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Hardy Sze On Chan^a; J. R. Lusty^b

^a Department of Chemistry, National University of Singapore, Kent Ridge, Singapore ^b School of Chemistry, Robert Gordon's Institute of Technology, Aberdeen, Scotland

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Acid-Catalyzed Cyclodehydration of Quinazolone Prepolymers

HARDY SZE ON CHAN*

Department of Chemistry
National University of Singapore
Kent Ridge, Singapore 0511

J. R. LUSTY

School of Chemistry
Robert Gordon's Institute of Technology
Aberdeen, AB1 1HG, Scotland

ABSTRACT

The effect of p-toluenesulfonic acid and phosphoric acid on the cyclodehydration of quinazolone prepolymers has been investigated. Isothermal weight loss during the curing process was monitored closely to follow the extent of cyclization. The optimum weight loss corresponding to 2 mol water is used as an indication of the formation of a fully cyclized quinazolone structure without concurrent decarboxylation. This can be achieved by incorporating the catalyst at 2 wt% concentration, which permits a lower curing temperature than those previously reported. The polymers formed in the presence of catalyst have thermal stability superior to those prepared without catalyst. The glass transition temperature is

*To whom correspondence should be addressed.

also raised. This we conclude to be a direct result of the decrease in the amount of incomplete quinazolone rings along the polymer backbone as a result of more efficient cyclization catalyzed by the acids.

INTRODUCTION

Previous papers [1-3] described the preparation of prepolymer precursor to heat-resistant polyquinazolones and studies to yield optimum conditions for their cyclodehydration. Differential thermal analysis (DTA) combined with mass spectroscopic (MS) and IR studies led us to conclude that the resultant cyclized polymers had structures significantly different from those of model quinazolones. Cyclization involving cyclodehydration was shown to be accompanied by concurrent decarboxylation, mainly due to the high temperatures required to effect the cyclization. Incomplete cyclization would have given polyquinazolones of inferior thermal stability compared to those which are fully cyclized.

This paper reports the use of acids to accelerate cyclodehydration at lower temperatures to prevent concurrent decarboxylation. Isothermal weight loss and microanalysis data were used to monitor the extent of cyclization. Optimum cyclization conditions were obtained, and the thermal stability and transitions of the resultant polymers were assessed by thermogravimetry (TG) and differential scanning calorimetry (DSC), respectively.

EXPERIMENTAL

Materials

Prepolymers

Quinazolone prepolymers were prepared as previously reported [1]. This involves melt condensation of equimolar amounts of BDC (4,4'-diaminodiphenyl-3,3'-dicarboxylic acid) and the diacetamido derivative of a diamine under nitrogen at a pressure of 0.1 torr. Nine prepolymers were prepared in the previous work, but only three have been chosen for the present study. The general structure of the prepolymers is shown in Fig. 1.

Prepolymer DP_p (subscript p indicates prepolymer) was obtained in 87% yield as a green glassy material from BDC and p-DAP (1,4-diacetamidophenylene) after 2 h at 243°C. Analysis: Calculated for DP_p prepolymer (C₂₄H₂₀N₄O₄): C, 67.3; H, 4.7; N, 13.1; O, 14.9%. Found: C, 68.3; H, 5.0; N, 12.9%.

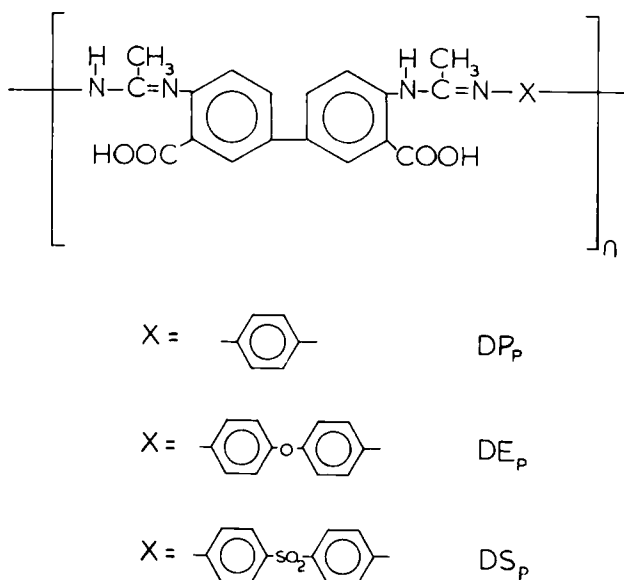


FIG. 1. Structure of quinazolone prepolymer.

Prepolymer DS_p was obtained in 85% yield as a lime green glassy material from BDC and p-DADS (4,4'-diacetamidodiphenyl sulfone) after 2 h at 243°C. Analysis: Calculated for DS_p ($C_{30}H_{24}N_4O_6S$): C, 63.4; H, 4.3; N, 9.9; S, 5.4; O, 16.9%. Found: C, 64.0; H, 4.9; N, 10.2; S, 5.9%.

Prepolymer DE_p was obtained from BDC and DADE (4,4'-diacetamidodiphenyl ether) after 2 h at 243°C as a grey glassy material in 73% yield. Analysis: Calculated for ($C_{30}H_{24}N_4O_5$): C, 69.2; H, 4.7; N, 10.8; O, 15.3%. Found: C, 69.9; H, 4.9; N, 11.0%.

Acid Catalysts

In their studies of poly-1,3,4-oxadiazole, Frazer and Wilson [4] found that phosphoric acid (PA) and p-toluenesulfonic acids (PTSA) are the most effective in catalyzing the cyclodehydration step. These two acids were chosen for the present work. The level of catalyst used throughout was 2 wt%, except on one occasion when dynamic TG was carried out on polymer DP_c (the subscript c indicates cyclized polymer) cyclized with 10 wt% catalyst.

TABLE 1. Intrinsic Viscosities of Prepolymers

Prepolymer	$[\eta]$, dL/g	
	Previous data ^a	Present data
DP _p	0.0702	0.0786
DS _p	0.0731	0.0765
DE _p	0.0723	0.0718

^aSee Ref. 1.

Prepolymer Characterization

Viscosity Measurement

In order to ensure that prepolymers of reasonable molecular weight have been prepared, intrinsic viscosities were determined in distilled dimethylformamide (DMF, bp 136°C) at 25 ± 0.03°C. The results are compared with previous data [1] in Table 1. It can be seen that the intrinsic viscosities are comparable and suggest that the molecular weight of the present prepolymers are sufficiently high for further studies. The viscosity-average molecular weight cannot be determined because the constants K and α in the Mark-Houwink equation for quinazolone polymers are unknown.

Infrared Spectroscopy

In order to study the structure of the quinazolone prepolymers, the IR spectrum of DP_p was compared with that of the model compound 3-phenyl-2-methyl-quinazoline-4-one, as shown in Fig. 2. The prepolymer showed the following absorptions: 3 300, 1 640, and 1 540 cm⁻¹ for the -NH-C=N- grouping, 1 680 cm⁻¹ for the carbonyl group of the aromatic acid, and 3 100 cm⁻¹ for the -OH of the acid. The sharp peaks at 1 380 and 1 420 cm⁻¹ are characteristic of C-H stretching in methyl groups. In addition, absorptions at 1 190, 1 285, and 1 340 cm⁻¹ indicate the presence of C-N stretching in the -C₆H₄-N- unit. The absorption at 1 600 cm⁻¹ arises from C=C stretching of the aromatic nucleus, and the strong peak at 840 may be due to C-H deformation of the aromatic nucleus. A comparison of the spectrum of the model compound with that of the prepolymer showed three important differences. 1) The absence of absorption between 2 500-4 000 cm; 2) a slight shift of C=O absorption from 1 660 cm⁻¹ to 1 680 cm⁻¹; and 3) the absence of absorption at 840 cm⁻¹, which may be attributed

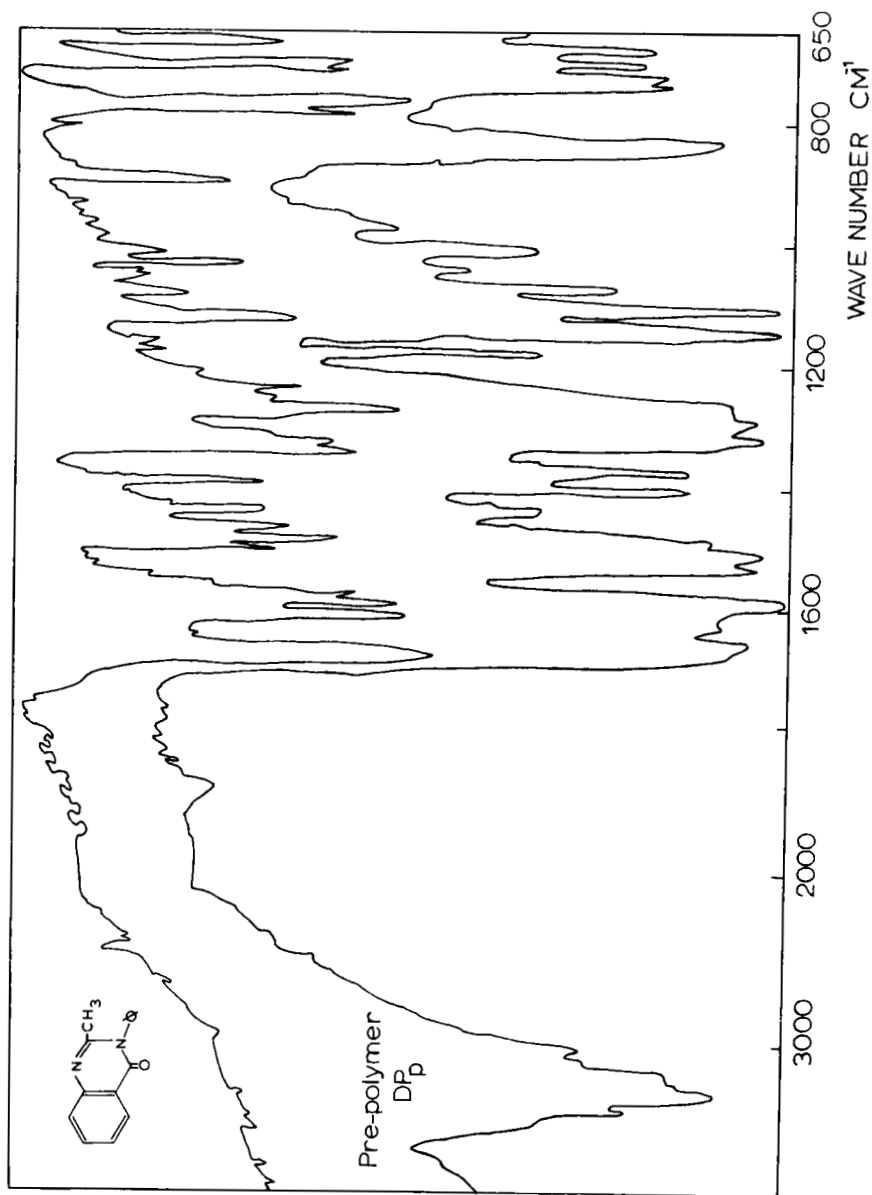


FIG. 2. Comparison of IR spectra of DP_p and model compound.

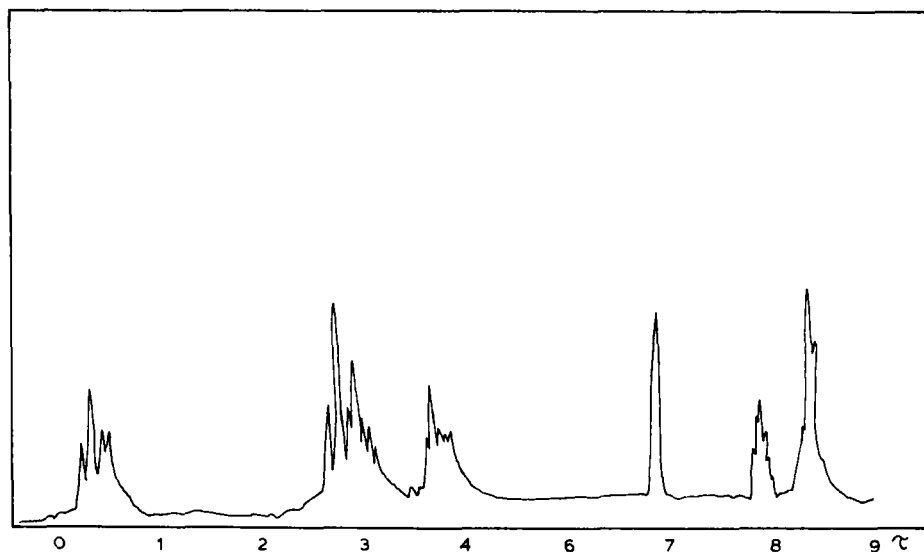


FIG. 3. NMR spectrum of DP_p .

to C-H deformation of the 1,2,4-trisubstituted aromatic nucleus. The other prepolymers, DE_p and DS_p , give similar IR absorption spectra.

Nuclear Magnetic Resonance Spectroscopy

A Perkin-Elmer NMR spectrometer (Model R-32) was used. The DP_p prepolymer was dissolved in deuterated dimethylsulfoxide to give a saturated solution. The NMR spectrum is shown in Fig. 3. The proton shifts can be assigned as follows:

<u>τ Values</u>	<u>Proton</u>
8.4	CH
7.8	NH
6.9	Solvent
2.5-3.8	Aromatic
0.5	C-OH O

Preparation of Polyquinazolone

Thermal conversion to polymer was carried out by spreading a DMF solution of the prepolymer together with the catalyst as a thin layer on a cleaned microscope slide which was then heated in an oven under nitrogen for different periods at several temperatures. The polyquinazolone so formed was scraped from the glass slide and ground into a fine powder for microanalysis and TG.

Isothermal Weight Loss Determination by TG

In order to assess the extent of cyclodehydration, the prepolymer was heated in the microfurnace of a Perkin Elmer (TGS-1) thermobalance under the same conditions as above. The weight of the sample was recorded continuously until about 20% weight loss. The results are summarized in Tables 2 and 3 and shown in Figs. 4-6. The steep loss at the beginning is attributed to the total volatilization of DMF. The weight loss curve for DP_p without catalyst is shown in Fig. 7 for comparison.

Characterization of Cyclized Polyquinazolones

Microanalysis

Microanalysis data were obtained for selected polyquinazolones cyclized under different conditions, and the results are summarized in Table 4.

Dynamic TG

The cyclized polyquinazolones were heated dynamically at $10^\circ\text{C}/\text{min}$ (unless otherwise stated) in static air, and their thermal stability was assessed based on the procedural decomposition temperature (pdt) (defined as the temperature at which the first observable weight loss occurs in dynamic TG) and T_{50} (the temperature at which 50% decomposition has occurred in dynamic TG). The results are shown in Figs. 8 and 9 as well as in Table 5.

Isothermal TG

The thermal indices used are W_{30} (the % weight loss after 30 min at 400°C in isothermal TG) and t_{50} (the time required for 50% weight loss to occur). The results are shown in Figs. 10 and 11 and Table 6.

Differential Scanning Calorimetry

Since the glass transition temperature and melting point of a polymer are functions of its chain rigidity, the cyclized polyquinazolones

TABLE 2. Isothermal Weight Loss Data of Prepolymers Cyclized with and without PTSA under Nitrogen

Cyclization conditions		Prepolymer					
		DP _p		DS _p		DE _p	
Temperature, °C	Time, h	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst
240	1	-	-	-	-	-	-
240	2	1.2	-	-	-	1.8	-
240	3	3.9	-	3.0	-	3.4	-
240	4	4.1	-	3.6	-	3.8	-
260	1	4.0	-	3.9	-	3.8	-
260	2	5.0	4.0	6.0	3.5	4.2	2.0
260	3	8.1	10.0	6.5	7.5	5.8	3.9
260	4	8.9	10.0	8.7	10.0	7.0	8.2
280	1	9.0	8.0	7.0	3.2	7.2	8.9
280	2	9.3	9.5	9.0	9.2	8.5	9.2
280	3	14.0	13.6	11.0	10.8	12.0	17.0
280	4	15.0	15.0	16.0	15.7	17.0	18.9
300	1	11.0	10.5	10.0	10.0	11.9	8.4
300	2	14.0	14.5	12.4	11.0	13.5	10.5
300	3	14.5	18.0	16.0	17.8	17.9	18.0
300	4	20.1	20.0	18.0	20.0	20.2	20.7

TABLE 3. Isothermal Weight Loss Data of Prepolymers Cyclized with and without PA under Nitrogen

Cyclization conditions		Prepolymer					
		DP _p		DS _p		DE _p	
Temperature, °C	Time, h	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst
240	1	-	-	-	-	-	-
240	2	-	-	-	-	2.0	-
240	3	3.0	-	2.8	-	3.0	-
240	4	3.8	-	3.5	-	4.0	-
260	1	3.8	-	4.1	-	3.9	-
260	2	4.7	4.0	6.2	3.5	5.0	2.0
260	3	8.3	10.0	6.8	7.5	6.0	3.9
260	4	8.8	10.0	9.0	10.0	7.4	8.2
280	1	8.6	8.0	6.5	3.2	7.1	8.9
280	2	9.3	9.5	8.7	9.2	8.0	9.2
280	3	14.3	13.6	11.0	10.8	12.2	17.0
280	4	15.0	15.0	15.8	15.7	16.5	18.9
300	1	10.0	10.5	10.0	10.0	11.5	8.4
300	2	13.0	14.5	13.0	11.0	14.0	10.5
300	3	14.1	18.0	17.0	17.8	17.5	18.0
300	4	19.8	20.0	18.5	20.0	21.0	20.7

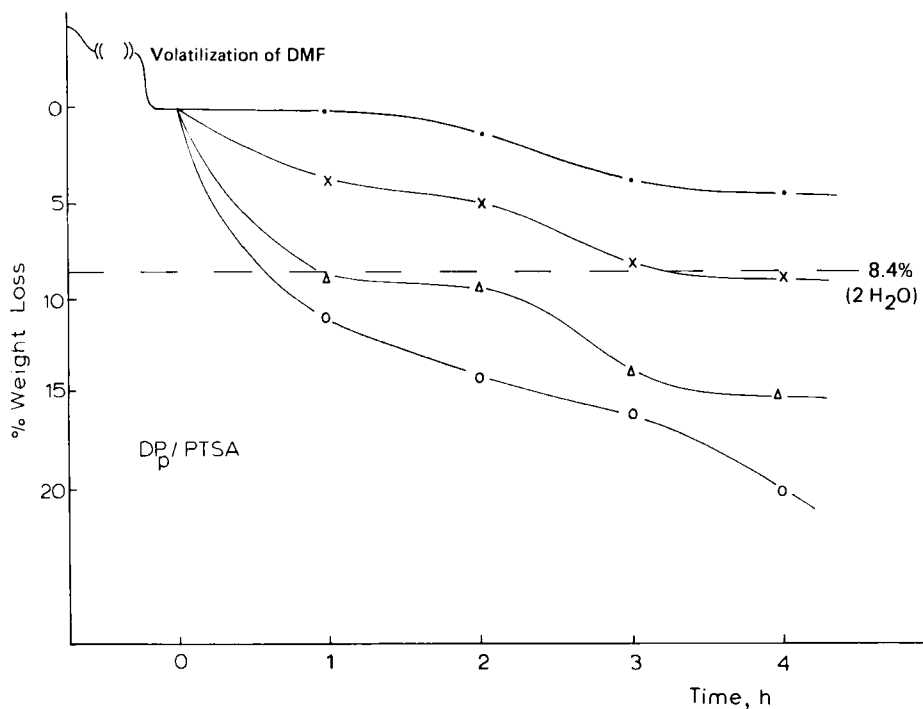


FIG. 4. Isothermal weight loss curves of DP_p cyclized with PTSA in nitrogen: (•) 240°C , (×) 260°C , (Δ) 280°C , (\circ) 300°C .

were further characterized by DSC to assess the effect of the acid catalysts.

A Perkin-Elmer DSC-4 differential scanning calorimeter was used at $10^\circ\text{C}/\text{min}$ from room temperature to 450°C . The sample (10 mg) was placed in a crimped aluminum pan and an empty crimped pan was used as reference. DSC thermograms for DP_c with and without PA are shown in Fig. 12.

DISCUSSION

The IR and NMR studies confirm the structure of the repeating unit proposed in Fig. 1 with pendent carboxylic groups for further cyclization.

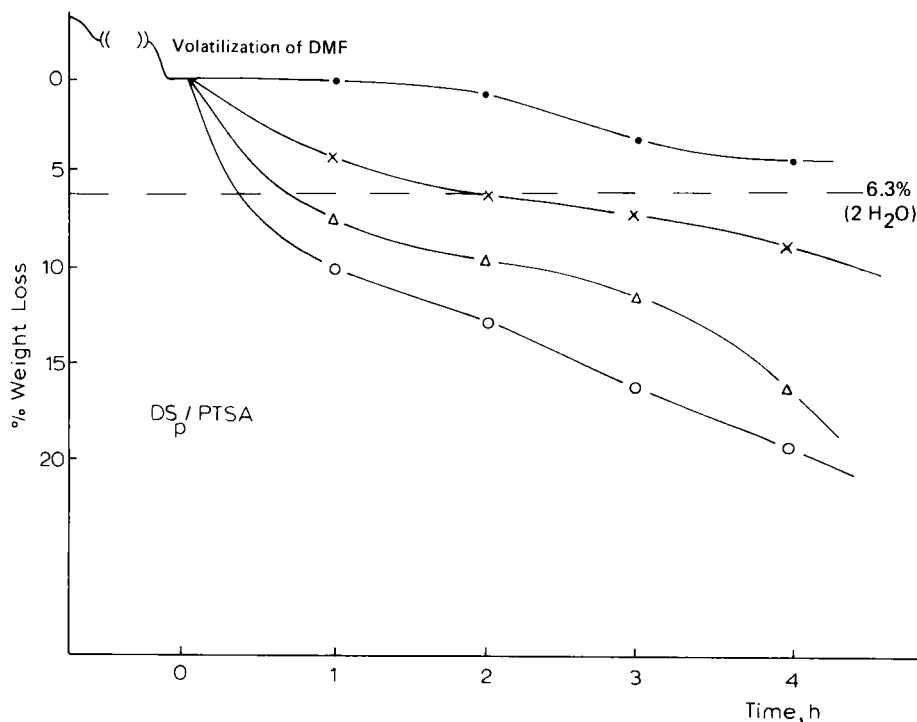


FIG. 5. Isothermal weight loss curves of DS_p cyclized with PTSA in nitrogen: (●) 240°C, (×) 260°C, (△) 280°C, (○) 300°C.

The results in Tables 2 and 3 show that the acid accelerates the weight change in two ways. First, weight loss starts at a lower temperature, and second, the time required to complete cyclization is shorter. In the case of DP_p prepolymer with 2 wt% catalyst, for example, weight loss corresponding to 2 mol water as a result of intramolecular cyclodehydration to give two quinazolone rings per repeating unit is achieved after 4 h at 260°C or 1 h at 280°C, compared to cyclization without catalyst in which, under similar conditions, the weight loss was more than 2 mol of water, indicating the concurrent loss of CO_2 . This decarboxylation also occurs in systems containing acid if the cyclization is carried out either at too high a temperature or for too long a period. It is, therefore, best to cyclize the prepolymer at the lower temperatures for the shortest possible time to ensure that cyclodehydration is the major process to give polyquinazo-

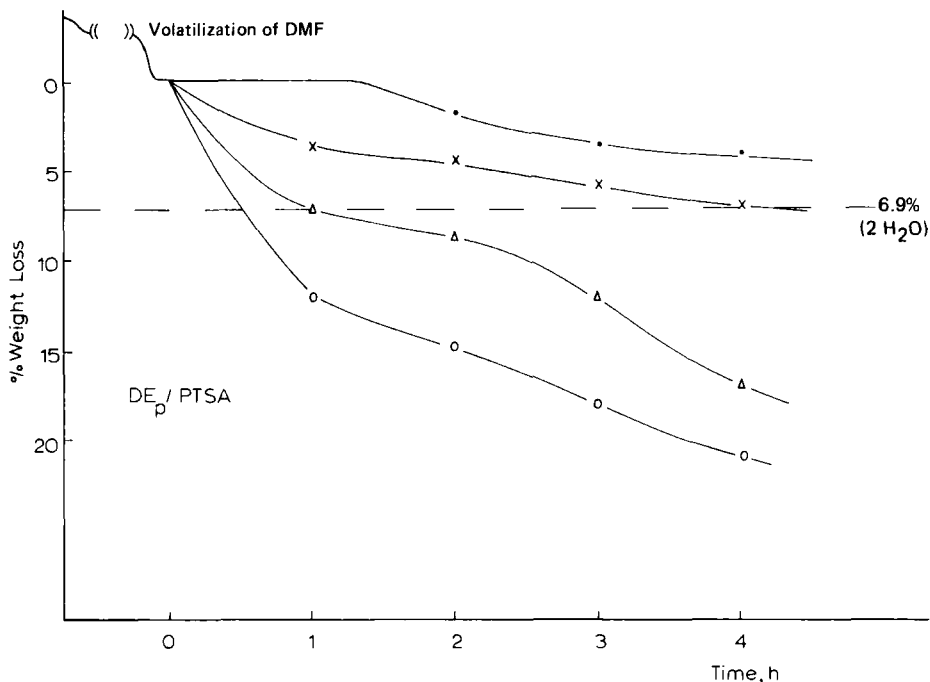


FIG. 6. Isothermal weight loss curves of DE_p cyclized with PTSA in nitrogen: (●) 240°C, (×) 260°C, (Δ) 280°C, (○) 300°C.

lone with close to fully cyclized rings in the backbone. This concurrent loss of CO_2 was confirmed in earlier work [1] by a simple lime water test and combined DTA/MS and during the thermal cyclization of poly(amic) acid to polyimide [5].

The optimum cyclization conditions in nitrogen for the three prepolymers are as follows:

DP_p : 260°C for 3-4 h or 280°C for 1 h

DE_p : 260°C for 4 h or 280°C for 1 h

DS_p : 260°C for 2 h or 280°C for 3/4 h

The microanalysis results show significant differences between polymers prepared with and without catalyst. The analyses for the

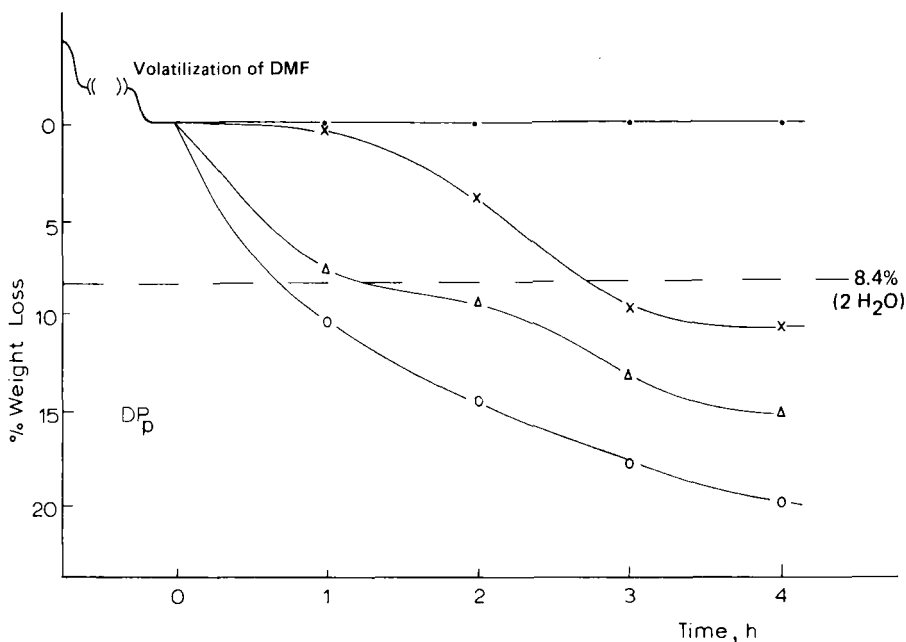


FIG. 7. Isothermal weight loss curves of DP_p cyclized without PTSA in nitrogen: (●) 240°C, (×) 260°C, (△) 280°C, (○) 300°C.

polymers cyclized in the presence of catalyst were closer to theoretical values based on the fully cyclized structure. The low oxygen and slightly high carbon values found for the three polymers prepared without catalyst and for those with catalyst but beyond the optimum conditions suggest 50% decarboxylation per repeating unit, as shown in Fig. 13.

The dynamic heat stability of the polymers cyclized with catalyst is superior to those cyclized by heat only in all three systems studied. The pdt values are raised by almost 50°C and T₅₀ values by about 75°C. The isothermal stability indices W₃₀ and t₅₀ of the catalyzed polyquinazolones are also substantially higher than those reported previously [3] (Table 6). These results substantiate the aforementioned suggestion that polyquinazolones prepared with acid have a higher proportion of heterocyclic rings which impart stability to the polymer. The stability determined by TG is of the order DP_c > DS_c > DE_c, the same as in Ref. 2, which attributed the stability of DP_c to

TABLE 4. Microanalysis Data of Polymers Cyclized with and without PTSA

Polymer	Cyclization conditions		Theoretical % C, H, N, S, O	Found % C, H, N, S, O
	°C	h		
DP _c	240, 4 ^a		73.5, 4.1, 14.3, -, 8.1	70.4, 4.3, 13.5, -, 11.8
	260, 3 ^a			73.2, 4.3, 14.2, -, 8.3
	260, 3 ^b			75.1, 4.8, 15.1, -, 5.0
	280, 3 ^a			75.4, 5.0, 14.9, -, 4.7
	300, 3 ^a			79.2, 6.0, 14.6, -, 0.2
DS _c	260, 3 ^a		67.7, 3.8, 10.5, 6.0, 12.1	67.4, 3.9, 10.3, 5.8, 12.6
	260, 3 ^b			66.2, 4.5, 10.7, 6.0, 12.6
	280, 3 ^a			67.0, 4.3, 11.0, 6.2, 11.5
DE _c	260, 4 ^a		74.4, 4.2, 11.6, -, 9.8	74.0, 4.4, 11.5, -, 10.1
	260, 4 ^b			76.1, 4.6, 12.0, -, 7.3
	280, 2 ^b			75.6, 4.9, 12.0, -, 7.5

^aWith catalyst.^bWithout catalyst.

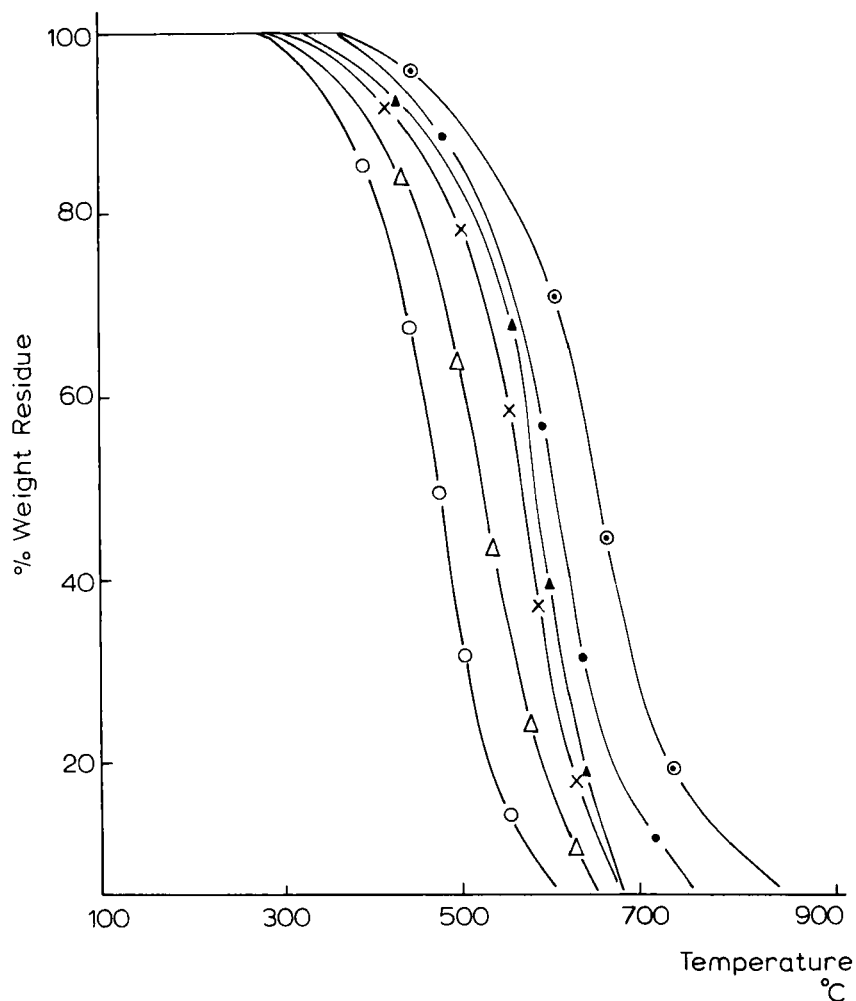


FIG. 8. Dynamic TG thermograms of polyquinazolones in air: (⊙) DP_c with catalyst, (x) DP_c without catalyst, (●) DS_c with catalyst, (Δ) DS_c without catalyst, (▲) DE_c with catalyst, (○) DE_c without catalyst.

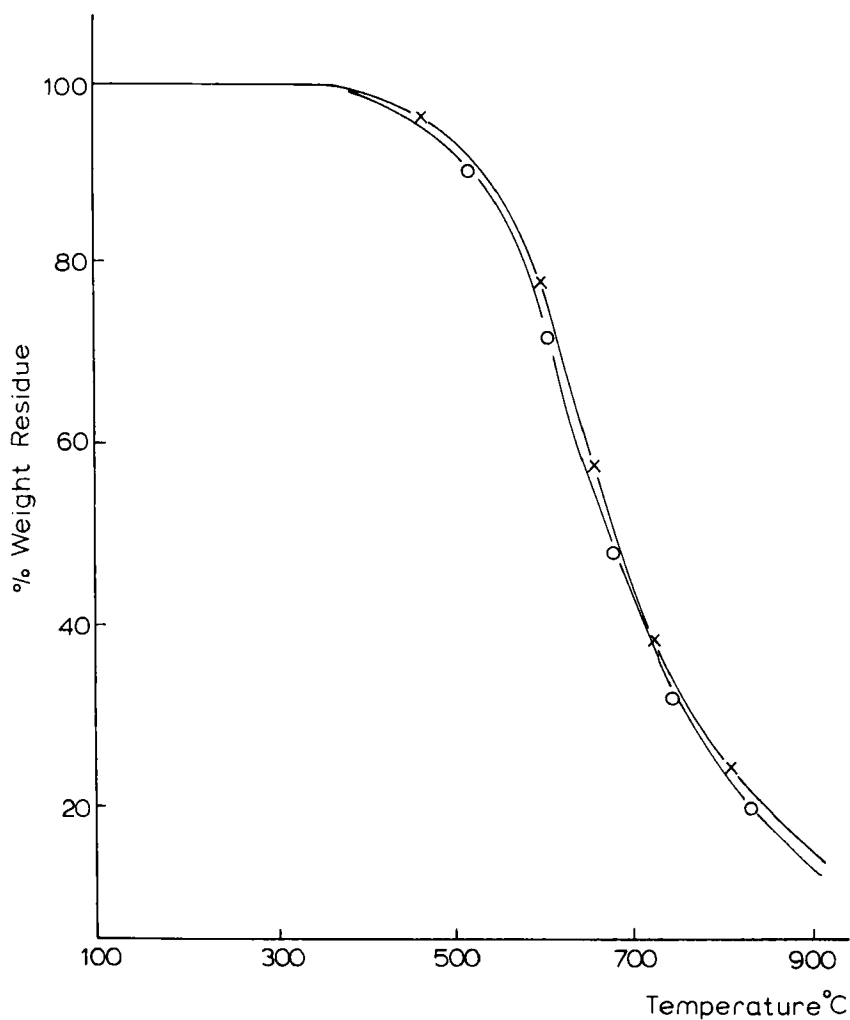


FIG. 9. Dynamic TG thermograms of DP_c with 2% and 10% PTSA in air: (o) with 2% PTSA, (x) with 10% PTSA.

TABLE 5. Dynamic Thermal Stability Indices pdt and T_{50} of Polymers Cyclized with and without PTSA

Polymer system	pdt, °C	T_{50} , °C
DP _c ^a	350	645
DP _c ^b	310	575
DS _c ^a	355	605
DS _c ^b	280	525
DE _c ^a	325	580
DE _c ^b	270	480

^aWith catalyst.^bWithout catalyst.TABLE 6. Isothermal Stability Indices W_{30} and t_{50} of Polymers Cyclized with and without PTSA

Polymer, with catalyst	W_{30}	t_{50} , h
DP _c	5.0 (13.5) ^a	4.5 (2.3) ^a
DS _c	10.0 (27.0)	3.1 (1.5)
DE _c	16.0 (20.0)	2.5 (1.8)

^aValues in parentheses determined in previous work [6].

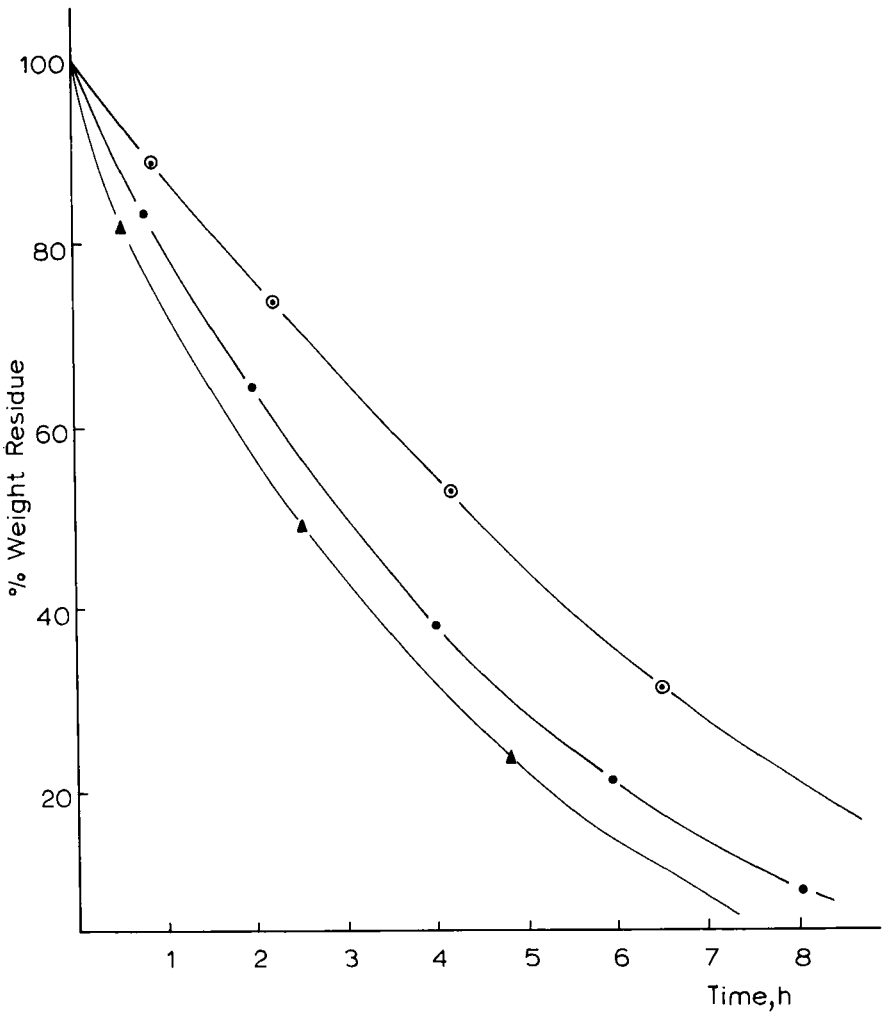


FIG. 10. Isothermal weight loss curves of polyquinazolones at 400°C in air: (○) DP_c, (●) DS_c, (▲) DE_c.

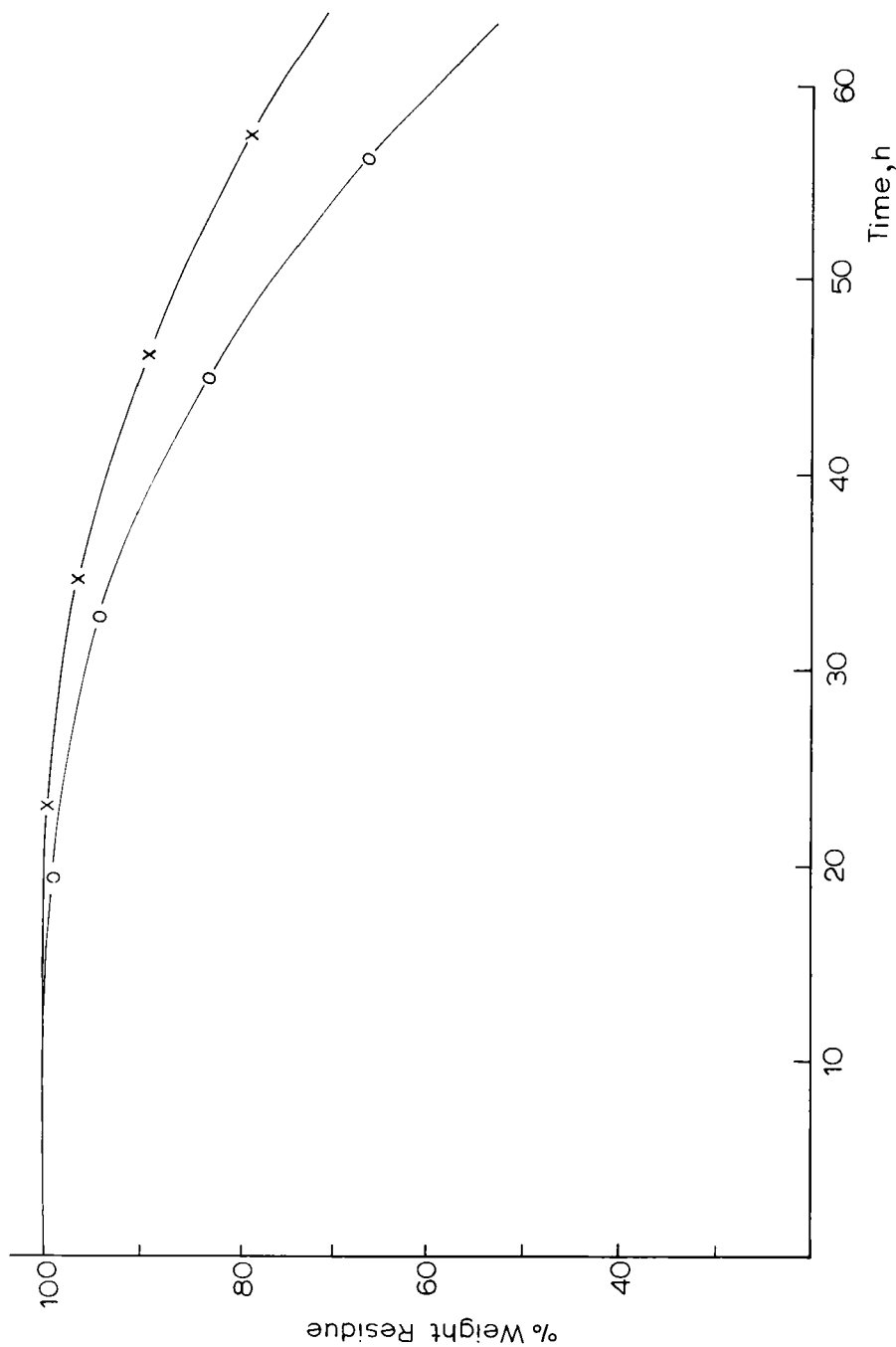


FIG. 11. Long-term stability of DP_c cyclized with and without PTSA at 300°C in air: (x) with catalyst PTSA, (o) without catalyst PTSA.

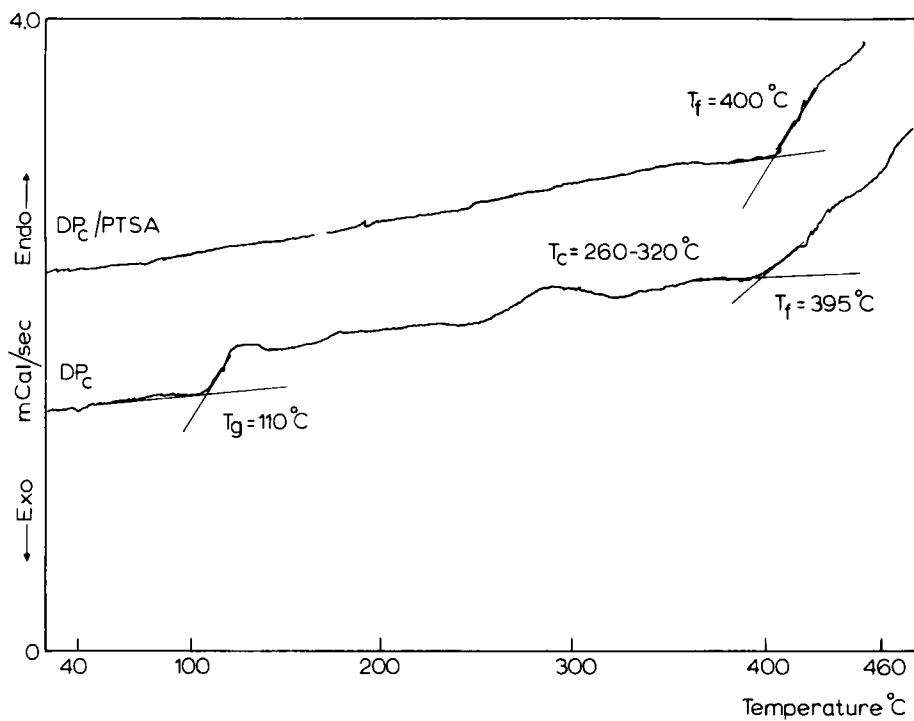


FIG. 12. DSC thermogram of DP_c in nitrogen.

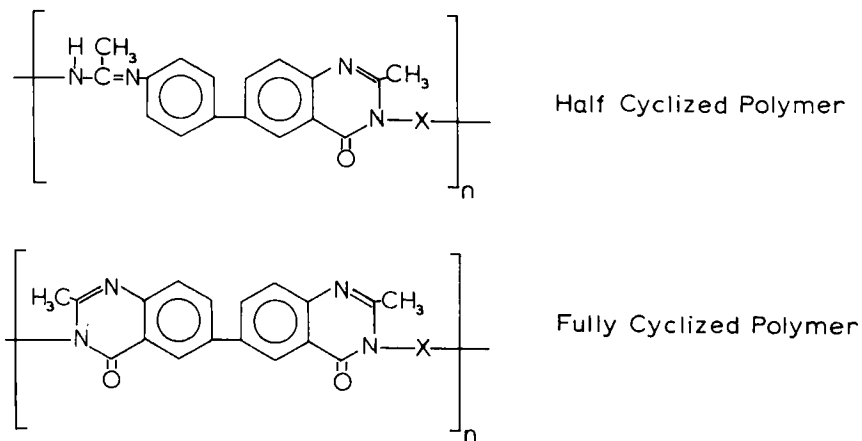


FIG. 13. Structure of half-cyclized polyquinazolone.

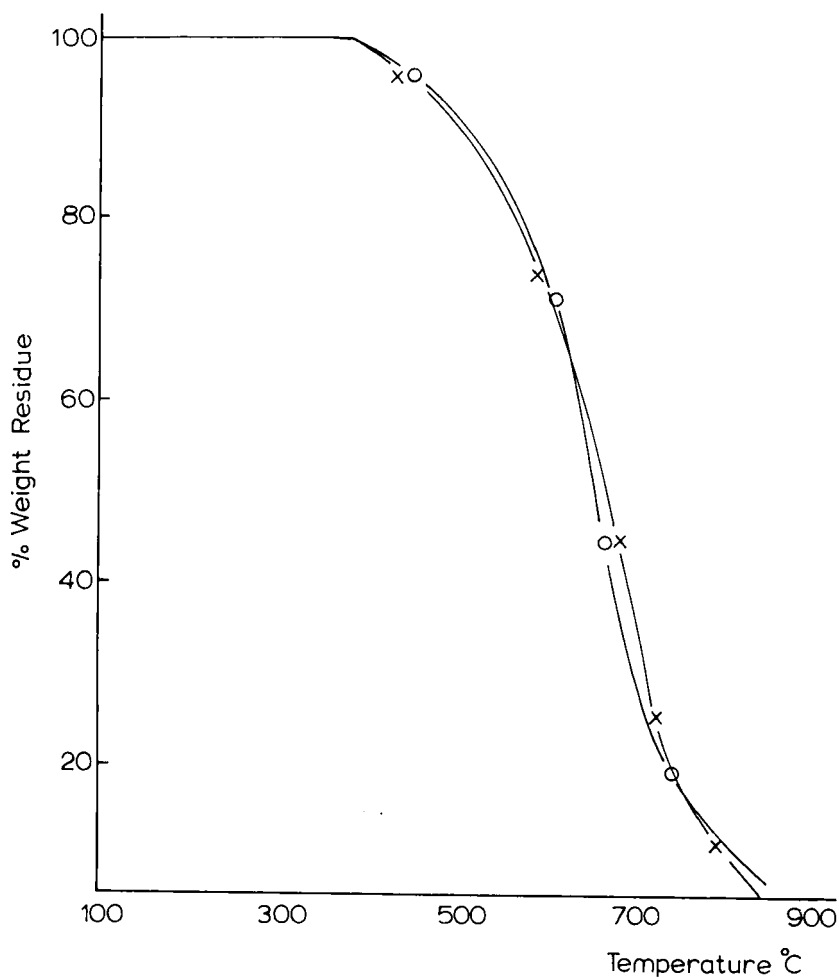


FIG. 14. Dynamic TG thermogram of DP_c cyclized with PTSA and PA in air: (○) PTSA, (×) PA.

symmetry and resonance stabilization. The acid-catalyzed polyquinazolone DP_c also has better long-term stability as shown in Fig. 11.

The DP_c /PTSA system shows no glass transition temperature (T_g), whereas DP_c has its T_g at around 110°C . This can be explained by the increased rigidity resulting from the increased number of fully cyclized units in the main chain, which makes rotation more difficult. Segmental jump is, therefore, restricted to much higher temperatures. The shallow endothermic peak starting at about 230°C in polymer DP_c can be attributed to cyclodehydration in situ, which is absent in DP_c /PTSA system. The flow temperature (T_f) for both polymers starts around 400°C , at which point black polymer melt was observed flowing out of the crucible.

The two catalysts PTSA and PA showed similar reactivity on an equal weight basis. The stabilities of the resultant polymers are compared in Fig. 14. The polymer DP_c cyclized by PA is slightly better, but the difference is too small to be significant, especially since, at equal weight, PA has a higher molar concentration than PTSA.

The higher level of catalyst, i.e., 10 wt%, seems to offer no advantage to overall heat stability as shown in Fig. 9. It is possible that 2 wt% is already beyond the optimum, and work is in progress to study the effect of lower levels of acid catalysts on the cyclodehydration step as well as the thermal stability of the polyquinazolones so formed.

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