

## **THERMAL STABILITY OF SOME POLYQUINAZOLONE POLYMERS: EFFECT OF ACID CATALYSIS\***

*Hardy S. O. Chan\*\* , Yee-Hing Lai, J. R. Lusty\*\*\* and E. Khor*

DEPARTMENT OF CHEMISTRY, NATIONAL UNIVERSITY OF SINGAPORE,  
KENT RIDGE, SINGAPORE 0511

Thermal properties of polyquinazolones (PQ) polymers prepared from 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid (BDC) and 4,6-diamino-isophthalic acid (DAIA) with diacetamido derivative of a number of diamines have been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). The effect of acid catalysis was also investigated. The results show that polyquinazolones prepared from DAIA have higher thermal stabilities and glass transition temperatures compared to those prepared from BDC. This can be attributed to the more stable and rigid fused quinazolone backbone unit in the PQ/DAIA system. Both polymer systems show improved thermal stability in the presence of catalyst which is a direct result of increased number of fully cyclised quinazolone rings in the polymer.

In previous papers [1-3] the preparation of pre-polymers to heat resistant polyquinazolones and studies to establish optimum conditions for their cyclisation step were discussed. Cyclisation involving cyclodehydration was shown to be accompanied by concurrent decarboxylation to give polyquinazolones of less than ideal structure. This is mainly due to the high temperatures which are required to initiate the cyclisation. Incomplete cyclisation would have given polyquinazolones of inferior thermal stability compared to those which are fully cyclised.

In a recent paper [4] we have described the use of *p*-toluene sulphonic acid and phosphorous acid to accelerate the cyclisation of the pre-polymer to enable the process to be carried out at lower temperatures. The results showed that PQ/BDC polymers prepared in the presence of an acid catalyst have superior thermal stabilities and higher glass transition temperatures.

This paper reports the preparation of two series of polyquinazolones, PQ/BDC and PQ/DAIA based on 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid and 4,6-

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\*\* Author to whom correspondence could be addressed.

\*\*\* School of Chemistry, Robert Gordon's Institute of Technology, St. Andrew Street, Aberdeen AB1 1HG, Scotland.

diaminoisophthalic acid with three co-monomers which were used in previous work. The corresponding polymers were compared in terms of thermal stability and glass transition temperature. The use of an acid catalyst was also investigated.

## Experimental

### Chemicals and reagents

*p*-Phenylenediamine, 4,4'-diaminodiphenyl sulphone and 4,4'-diamino-diphenyl ether were obtained from Aldrich Chemical Co. The purification was carried out as reported previously [1].

### Monomers

The diamines were converted to the diacetamido derivative as reported [1]. 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid was prepared following the procedure used by Kurihara and Yoda [5]. 4,6-diaminoisophthalic acid was synthesised according to the work of Bogert and Kropff [6].

### Acid catalyst

*p*-Toluene sulphonic acid was used to accelerate cyclodehydration of the quinazolone pre-polymers. The level of catalyst employed was 2% (w/w).

### Pre-polymers

Quinazolone pre-polymers were prepared as previously reported [1]. This involves the melt condensation of equimolar amounts of DAIA or BDC with any one of the three diacetamido derivatives under nitrogen at a pressure of 0.1 Torr. Six pre-polymers were synthesised in the present work and their general structure is shown in Figure 1.

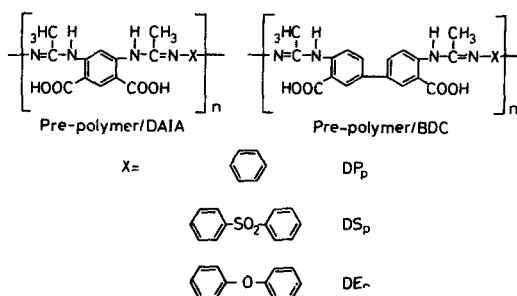


Fig. 1 Structure of quinazolone pre-polymer

*Polyquinazolones*

Thermal conversion of the pre-polymer to fully cured polymer was carried out by spreading a solution of the pre-polymer with or without the catalyst in dimethyl formamide (DMF) as a thin layer on a clean microscope slide. This was then heated in an oven under nitrogen according to the following optimum conditions [2, 4]:

with catalyst	without catalyst
DP <sub>p</sub> 250° for 3 hours	DP <sub>p</sub> 290° for 2 hours
DS <sub>p</sub> 260° for 3 hours	DS <sub>p</sub> 280° for 2 hours
DE <sub>p</sub> 260° for 4 hours	DE <sub>p</sub> 290° for 2 hours

Subscript *p* denotes pre-polymer

The cured dark brown glassy polymer was scrapped from the slide for thermal analysis and other characterisations.

*Thermal analysis*

TG studies were made in air on a Shimadzu TGA-30 thermobalance at a heating rate of 5 deg min<sup>-1</sup> unless otherwise stated. The DSC runs were carried out on a Shimadzu DSC-30 differential scanning calorimeter at a heating rate of 5 deg min<sup>-1</sup>. The thermolytic reactions were run with samples varying in weight from 4.36 to 11.98 mg. The thermal curves are shown in Figures 2 to 4.

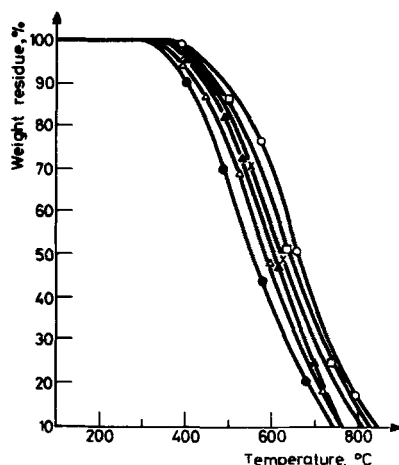


Fig. 2 Dynamic TG curves of acid catalysed polyquinazolones in air.

—○—○— DP<sub>c</sub>/DAIA; —×—×— DP<sub>c</sub>/BDC; —□—□— DS<sub>r</sub>/DAIA; —▲—▲—  
DS<sub>r</sub>/BDC; —△—△— DE<sub>c</sub>/DAIA; —●—●— DE<sub>c</sub>/BDC

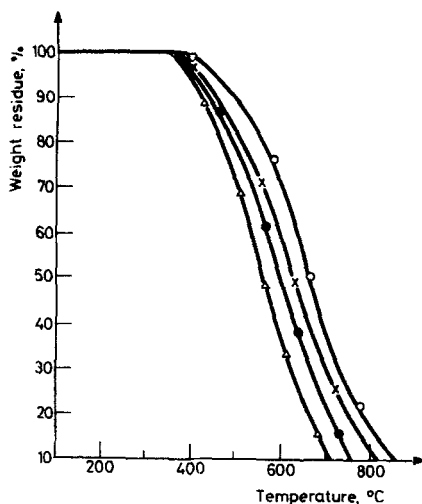


Fig. 3 Dynamic TG curves of polyquinazolones in air.

—○—○— DP<sub>c</sub>/DAIA/wc; —●—●— DP<sub>c</sub>/DAIA/woc; —×—×— DP<sub>c</sub>/BDC/wc;  
 —△—△— DP<sub>c</sub>/BDC/woc

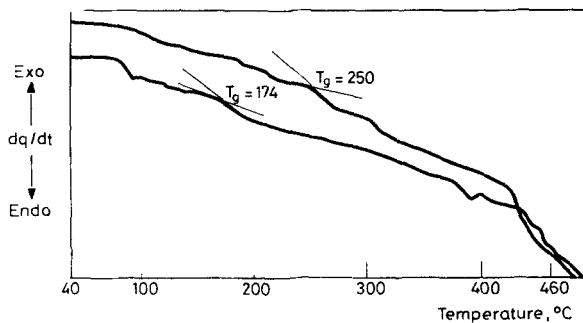


Fig. 4 DSC curves of acid catalysed DE<sub>c</sub>/DAIA and DE<sub>c</sub>/BDC

### Infrared spectroscopy

Infrared spectra of the pre-polymers were recorded in KBr medium in the region 4000–600  $\text{cm}^{-1}$  using a Perkin-Elmer 1310 spectrophotometer. The spectrum of DS<sub>p</sub>/DAIA is shown in Figure 5. Attempts to obtain the IR spectrum of the fully cured polyquinazolone were unsuccessful due to the poor dispersion of the polymer making the KBr disc almost opaque to the light source.

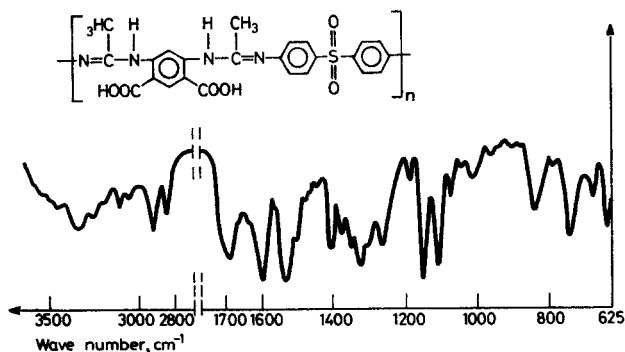


Fig. 5 IR spectrum of DS<sub>p</sub>/DAIA

*Micro-analysis*

Microanalysis of C, H, N and S was performed in the Micro-Analytical Laboratory of Chemistry Department, National University of Singapore with a Perkin-Elmer 240C Elemental Analyser. The results for the pre-polymers are given in Table 1.

**Table 1** Micro-analysis of pre-polymers

Pre-polymer	C, %	H, %	N, %	O, % (by difference)	S, %
DP <sub>p</sub> /DAIA	61.0 (61.7)	3.8 (4.0)	15.9 (16.0)	19.3 (18.3)	
DP <sub>p</sub> /BDC	68.1 (67.3)	5.2 (4.7)	12.7 (13.1)	13.8 (14.9)	
DS <sub>p</sub> /DAIA	57.6 (58.8)	3.4 (3.7)	10.9 (11.4)	21.7 (19.6)	6.4 (6.5)
DS <sub>p</sub> /BDC	64.0 (63.4)	4.9 (4.3)	10.2 (9.9)	15.0 (16.9)	5.9 (5.6)
DE <sub>p</sub> /DAIA	63.9 (65.2)	3.9 (4.1)	12.0 (12.7)	20.2 (18.1)	
DE <sub>p</sub> /BDC	69.9 (69.2)	5.0 (4.7)	11.0 (10.8)	14.1 (15.3)	

In parenthesis, calculated values.

## Results and discussion

The pre-polymer  $DS_p/DAIA$  showed the following i.r. absorptions which are common to the other pre-polymers:  $3300$ ,  $1620$  and  $1540\text{ cm}^{-1}$  for the  $-\text{NH}-\text{C}=\text{N}-$  grouping,  $1680\text{ cm}^{-1}$  for the carbonyl group of the aromatic acid and  $3100\text{ cm}^{-1}$  for the OH of the acid. The sharp peaks at  $1380$ ,  $1420$  and  $2920\text{ cm}^{-1}$  are characteristics of C—H stretching in the methyl group. These results suggest that the structure of the pre-polymer is consistent with that shown in Figure 1. The structure is further confirmed by the close agreement between the determined and calculated C, H, N, S % values shown in Table 1.

The  $T_g$  of  $DE_c/DAIA$  and  $DE_c/BDC$  (the subscript  $c$  denotes cured polymer) were determined from the DSC curve obtained (Figure 4). It can be seen that  $DE_c/DAIA$  has a higher  $T_g$  because of the more rigid backbone structure of this polymer. In comparison, the carbon-carbon single bond rotation in  $DE_c/BDC$  (as shown in Figure 6) is likely to make the molecule more mobile. No  $T_g$  was observed

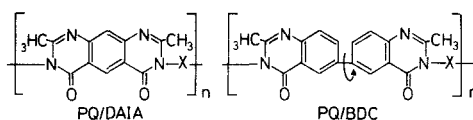


Fig. 6 Structure of cyclised polyquinazolones

for the other two polyquinazolone polymers. The thermal stabilities of the polymers are compared in terms of procedural decomposition temperature (PDT) and temperature at which 50% weight loss had occurred ( $T_{50\%}$ ). The results are summarised in Table 2 and the TG curves are shown in Figure 2. The PQ/DAIA group of polymers has higher PDT and  $T_{50\%}$  than the corresponding PQ/BDC group both with and without an acid catalyst. This we believe is due to the more stable fused quinazolone unit in the PQ/DAIA polymer towards thermooxidation. The effect of acid accelerated cyclodehydration is best illustrated in Figure 3 where it can be seen that for both PQ/DAIA and PQ/BDC the stability index  $T_{50\%}$  has been increased by about  $50^\circ$ .

## Conclusion

The PQ/DAIA series is thermally more stable than the corresponding PQ/BDC series. This can be explained by considering the quinazolone structure in the repeating unit of the two polymers.

**Table 2** Thermal stability indices of polyquinazolones

Polymer system	PDT, °C	$T_{50\%}$ , °C
DP <sub>c</sub> /DAIA/wc <sup>a</sup>	360	660
DP <sub>c</sub> /BDC/wc	350	620
DP <sub>c</sub> /DAIA/woc <sup>b</sup>	330	600
DP <sub>c</sub> /BDC/woc	320	560
DS <sub>c</sub> /DAIA/wc	345	630
DS <sub>c</sub> /BDC/wc	320	605
DS <sub>c</sub> /DAIA/woc	310	585
DS <sub>c</sub> /BDC/woc	290	525
DE <sub>c</sub> /DAIA/wc	340	590
DE <sub>c</sub> /BDC/wc	300	555
DE <sub>c</sub> /DAIA/woc	315	540
DE <sub>c</sub> /BDC/woc	290	490

<sup>a</sup> with catalyst<sup>b</sup> without catalyst

The fused quinazolone units in the former system are more stable than the quinazolone units which are separated by a vulnerable carbon-carbon bond in the latter (Figure 6). Moreover, the fused quinazolone rings are more restricted to internal segmental rotation which accounts for the higher  $T_g$  determined. The effect of an acid catalyst in the PQ/DAIA series is similar to that found previously in the PQ/BDC series, i.e., thermal stability is generally enhanced in both cases.

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**Zusammenfassung** — Thermische Eigenschaften von aus 4,4-Diaminodiphenyl-3,3'-dicarbonsäure (BDC) und 4,6-Diaminoisophtalsäure (DAIA) mit Diacetoimido-Derivaten einer Auswahl von Diaminen hergestellten Polymeren von Polyquinazolone (PQ) wurden mittels TG und DSC untersucht. Die mit DAIA erhaltenen Polyquinazolone sind thermisch stabiler und weisen höhere Glasübergangstemperaturen auf als die mit BDC hergestellten. Das kann der stabileren und fester ancondensierten Quinazolonehauptketteneinheit im PQ/DAIA-System zugeschrieben werden. Beide Polymersysteme weisen in Gegenwart eines Katalysators eine verbesserte thermische Stabilität auf, was auf eine größere Anzahl von voll zyklisierten Quinazoloneinheiten im Polymer zurückzuführen ist.

**Резюме** — Методом ТГ и ДСК изучены термические свойства полихиназолоновых полимеров (ПХ), полученных реакцией взаимодействия 4,4-диаминодифенил-3,3-дикарбоновой кислоты (ДДК) и 4,6-диаминоизофталевой кислоты (ДАИК) с диацетамидопроизводными ряда диаминов. Изучено также влияние кислотного катализа. Результаты показали, что полихиназолонны, полученные на основе ДАИК, обладали более высокой термоустойчивостью и более высокой температурой стеклообразования по сравнению с таковыми, полученными на основе ДДК. Это может быть обусловлено большей устойчивостью к плавлению хиназолонового каркасного звена в системе ПХ/ДАИК. Обе полимерные системы показывают улучшенную термоустойчивость в присутствии катализатора, что является следствием увеличения числа полностью циклизированных хиназолоновых колец в полимере.