X-Ray Photoelectron Spectroscopic Studies of Polyquinazolones: An Assessment of the Degree of Cyclization

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(Received April 11, 1990)

ABSTRACT: Prepolymers of polyquinazolone have been prepared from 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid and aromatic diacetoamido compounds by melt condensation. Optimum preparative conditions were established for each individual system on the basis of reduced viscosity and thermogravimetry (TG) results. The soluble prepolymers were converted to the quinazolone structure by thermal cyclization under two heating programmes. A significant amount of uncyclized carboxylic groups have been identified by X-ray photoelectron spectroscopy (XPS). Quantitative measurements of the C=O/COOH ratio at the surface of the resultant polymers have been carried out by XPS, which provide a reliable measure of the degree of cyclization. Comparison of XPS results with TG data indicates a direct correlation between degree of cyclization on the polymer surface and thermooxidative stability of the bulk polymer.

KEY WORDS Heat Resistant Polymer / Polyquinazolone / X-Ray Photoelectron Spectroscopy / Thermogravimetry / Degree of Thermal Cyclization / Thermooxidative Stability /

One of the major limitations of synthetic polymers is their poor thermooxidative stability compared with other materials, especially metals, alloys and ceramics. To overcome this problem as well as to meet the rapid development of atomic reactors and space aviation, a new generation of heat resistant polymers has been prepared during the past decades.

The attempt to synthesize polymers capable of withstanding prolonged exposure to elevated temperature, has been three pronged.

1. To improve the existing polymers by structural modification.
2. To devise new organic systems tailored to resist the effect of heat and oxidation.
3. To synthesize new classes of inorganic and semi-inorganic polymers of high

thermal stability.

In the second mode of attack, the most fruitful of these three lines of research, a whole new generation of carbon-based polymers with inherently rigid chains have been developed. The polymers were prepared by incorporating highly stable rigid, carboxylic and/or heterocyclic ring systems directly into the polymer chain. An infinite variety of such structures is possible, and many have been synthesized. One of the most serious draw backs of heat resistant polymers is their insolubility and intractability conferred by the very structural features desirable for high thermal stability. In the case of the most promising heat resistant polymers such as polyimides,¹⁻³ the most commercially successful of all the heat resistant polymers, polybenzimidazole,⁴ polyquinazolones,⁵ poly-

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imidazolepyrrolones,⁶ and polyquinazoline-diones,⁷ the synthesis involved a novel two steps process in which soluble and fabricable high molecular weight prepolymers were first prepared. Rigid stable rings were then formed by thermally or chemically induced cyclodehydration or cyclisation of reactive group attached to the prepolymer chain to give an insoluble, infusible and intractable polymer. This approach enabled films, fibres and coatings to be produced.

In our previous work on polyquinazolones,⁸ concurrent decarboxylation during the cyclization step was detected by differential thermal analysis (DTA) coupled with mass spectrometry (MS), which meant that the actual structure deviated from theory. This problem was also encountered in polyimides,^{9,10} where a controversy exists as to whether the imidization reaction goes to completion. We consider this a potentially very serious concern in the field of thermally stable polymer which has received too little attention. We have used in the past TG¹¹ and elemental analysis¹² in an attempt to quantify the degree of cyclization with limited success due mainly to the small relative weight change incurred in the conversion of prepolymer to the fully cyclised polyquinazolone. The disappearance of the NH band between 3000–3400 cm⁻¹ in IR spectroscopy has also been used to monitor the degree of cyclization in polyquinazolones by the use of an internal reference peak.⁸ This, however, provides only a semi-quantitative assessment depending on an arbitrary internal reference which may give unreliable results. The usefulness of XPS for polymer characterization is well known^{13–16} and we would like to report in this communication recent XPS studies to determine more accurately the degree of cyclization in polyquinazolones and to correlate the results with thermooxidative stability assessed by TG.

EXPERIMENTAL

Preparation of Monomers

4,4'-Diaminodiphenyl-3,3'-dicarboxylic acid (BDC) (I) 4-diacetamidophenylene (*p*-DAP) (II) and 4,4'-diacetamidodiphenyl methane (DADM) (III) shown in Figure 1 were prepared according to methods previously reported.^{17,18} For BDC; yield = 64%, mp 302°C (with decomposition), lit. mp¹⁷ 300°C. For *p*-DAP; yield = 69%, mp 305°C, lit. mp¹⁹ 303°C. For DADM; yield = 71%, mp 227°C, lit. mp¹⁹ 227–228°C.

Preparation of Prepolymer

Quinazolone prepolymers were prepared as

Figure 1. Structures of monomers.

Figure 2. General structure of the prepolymer.

previously reported.¹⁸ Equimolar amounts of BDC (0.005 mol) and each comonomer (0.005 mol) were mixed thoroughly together and the polymerization was effected by melt condensation under a nitrogen atmosphere at 255°C. In the present work the polymerization was carried out for 1, 2, and 3 h, respectively to study the effect of polymerization time. The structure of the prepolymer is given in Figure 2. DP_p(2) (subscript p to indicate prepolymer; figure in bracket indicates polymerization time in hour) was obtained in 91% yield as a dark green glassy material for both cyclization conditions. Calculated % composition for DP_p prepolymer (C₂₄H₂₀N₄O₄): C, 67.3%; H, 4.7%; N, 13.1%; O, 14.9% (by difference). Found for DP_p(2): C, 68.3%; H, 5.0%; N, 12.9%; O, 13.8% (by difference). Prepolymer DADM_p was obtained as a grey glassy material in 70.8% yield. Calculated for (C₃₁H₂₆N₄O₅): C, 71.8%; H, 5.1%; N, 10.8%; O, 12.3%. Found for DADM_p(2): C, 71.0%; H, 5.5%; N, 10.6%; O, 12.9%.

Viscosity Measurement

In order to determine the optimum polymerization time the reduced viscosities of the prepolymers obtained for different periods were measured in distilled *N*-methyl-2-pyrrolidone (NMP) (1% solution by weight) at 25 ± 0.03°C using an Ostwald viscometer (bore

diameter 0.4 mm). The flow times reported are averages of 6 repeated determinations to an accuracy of ± 0.02 s. The results are summarized in Table I.

Preparation of Polyquinazolone (Cyclization)

The optimum prepolymers determined by viscosity measurements, DP_p(2) and DADM_p(2) were dissolved in NMP (20–30% by weight) and the viscous polymer solution was deposited onto a thin glass slide as a thin viscous film. The prepolymer was then cyclized under vacuum in a tube furnace under two different regimes: Condition (A); 30 min at 250°C followed by 20 min at 280°C followed by 40 min at 305°C, and condition (B); 90 min at 305°C. The structures of the ideal and partially cyclized polyquinazolone are given in Figure 3. Calculated for DP_c(A) (C₂₄H₁₆N₄O₂): C, 73.5%; H, 4.1%; N, 14.3%; O, 8.1% (by difference). Found: C, 73.8%; H, 4.8%; N, 14.1%; O, 7.3%. Found for DP_c(B): C, 75.0%; H, 4.3%; N, 14.5%; O, 6.2%. Calculated for DADM_c(A) (C₃₁H₂₂N₄O₂): C, 77.1%; H, 4.6%; N, 11.6%; O, 6.6% (by difference). Found: C, 77.1%; H, 5.2%; N, 12.1%; O, 5.7%. Found for DM_c(B): C, 78.3%; H, 5.0%; N, 11.8%; O, 4.9%.

Elemental Analysis

The elemental analyses were conducted by

Table I. Viscosity measurements for prepolymers DAP_p and DADM_p

System ^a	Flow time, <i>t</i> _p /s	<i>η</i> _{sp} ^b
DAP _p (1)	58.88	0.0723
DAP _p (2)	60.79	0.1071
DAP _p (3)	58.81	0.0710
DADM _p (1)	56.21	0.0237
DADM _p (2)	59.93	0.0914
DADM _p (3)	57.14	0.0416

^a Numbers in brackets indicate polymerization time in hour.

^b $\eta_{sp} = (t_p - t_s)/t_s$. Average flow time for solvent (*t*_s) = 54.91 s.

Incomplete cyclisation

Polyquinazolone

Figure 3. Polyquinazolone: complete vs. incomplete cyclization.

the Microanalytical Laboratory using a Perkin-Elmer model 240C C, H, N analyzer.

X-Ray Photoelectron Spectroscopy

In the case of the prepolymers, the powders were mounted onto a standard VG holder by double-sided Scotch tape. For the polyquinazolones, cyclization was carried out *in-situ* on the sample holder under the optimum conditions and transferred immediately into the vacuum chamber ($\approx 10^{-7}$ Torr) in the XPS machine to minimise contamination. Core levels spectra were obtained on a VG ECSA/SIMSLAB MK II spectrometer using Mg- K_{α} radiation, operating on a fixed retardation ratio of 40. The binding energies were referred to the hydrocarbon component in the C_{1s} envelope, defined at 285.0 eV to compensate for surface charging. Surface stoichiometries were obtained from peak area ratios corrected with appropriate experimentally-determined sensitivity factors. Deconvolution of overlapping spectral components were performed on VG softwares.

Thermogravimetry

TG studies were performed on a du Pont 9900 thermal analyzer under a dynamic air flow

of $75 \text{ cm}^3 \text{ min}^{-1}$ at a linear heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 700°C . The samples were run in powder form of weight $\approx 5 \text{ mg}$.

RESULTS AND DISCUSSION

Viscosity

From the results shown in Table I, it can be seen that the optimum polymerization time is 2 h for both DAP_p and DADM_p based on their specific viscosities which can be used as an indication of molecular weight of the prepolymers. Further determination of viscosity average molecular weight for the prepolymers from intrinsic viscosity measurements was not possible due to the unavailability of the constants K and α in the Mark-Houwink equation.

Thermogravimetry

The TG thermograms are shown in Figures 4–6 and the results are summarized in Table II. It can be seen in Figure 4 that both the $\text{DAP}_p(1)$ and $\text{DAP}_p(3)$ exhibit lower thermal stability than the corresponding $\text{DAP}_p(2)$. The stability of a polymer, amongst other considerations, is related to its molecular weight.

Figure 4. TG thermogram of $\text{DAP}_p(1)$, $-\bigcirc-\bigcirc-$; $\text{DAP}_p(2)$, $-\triangle-\triangle-$; $\text{DAP}_p(3)$, $-x-x-$.

Figure 5. TG thermogram of DAP_p cyclized under programme A, $-x-x-x-$. TG thermogram of DAP_p cyclized under programme B, $-o-o-o-$.

Figure 6. TG thermogram of DAP_c , $-x-x-x-$; DADM_c , $-o-o-o-$.

This is particularly relevant when we compare prepolymers of similar structures. The TG results are in good agreement with the viscosity data. It can be concluded that for the present series of polyquinazolones, the optimum polymerization time is around two hours.

The thermograms (Figure 5) and the thermal index ($T_{50\%}$) in Table II of the polyquinazolone DAP_c cyclized under different heating pro-

grammes show clearly that programme (A) produced more thermooxidatively stable polymers. It can be seen from Figure 6 that DAP_c has a higher overall stability than DADM_c . The $-\text{CH}_2-$ group may act as a weak link during the degradation of the polymer.

XPS

The O_{1s} , N_{1s} , and C_{1s} core spectra for the

prepolymers and cyclized polymers are compared in Figures 7–9 and the surface stoichiometries have been compared with the bulk composition in Table III. The surface

Table II. Thermal stability indices of pre- and cyclized DAP and DADM

System ^a	pdt (°C) ^b	$T_{50\%}$ ^c
DAP _p (1)	≈ 200	395
DAP _p (2)	≈ 200	495
DAP _p (3)	≈ 200	369
DADM _p (1)	≈ 200	372
DADM _p (2)	≈ 200	430
DADM _p (3)	≈ 200	360
DAP _c (A)	≈ 200	526
DAP _c (B)	≈ 350	558
DADM _c (A)	≈ 200	500
DADM _c (B)	≈ 275	534

^a Numbers in brackets indicate polymerization time in hour. Letters in brackets indicate different cyclization programmes (A) and (B).

^b pdt = the temperature at which the first observable weight loss occurs in dynamic TG.

^c $T_{50\%}$ = temperature at which 50% weight loss has occurred in dynamic TG.

stoichiometries of the elements are calculated based on the peak area of the corresponding XPS peaks corrected with the appropriate sensitivity factor referenced to carbon which has a value of 1.0. The high carbon content found on the surface can be attributed to hydrocarbon contamination and the low oxygen may be due to concurrent decarboxylation during cyclization. The chemical shifts and % area ratios of the various core levels and

Table III. Comparison of surface and bulk stoichiometries

Sample	Bulk				Surface		
	C	H	N ^a	O	C	N	O
DAP _p (2)	24.8	21.8	4.0	3.8	25.0	4.0	4.1
DADM _p (2)	31.0	28.9	4.0	4.3	32.3	4.0	4.1
DAP _c (A)	24.4	19.0	4.0	1.81	25.1	4.0	1.86
DAP _c (B)	24.0	16.5	4.0	1.49	24.8	4.0	1.51
DADP _p (A)	29.8	23.3	4.0	1.78	29.2	4.0	1.80
DADM _p (B)	31.1	24.8	4.0	1.45	31.6	4.0	1.49

^a The atomic ratios are normalized to N_{4.0}.

Table IV. XPS data for pre- and cyclized polymers of DAP and DADM

XPS core level	DAP _p			DADM _p		
	BE (eV)	BE	Relative %	BE (eV)	BE	Relative %
C _{1s}	285.0		77.3	285.0		83.6
	286.4	1.4	12.6	286.4	1.4	9.2
	289.1	4.1	9.2	289.1	4.1	6.9
N _{1s}	399.7		49.6	399.7		45.7
	400.8	1.1	50.2	400.8	1.1	43.9
O _{1s}	532.1		46.4	532.1		48.6
	533.3	1.2	45.5	533.3	1.2	47.2
	535.1	2.7	7.7	535.1	2.7	4.2
	DAP _c			DADM _c		
	BE (eV)	BE	Relative %	BE (eV)	BE	Relative %
C _{1s}	285.0		80.0	285.0		84.9
	286.4	1.4	9.2	286.4	1.4	7.3
	287.9	2.9	7.2	287.9	2.9	5.2
	289.1	4.1	1.4	289.1	4.1	1.4
N _{1s}	399.6		50.2	399.7		50.6
	400.7	1.1	49.7	400.8	1.1	49.4
O _{1s}	532.3		82.8	532.2		78.2
	533.7	1.4	16.6	533.7	1.4	21.8

(a)

(b)

Figure 7. Curve fitted O_{1s} spectrum of (a) DAP_p and (b) DAP_c.

their deconvoluted components for both the DAP and DADM systems are summarized in Table IV. For the prepolymer, there should theoretically be two peaks of equal area in the O_{1s} spectrum, *i.e.*, the C=O (532.1 eV) and the C–O (533.3 eV) in the COOH moiety in DAP_p. We have attributed the highest binding energy peak at 535.1 eV to the presence of free water. This peak disappeared after the prepolymer was left in the desiccator for three days and also after cyclization. This free water has also been observed in low density polyethylene.²⁰

The N_{1s} spectrum consists of two peaks of which implies that two different environments are present. The nitrogen which is attached to the double bond in the structure $\text{–C–NH–C(CH}_3\text{)=N–C–}$ has been assigned the lower BE (399.7 eV) as compared to the nitrogen attached to the hydrogen at 400.8 eV. Although the double bond can tautomerize between the two nitrogens, the rate at room temperature is likely to be much lower than the photoelectron emission process which is in the region of 10^{-17} – 10^{-14} s. Hence, two distinguishable

Figure 8. Curve fitted N_{1s} spectrum of (a) DAP_p and (b) DAP_c .

peaks are observed. The peak at 285 eV in the C_{1s} spectrum corresponds to the C–C, C–H, and possibly N–C functionalities. The next peak at a shift of 1.4 eV can be attributed to C–O (from surface oxidation) and N–C=N functionalities. The highest binding energy peak at 289.1 eV is assigned to the carbon in the COOH group. It should be noted that the observation and interpretation made for the O_{1s} , N_{1s} , and C_{1s} spectra of $DADM_p$ are similar to that of DAP_p .

For the cyclised polymers, the N_{1s} spectrum

remained basically unchanged. Both the O_{1s} and C_{1s} , however, show significant differences which provide further information about the cyclization process. Comparison of Figures 7a and b indicate a large decrease but not total disappearance of the lower binding energy C–O component upon cyclization. It can be seen from Figure 9b that for DAP_c the COOH peak in the C_{1s} envelope has decreased considerably and an extra major component is observed at 289.7 eV which can be attributed to the C=O functionality specific to the polyquinazolone

XPS of Polyquinazolones

(a)

(b)

Figure 9. Curve fitted C_{1s} spectrum of (a) DAP_p and (b) DAP_c.

structure. However, the presence of the C–O and COOH peaks, no matter how small, suggests incomplete cyclization due to unreacted COOH group in addition to the decarboxylation suggested by the low oxygen content in both the elemental analysis and XPS surface stoichiometries in this work and DTA/MS studies previously reported.⁸ Table V gives the C=O/COOH ratios for the various polyquinazolones prepared under different cyclization conditions and their thermal data. The results clearly indicate that this quantity

can be used as a more accurate measure of the degree of cyclization of the polyquinazolones than other available techniques. It is important to note that although the degree of cyclization data obtained has been limited to the surface, this quantity correlates directly with the bulk thermooxidative stability of the present series of polymers. Moreover, many forms of degradation initiate at the surface of the polymer before significant damages occur in the bulk. It can be seen that the more fully cyclized the polyquinazolone, the better its high

Table V. Comparison of C=O/COOH ratio and thermal stability of cyclized polymer DAP_c and DADM_c

Polymer ^a system	C=O/COOH	T _{50%} (°C)
DAP _c (A)	5.1	558
DAP _c (B)	4.5	526
DADM _c (A)	4.6	534
DADM _c (B)	4.0	500

^a Letters in brackets indicate different cyclization programmes (A) and (B).

temperature performance. The ultimate goal in the area of heat resistant polymers must therefore be the ability to synthesize polymers with the ideal structure.

CONCLUSIONS

XPS has provided a rapid and accurate means of assessing quantitatively the degree of cyclization in polyquinazolones, a parameter vital to the preparation of heat resistant polymers involving a prepolymer step and which so far has not been determined to any degree of accuracy. We believe that the cyclization process should be studied and characterized more thoroughly in order to achieve a higher degree of cyclization which, based on the results reported in this paper, can be quantitatively determined by XPS. A more fully cyclised ring system would no doubt extract even better high temperature performance from some of the already commercially successful heat resistant polymers.

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