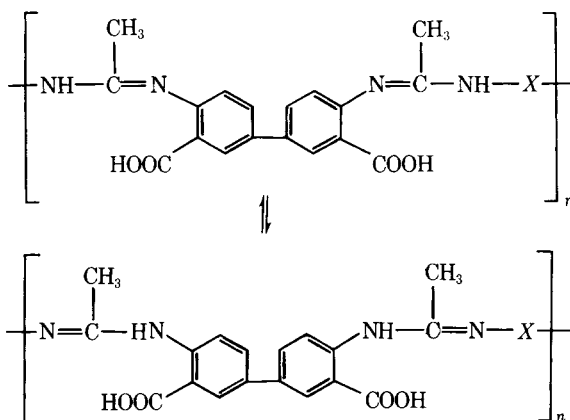
structure (II)



(II)

Spectroscopic analysis however has shown that the characteristic broad absorption for a primary amino grouping in the IR spectrum at $3500\text{--}3300\text{ cm}^{-1}$ is absent. Chemical tests for primary aromatic amines were also negative. In the proton nmr spectra the following absorptions were found on the τ scale, using $p\text{-DP}_p$ and $p\text{-DS}_p$ as typical examples: $p\text{-DP}_p$ gave 7.8 (singlet), CH_3 ; 4.8 (broad absorption), NH ; 2.5–3.8 (complex), aromatics; and 0.5 (multiplet), CO_2H . $p\text{-DS}_p$ gave 7.8 (singlet), CH_3 ; 4.8 (broad absorption), NH ; 2.0–4.0 (complex), aromatics; 0.0 (multiplet), CO_2H .

The position of the methyl group absorption is consistent with structure (I) since if the methyl grouping were adjacent to the carbonyl grouping it would absorb at lower field.⁸ The position of the other proton resonances, especially that at $\tau = 0 - 0.5$ due to the carboxyl protons suggest that structure (I) is predominantly present. This, together with the combustion analysis data, suggest that the "basic" structure of these pre-polymers is the tautomeric equilibrium



The overall complexity of the NMR spectra thus arises in part as a result of this tautomeric behavior. In addition the situation is further complicated by structures involving hydrogen bonded and zwitterionic forms and the possibilities of hydrogen exchange. Characterization of these systems by intrinsic viscosity measurements gave the typical graphs shown in Figure 2 for reduced viscosity vs. concentration with departure from linearity which may be ascribed to polyelectrolyte behavior associated with dissociation of the carboxyl groupings on progressive dilution. If the data is plotted according to the empirical equation of Fuoss,⁵ linear plots are obtained, leading to values of intrinsic viscosity re-

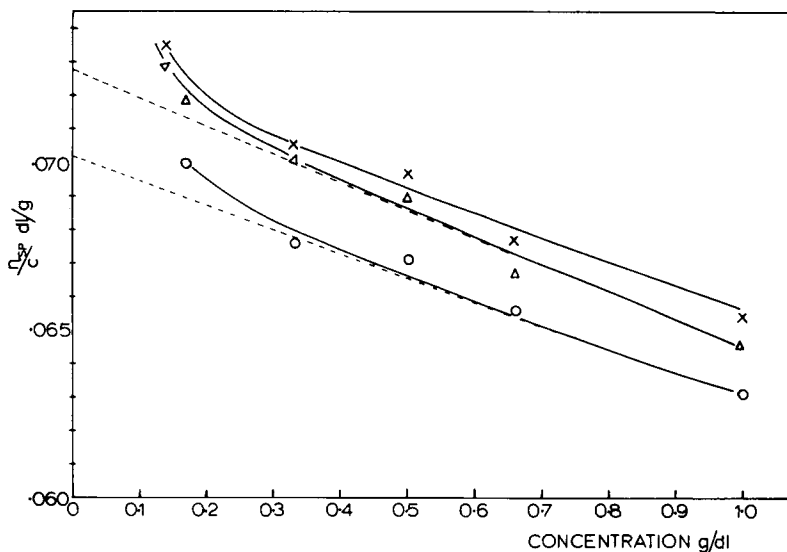
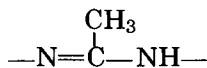


Fig. 2. Intrinsic viscosity determination. — O —, p -DP $_p$; — x —, p -DS $_p$; — Δ —, DM $_p$.

corded in Table I, which indicate low molecular weights for these systems as is confirmed by the vapor pressure osmometry data.

DSC in conjunction with HSPM studies were used to characterize the prepolymers in terms of glass transition temperatures (T_g), the temperature range in which liquefaction occurred (T_L), the temperature range in which cyclodehydration occurred (T_C), and the onset temperature for thermal degradation (T_D). Typical traces obtained by DSC are shown in Figure 3. They show a baseline shift at T_g followed by three endothermic processes. The two processes (2, 3) at temperatures in excess of 200°C both involve weight loss and the shallow endotherm may be ascribed to cyclodehydration while the process involving more energy is thermal degradation. Endotherm (1) is not associated with weight loss or with volatile formation as shown by TG and combined DTA/mass spectroscopic (MS) studies. The temperature range of this endotherm corresponds to the range in which liquefaction and flow are observed on the HSPM. These materials are not birefringent and this suggests that they are amorphous, as confirmed by x-ray analysis.^{1,6} This behavior, therefore, suggests that endotherm (1) may possibly be associated with a transition involving loss of local order in the system similar to that reported for polystyrene by Boyer⁹ and designated the T_{ml} , temperature of melt to liquid transition. The results obtained from DSC and HSPM studies are presented in Table II.

The low molecular weights obtained by VPO are substantiated by the low T_g values presented in Table II. For these systems the T_g would be expected to rise rapidly with increasing molecular weight as a result of the in-built chain stiffness associated with the aromatic units and the tautomeric forms of the



unit. The shallow endotherm observed between 230°–280°C designated (T_C) was initially attributed to cyclodehydration only. However combined DTA and

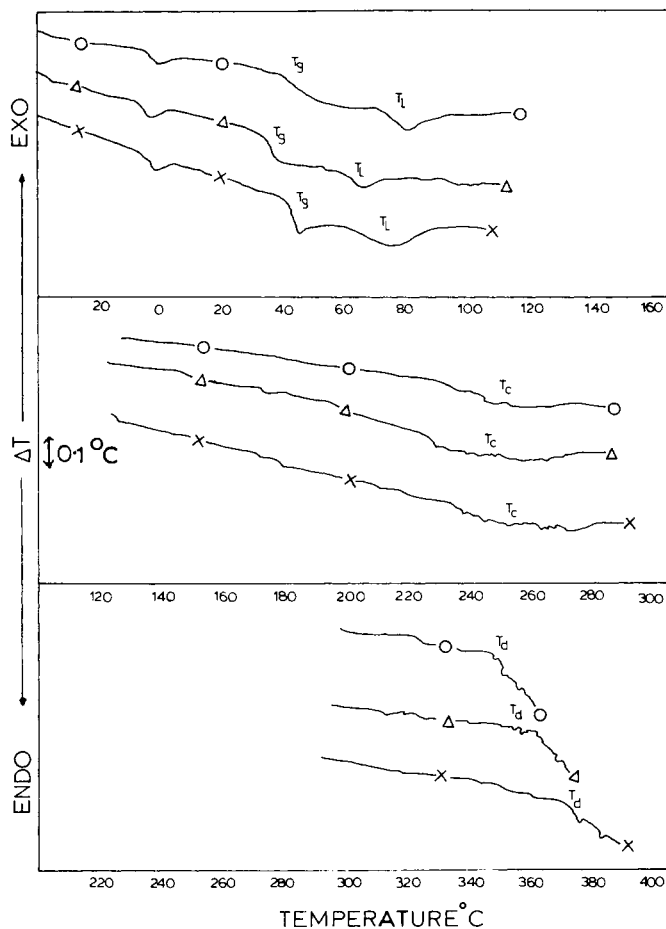


Fig. 3. DSC curves for pre-polymers in nitrogen. — O —, p -DP_p; — x —, p -DS_p; — Δ —, DM_p; T_g = glass transition; T_L = liquefaction temperature range; T_d = onset temperature for degradation.

mass spectrometry and dynamic TG and isothermal weight loss studies have revealed that this is not the only process occurring.

The experimental weight losses observed for isothermal studies in the cyclodehydration endotherm range, Table III, may be compared with the theoretical values for water loss in an attempt to give a convenient method for assessing the degree of conversion to the poly(quinazolone). However, the weight losses are in general in excess of that required by loss of 2 moles of water from each repeating unit, suggesting that weight loss involves at least two components.

The thermal cyclization of poly(amic acids) to poly(imides) has been shown by Bruck¹⁰ to involve concurrent dehydration and decarboxylation and a similar reaction could occur in these systems. Studies by passage of evolved gases from p -DS_p, p -DP_p, and DM_p through lime water showed that carbon dioxide was evolved during cyclization. Combined DTA/MS studies on p -DP_p and DDS_p showed that carbon dioxide was evolved from 260°C and leveled off at 290°C under dynamic conditions at 16°C/min heating rate. The poly(imide) precursor (RX-13) was shown to behave similarly. In addition, in the case of DDS_p hydrogen sulphide evolution was also shown to occur from 270°C.

TABLE II
 DSC and HSPM Studies on Pre-Polymers

Pre-polymer	T_g (°C) ^a	DSC		T_D (°C)	HSPM T_L (°C) ^c
		T_L (°C) ^b	T_C (°C)		
<i>o</i> -DP _p	20	80	202–225	320	85–104
<i>m</i> -DP _p	47	95	235–280	340	90–112
<i>p</i> -DP _p	41	80	240–280	400	85–110
<i>p</i> -DS _p	35	65	230–2.0	360	72–105
<i>m</i> -DS _p	29	95	236–274	350	80–105
DE _p	32	69	230–270	340	75–85
DM _p	40	77	240–280	380	82–92
DDS _p	39	60	240–290	350	71–82
DPY _p	34	90	232–272	360	92–118

^a T_g was taken as the temperature corresponding to the intersection of the extrapolation of the baseline and the longest straight line of the low-temperature side of the peak.

^b T_L was taken as the minimum in the endothermic process.

^c T_L represents the temperature range in which liquefaction and flow occurred.

 TABLE III
 Isothermal Weight Loss Studies on the Pre-Polymers in Nitrogen

Conditions		Polymer/% weight loss								
Temperature (°C)/time (hr)		<i>o</i> -DP _p	<i>m</i> -DP _p	<i>p</i> -DP _p	<i>p</i> -DS _p	<i>m</i> -DS _p	DE _p	DM _p	DDS _p	DPY _p
280	1	6.5 ^a	7.5	6.0	8.0	8.0	7.5	8.5	9.5	10.0
280	2	10.5 ^a	11.0	9.5	10.0	10.5	11.0	11.0	12.0	13.0
280	3	12.0 ^a	13.0	11.5	11.0	12.0	12.0	13.0	13.0	15.0
280	4	13.5 ^a	15.0	13.0	12.5	14.5	13.0	14.0	14.5	16.0
300	1	11.5 ^a	11.0	11.0	12.5	11.0	11.5	12.0	12.5	13.0
300	2	15.0 ^a	13.5	14.0	14.0	15.0	14.5	14.5	14.5	15.0
300	3	17.5 ^a	17.0	16.0	15.5	16.0	16.0	16.0	17.0	18.0
300	4	18.5 ^a	19.0	17.5	17.0	17.5	17.5	17.0	18.0	19.5
Theoretical % weight loss for 2H ₂ O		8.4	8.4	8.4	6.3	6.3	6.9	7.0	6.3	8.4
Theoretical % weight loss for 2H ₂ O + 2CO ₂		14.5	14.5	14.5	10.9	10.9	11.9	12.0	10.9	14.4

^a Isothermal studies at 240°C for specified time due to ease of cyclization.

Since TG records the total weight lost from these systems it does not therefore give an adequate assessment of cyclization behavior when used alone.

In an attempt to optimize conditions for cyclization, studies were also made by DSC/DTA and by IR spectroscopy. Typical results of DTA/DSC studies on polymers produced under different cyclization conditions are shown in Table IV together with observations of the flow behavior made by stopping the DTA or DSC experiment at suitable temperatures.

Typical traces for the DM_c system are shown in Figure 4. These show the disappearance of the T_g with increased severity of cyclization conditions and decreased susceptibility to oxidative degradation (T_D increases) as the system is no longer converted to the melt phase. Conditions for cyclization were chosen such that the T_g and cyclization endotherm were absent in the treated polymer and it was no longer observed to flow. Where a series of treatments gave similar

TABLE IV
 Optimization of Cyclization Conditions by DSC in Air

Polymer	Cyclization conditions °C/time (hr)	Temperature range (°C)		
		-40°-100°C	100°-350°C	350°-500°C
<i>p</i> -DP _p	280/1	<i>T_g</i> 42°C	—	<i>T_F</i> 380°C
	280/3	<i>T_g</i> 42°C	—	<i>T_F</i> ^a 380°C
	300/1	No <i>T_g</i>	—	no flow observed
	300/2	observed	—	<i>T_D</i> 400°C
<i>p</i> -DS _p	280/1	<i>T_g</i> 42°C	shallow endotherm ^b 260°-280°	<i>T_F</i> 360°C
	280/2	<i>T_g</i> 42°C	—	<i>T_F</i> 360°C
	280/4	<i>T_g</i> 42°C	—	<i>T_F</i> 360°C
	300/1	<i>T_g</i> 45°C (small)	—	<i>T_F</i> 360°C
	300/2	No <i>T_g</i>	—	no flow observed
	300/3	observed	—	<i>T_D</i> 400°C
DM _p	280/1	<i>T_g</i> 44°C (very small)	endotherm ^b 240-280°	<i>T_F</i> 370°C
	280/4	<i>T_g</i> 42°C (very small)	—	<i>T_F</i> 380°C
	300/2	No <i>T_g</i>	—	no flow observed
	300/2	observed	—	<i>T_D</i> 400°C

^a *T_F* is the temperature at which flow was observed in terms of the system flowing up the macrotube in a DTA experiment or flowing out of the aluminum pan in a DSC experiment.

^b Cyclization endotherm.

results the least severe conditions giving the smallest weight loss (Table IV) were chosen to minimize decarboxylation. The conditions optimized using TG/DTA/DSC are presented in Table V.

IR was also used in an attempt to optimize cyclization conditions. In Figure 5 typical spectra obtained from DM_p and the cyclized polymer DM_c (cyclized under the conditions optimized by TG/DSC) are shown and compared with that from the model compound 3-phenyl-2-methylquinazoline-4-one. It can be seen that DM_c still shows absorptions due to the NH grouping, indicating cyclization to be incomplete. Attempts were made to assess the degree of cyclization by measuring the peak area ratio, N—H peak (cyclized polymer): N—H peak (pre-polymer). However, this ratio was found to be unsuitable since when the polymers were cyclized they became more difficult to disperse in potassium bromide, leading to an overall smaller absorption. In an attempt to compensate for dispersion effects, a peak at 1600 cm⁻¹, which should not change in intensity if cyclization is the only process occurring, was chosen as a reference peak. A parameter *X* was defined where

$$X = \frac{\text{wt. peak at } 3300 \text{ cm}^{-1} \text{ (cyclized polymer)}}{\text{wt. peak at } 3300 \text{ cm}^{-1} \text{ (pre-polymer)}} \times \frac{\text{wt. reference peak (pre-polymer)}}{\text{wt. reference peak (cyclized polymer)}}$$

which should monitor the degree of cyclization allowing for dispersion. *X* should vary from unity to zero, but for all the systems studied the results indicated that the reference peak also changed under the cyclization conditions. Similarly if

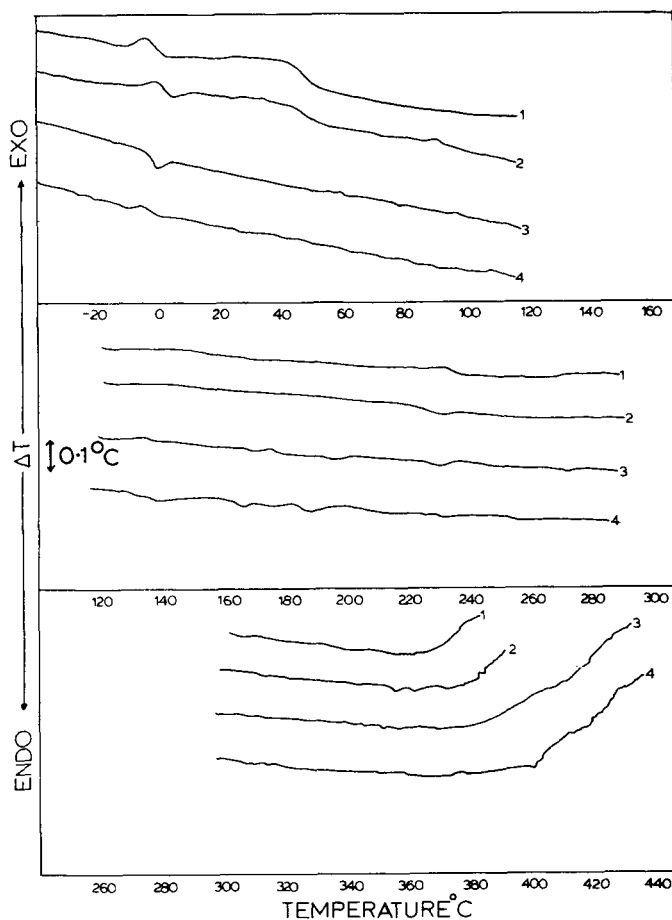


Fig. 4. Optimization of cyclization conditions for DM_p by DSC in air. Curve 1, after cyclization at 280°C for 1 hr; curve 2, after cyclization at 280°C for 4 hr; curve 3, after cyclization at 300°C for 1 hr; curve 4, after cyclization at 300°C for 2 hr.

TABLE V
Optimum Cyclization Conditions

Polymer	Temperature ($^\circ\text{C}$)/time (hr)
$o\text{-}DP_c$	240 2
$m\text{-}DP_c$	300 2
$p\text{-}DP_c$	280 4
$p\text{-}DS_c$	300 2
$m\text{-}DS_c$	300 1
DE_c	300 2
DM_c	300 1
DDS_c	280 4
DPY_c	280 3

the C—H aromatic absorption peak at $820\text{--}830\text{ cm}^{-1}$ is used as the reference peak the values of X observed at low extents of cyclization are again greater than unity. Both observations may be cited as evidence for the loss of the carboxyl function by decarboxylation, leading to changes in the width of the reference peaks. It

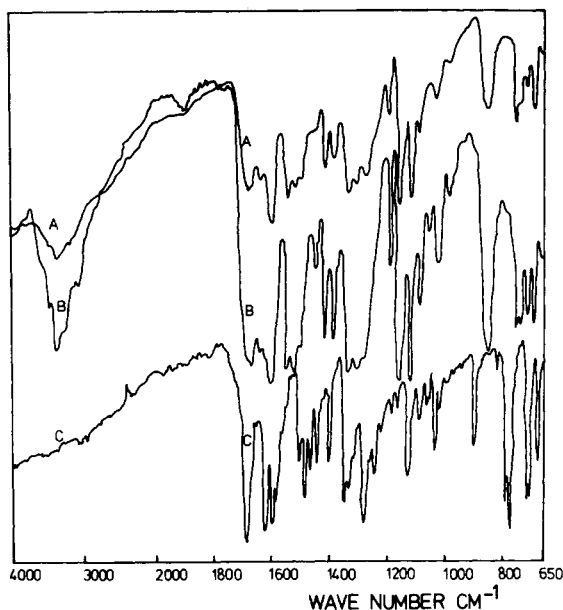


Fig. 5. IR spectra for DM_p , DM_c , and 3-phenyl-2-methyl quinazoline-4-one. A = DM_c ; B = DM_p ; C = 3-Phenyl-2-methyl quinazoline-4-one.

was thus found that this IR method as used above cannot give a suitable measure of cyclization and a combination of DSC/DTA and TG gives more realistic results but indicates that concurrent decarboxylation and loss of low molecular weight water insoluble species occurs.

Chemical cyclization studies were also made on these systems in an attempt to reduce the temperature required for cyclodehydration and to prevent decarboxylation. Polyamic acids may be converted to the corresponding polyimide in the bulk phase or in solution using chemical reagents.¹¹⁻¹⁴ Experiments were carried out using similar procedures to those used by Dine-Hart and Wright¹¹ but the results showed that cyclization could not be effected at lower temperatures as in the case of polyimides.

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