

## New Poly(ether-alkyl)hydrazides: Synthesis and Characterization

P. LAURIENZO, M. MALINCONICO, E. MARTUSCELLI,\*  
N. PERENZE, and M. G. VOLPE

*Istituto di Ricerche su Tecnologia dei Polimeri e Reologia, C.N.R.,  
Via Toiano, 6 80072 Arco Felice (Naples), Italy*

(Received May 29, 1992)

**ABSTRACT:** A series of new acyclic dichlorides were prepared from 4,4'-dihydroxybiphenyl and the ethylester of an  $\omega$ -Bromo alkyl-carboxylic acid. These dichlorides condensed with terephthalic dihydrazide. The resulting poly(ether-alkyl)hydrazides (PEHZ), whose general formula is:  $[-\text{NHNH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{NHNH}-\text{CO}-(\text{CH}_2)_n-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_n-\text{CO}-]_x$  were characterized by inherent viscosity, elemental analysis, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and WAXS experiments.

**KEY WORDS** Poly(ether-alkyl)Hydrazides / Polycondensation / Thermal Properties / Wide Angle X-Ray Scattering Analysis /

In the last decade, large interest has grown on heat resistant polymers for application in extreme environment. Kevlar<sup>1</sup> was the most successful example and more recently poly(aryl ether ketone)s, like poly(ether ether ketone) (PEEK).<sup>2</sup> In order to improve the processability of such aromatic polymers it is common practice to decrease their melting points either by the introduction of defects along the chain, *e.g.* *m*-oriented aromatic rings or alkyl substituents on a *p*-oriented ring, or by the insertion of aliphatic units. Aromatic polyoxadiazoles<sup>3-5</sup> are interesting candidates for application in extreme conditions. They can be obtained by thermal treatment of intermediate polyhydrazides<sup>3</sup> in a fashion very similar to formation of polyimides from intermediate poly(amic acid).<sup>6</sup>

Polyoxadiazoles, as well as aromatic polyhydrazides, suffer from an almost complete lack of processability. In fact they do not melt and are soluble only in solvents not suitable for industrial applications (strong inorganic acids or amides). In order to impart moldability

and improve solubility of polyoxadiazoles, a new class of chemically modified polyhydrazides has been synthesized. They are based on 4,4'-dihydroxybiphenyl (biphenol) which is incorporated in the polyhydrazide between two sequences of methylene units of variable length.

It is well established that the combination of biphenol and alkane spacer leads to thermotropic polyesters and poly(esterimide)s.<sup>7-9</sup> It was found that the number of methylenes in the repeating unit is very critical for the existence of a stable mesophase.

In the present paper we investigate poly(ether-alkyl)hydrazides (PEHZ) incorporating methylene sequences  $(\text{CH}_2)_n$  with *n* values of 3, 4, and 5 and we report their synthesis and characterization.

## EXPERIMENTAL

### Materials

4,4'-(dihydroxy)biphenyl (biphenol) is an Aldrich reagent grade product and was used

\* Correspondence author.

as received.

$\omega$ Br-ethyl esters (Aldrich) were reagent grade and used without further purification.

LiCl was desiccated at 100°C overnight and stored over P<sub>2</sub>O<sub>5</sub>.

Thionyl chloride (Aldrich) was used as received.

Sodium methoxide was freshly prepared according to standard procedure just before use.

Anhydrous *N,N*-dimethylformamide (DMF) was prepared by refluxing for four hours over CaH<sub>2</sub>.

*N,N*-dimethylacetamide (DMAc) and *n*-hexane were stored over activated molecular sieves.

All other solvents were of analytical grade and used as received.

#### *Thermal Analysis*

Thermal analysis was performed on a Mettler T. A. –3000 Differential Scanning Calorimeter (DSC), equipped with a control and programming unit (microprocessor Tc 10A), that manages the apparatus and allows elaboration of the memorized data, and a calorimetric cell DSC-30, which allows scans from –170 to 600°C. All the experiments were run under N<sub>2</sub> and at a rate of 20°C min<sup>-1</sup>.

#### *Thermogravimetric Analysis*

Thermal degradation under N<sub>2</sub> was performed on a Mettler Thermogravimetric Analyzer (TGA) TG50 model, which consists of a measuring cell, a Mettler microbalance and an AX2 Epson computer for data storage and evaluation. The heating rate was 20°C min<sup>-1</sup>.

#### *Infrared Analysis*

Infrared spectra were obtained with a Fourier Transform Infrared spectrometer (FTIR) Nicolet 5DX-B, with a resolution of 4 cm<sup>-1</sup> (32 scans collected). Samples were prepared by compressing the powders into KBr disks.

#### *Wide Angle X-ray Scattering Analysis*

Wide angle X-ray scattering (WAXS) analysis was carried out on a Philips (PW1050 model) powder diffractometer (CuK Ni-filtered radiation) to evaluate the crystallinity of polymers. The scanning rate was 0.5 degree per min.

#### *Viscosity Measurements*

Viscosity measurements were performed at 30°C with a Cannon-Ubbelohde viscometer, at about 0.20 g dl<sup>-1</sup> hexamethylenephosphoramide (HMPA).

#### *<sup>1</sup>H NMR Analysis*

<sup>1</sup>H NMR spectra were performed on a Bruker AMX32 operated at 500:13 MHz. Chemical shifts refer to CDCl<sub>3</sub> at  $\delta$  7.26 ppm.

#### *Preparation of 4,4'-Bis(5-ethoxycarbonylpentanoxy)biphenyl (Ic)*

In a three necked flask equipped with a condenser, a magnetic stirrer and a N<sub>2</sub> inlet, 5.00 g of 4,4'-biphenol (0.027 mol) were dissolved in 130 ml of anhydrous DMF. When dissolution was complete, 3.20 g of sodium methoxide (0.059 mol) were added to the solution. The temperature was raised to 150°C and the mixture was kept at this temperature under stirring for 24 hours. A fine pink suspension of sodium biphenoxide gradually formed. Then, 14.50 g of ethyl-6, bromohexanoate (0.065 mol) were added. A clear solution was immediately obtained, and the reaction proceeded for 4 hours, to allow the reaction of both the hydroxyl groups of biphenol. Upon cooling, the solution was poured into 2 liters of water. The product was recovered by filtration, repeatedly washed with water and finally dried in air at 60°C.

The white powder obtained was twice recrystallized from methanol.

The purity of the product was checked by <sup>1</sup>H NMR and elemental analysis (yield = 40%).

*Preparation of 4,4'-Bis(5-chlorocarbonylpentanoxy)biphenyl (IIIc)*

(IIIc) was put in a flask, equipped with condenser and N<sub>2</sub> inlet, containing 200 ml of a 10% (w/v) solution of potassium hydroxide in absolute ethanol and stirred at reflux for 4 hours. The cold mixture was dissolved in water and concentrated hydrochloric acid was added until clear acidic reaction of pH test paper. The solid diacid so obtained was recovered by filtration, washed with water until neutral and dried at 100°C (yield = 100%). Purity was checked by <sup>1</sup>H NMR analysis.

A large excess of thionyl chloride was added to the diacid to reflux. The reaction was allowed to proceed for 2 hours (complete solubilization was obtained after almost 30 minutes). The unreacted thionyl chloride was removed under vacuum and the solid dichloride was washed three times with anhydrous *n*-hexane before drying under nitrogen stream (yield = 100%). Rapid hydrolysis prevented the accurate determination of melting point and obtaining of spectral data.

*Polycondensation Reaction of PEHZ from (IIIc) Sample (PEHZH)*

A low temperature solution polycondensation method was used for the synthesis of the polyhydrazides.

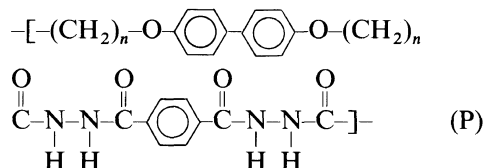
In a flask equipped with a mechanical stirrer and N<sub>2</sub> inlet 45.67 g of DMAc containing 5% by weight of LiCl were dissolved and 1.51 g (7.80 mmol) of TDH were added under stirring. When a fine suspension of TDH was obtained, the flask was immersed in a water/ice bath and 3.51 g (7.80 mmol) of (IIIc) were added. The bath temperature was kept at 0°C during the first two hours of reaction. At early stages, the solution became transparent and the viscosity gradually increased, until it turned to a stirrable gel-like mixture. The water/ice bath was then removed and the mixture was kept at room temperature over night and finally poured into water. The recovered polymer was washed with water until neutral and dried *in vacuo* at 100°C

( $\eta_{inh} = 0.48 \text{ dl g}^{-1}$ , yield = 100%).

## RESULTS AND DISCUSSION

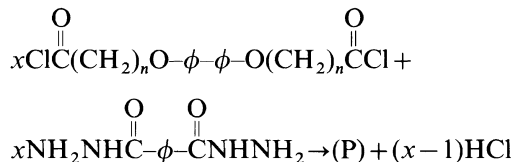
### Synthesis

Poly(ether-hydrazide)s with the following basic repeating unit:



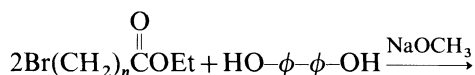
have been prepared with  $n = 3, 4,$  and  $5$ .

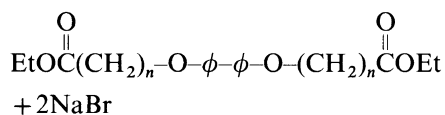
They are obtained by the low temperature polycondensation method, well known to give high molecular weight polyhydrazides,<sup>3)</sup> between the dichloride and terephthalic dihydrazide (TDH):



TDH was prepared starting from hydrazine hydrate and dimethyl terephthalate, according to standard procedures.<sup>10</sup> The rigid biphenolic unit is the repeating unit followed by a flexible space (in this case short aliphatic chain) is reported to be able to impart liquid crystalline properties to polyesters.<sup>7</sup> Nevertheless, it is reported that the number of methylene units able to give a mesophase in rigid polymers as polyesters or poly (ester imide)s in very critical and, sometimes, the mesophase starts to appear only for  $n$  above 6. In our case, we found no evidence of a mesophase, for all investigated  $n$ .

Dichlorides were obtained from the corresponding diethylesters starting from biphenol and ethyl ester of an  $\omega$ -Bromo alkylcarboxylic acid, through William's reaction:





The reaction occurred in two steps. In the first step there was formation of monoester; the conditions to shift the equilibrium towards diester formation were very critical; an excess of both sodium methoxide and bromoester improved the yield. Sodium methoxide was chosen as it is most effective to promote the formation of biphenate salt, an intermediate of the reaction.

The products were recovered by pouring the reaction mixture into water and purified by

**Table I.** Melting points (mp), proton chemical shifts ( $\delta_{\text{H}}$ ) and elemental analysis of ether esters of general formula  $\text{H}_5\text{C}_2\text{OOC(CH}_2)_n\text{-O-}\phi\text{-}$  with  $n=3$  (**Ia**), 4 (**Ib**), and 5 (**Ic**)

Sample	mp °C	$\delta_{\text{H}}(\text{CDCl}_3)$ ppm	Elemental analysis <sup>a</sup>	
			%	
			C	H
<b>Ia</b>	94.5	1.27 (6H, t), 1.84 (4H, m), 2.34 (4H, t), 4.08 (4H, t), 4.11 (4H, q), 6.69–7.62 (8H, m)	69.6 (69.56)	7.3 (7.25)
<b>Ib</b>	89.0	1.25 (6H, t), 1.85 (8H, m), 2.32 (4H, t), 4.09 (4H, t), 4.14 (4H, q), 6.71–7.65 (8H, m)	70.4 (70.59)	7.7 (7.69)
<b>Ic</b>	93.5	1.28 (6H, t), 1.85 (12H, m), 2.38 (4H, t), 4.05 (4H, t), 4.11 (4H, q), 6.87–7.45 (8H, m)	71.5 (71.49)	8.1 (8.08)

<sup>a</sup> Figures in parentheses indicate calculated values.

repeated recrystallizations from diluted methanol solution.

The ether esters were characterized by DSC,  $^1\text{H}$  NMR, elemental analysis (Table I) and infrared spectroscopy. Characteristic absorption bands due to aromatic rings stretching ( $1602\text{ cm}^{-1}$ ), C=O stretching ( $1738\text{ cm}^{-1}$ ) and  $\phi\text{-O-C}$  stretching ( $1256\text{ cm}^{-1}$ ) were observed. The infrared spectrum of the sample with  $n=4$  is given in Figure 1a. No significant changes were found in the spectra of the samples with different values of  $n$ .

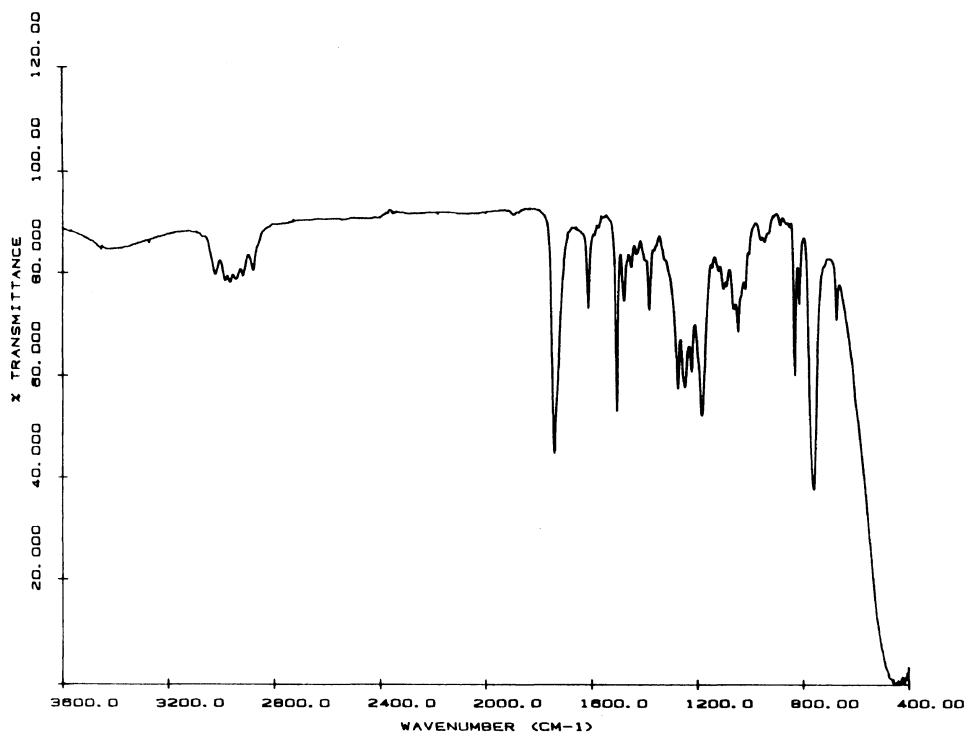
Subsequent saponification with potassium hydroxide in ethanol and reaction of the diacid with thionyl chloride were carried out according to standard procedures. Also the diacids were characterized by DSC,  $^1\text{H}$  NMR (Table II) and infrared spectroscopy. Figure 1b shows the spectrum of the sample with  $n=4$  as an example. Additional bands due to C=O and -OH of the acid groups ( $1702$  and  $3070\text{ cm}^{-1}$ , respectively) were observed, while the ester band at  $1738\text{ cm}^{-1}$  was absent.

Sample codes,  $\eta_{\text{inh}}$  and elemental analysis of polymers are reported in Table III. The obtained viscosities were found to be independent of the length of  $\text{CH}_2$  sequences and not very high. This may be, at least partially,

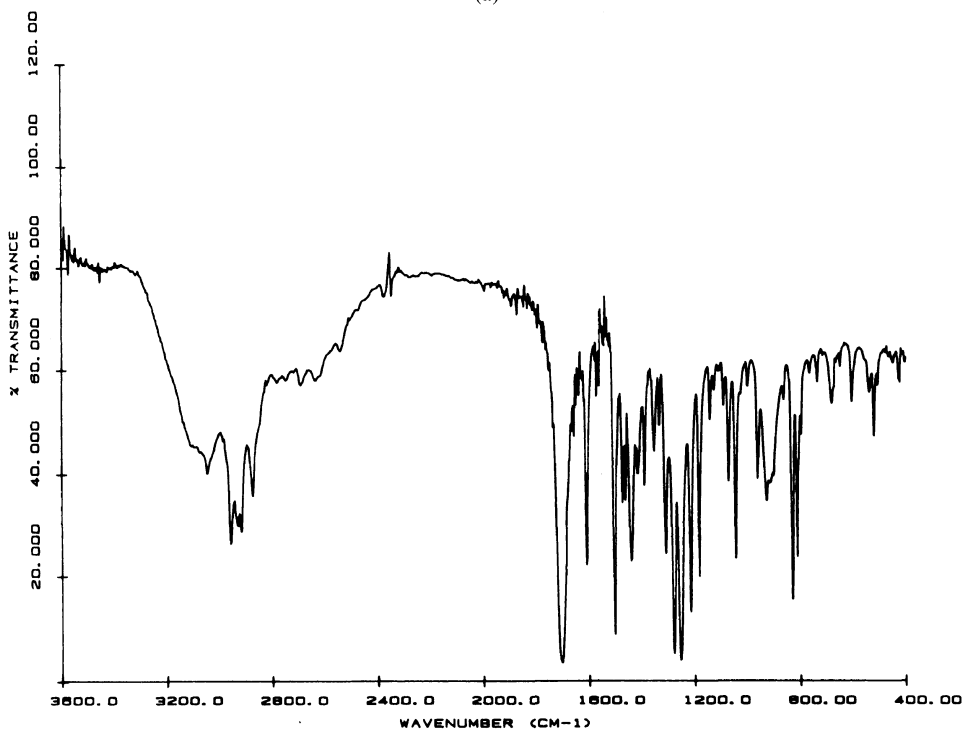
**Table II.** Melting points (mp) and proton chemical shifts ( $\delta_{\text{H}}$ ) of intermediates ether-acids of general formula  $\text{HOOC(CH}_2)_n\text{-O-}\phi\text{-}$  with  $n=3$  (**IIa**), 4 (**IIb**), and 5 (**IIc**)

Sample	mp °C	$\delta_{\text{H}}$ (DMSO)	
		ppm	
<b>IIa</b>	252.5	1.70 (4H, m), 2.28 (4H, t), 3.99 (4H, t), 6.96–7.52 (8H, m), 12.11 (2H, s)	
<b>IIb</b>	209.9	1.71 (8H, m), 2.30 (4H, t), 3.97 (4H, t), 6.98–7.56 (8H, m), 12.10 (2H, s)	
<b>IIc</b>	201.0	1.68 (12H, m), 2.31 (4H, t), 3.97 (4H, t), 6.95–7.61 (8H, m), 12.11 (2H, s)	

Poly(ether-alkyl)hydrazides



(a)



(b)

Figure 1. (a) FTIR spectrum of **Ib** sample; (b) FTIR spectrum of **IIb** sample.

due to gelation during polymerization, that can kinetically limit molecular weight.

No correlation could be found between  $\eta_{inh}$

**Table III.** Codes, number of methylenic groups in the repeating unit ( $n$ ),  $\eta_{inh}$  and elemental analysis of the polyhydrazides

Codes	$n$	$\eta_{inh}^a$ dl g <sup>-1</sup>	Elemental analysis <sup>b</sup>		
			%		
			C	H	N
PEHZB	3	0.47	65.1 (65.12)	5.3 (5.43)	10.8 (10.85)
PEHZV	4	0.35	66.1 (66.18)	5.7 (5.88)	10.3 (10.29)
PEHZH	5	0.48	67.2 (67.13)	6.3 (6.29)	9.7 (9.79)

<sup>a</sup>  $T = 30^\circ\text{C}$ ,  $c = 0.20$  g dl<sup>-1</sup> in hexamethylenephosphoramide.

<sup>b</sup> Figures in parentheses indicate calculated values.

and  $M_w$ , as values of “ $\alpha$ ” and “ $K$ ” are not reported in literature.

IR spectroscopic analysis was performed on polymers. The polyhydrazides showed N–H stretching at around 3200 cm<sup>-1</sup>, carbonyl stretching at 1650 cm<sup>-1</sup> and C–N stretching at 1270 cm<sup>-1</sup> (see Figure 2 as example).

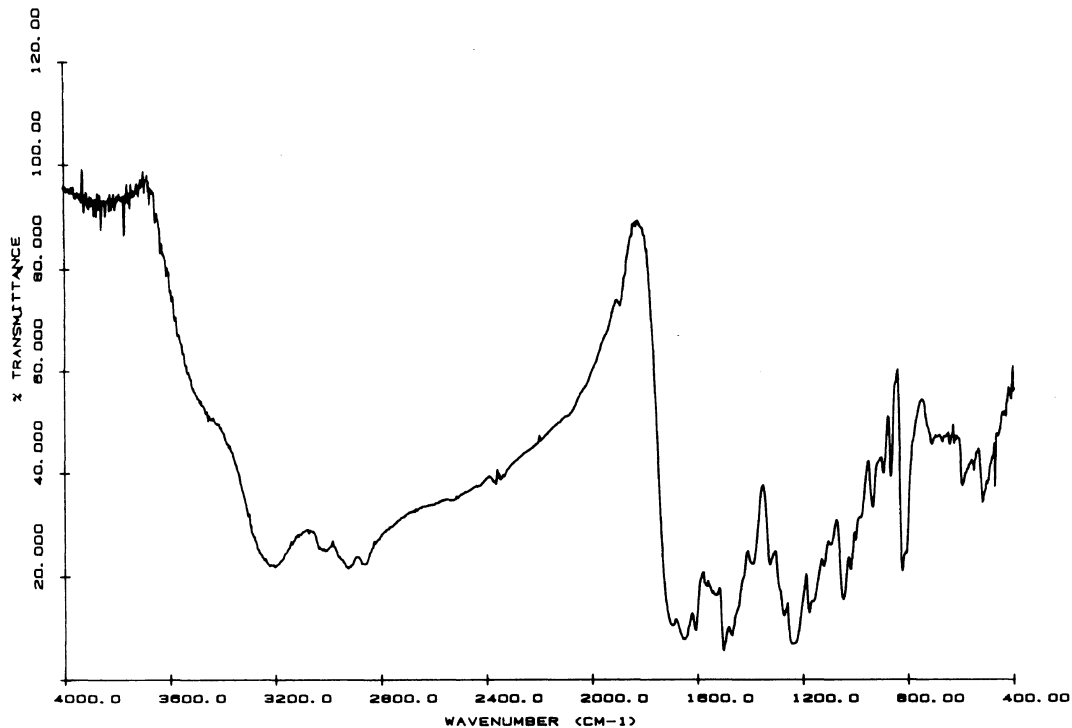
#### Thermogravimetric Analysis

Figure 3 shows the TG traces in N<sub>2</sub> for all samples.

**Table IV.** Cyclization and degradation temperatures of the PEHZ samples<sup>a</sup>

Sample	$T_{cycl}$	$T_{deg}$
	°C	°C
PEHZB	340	440
PEHZV	324	444
PEHZH	320	440

<sup>a</sup> PEHZ, poly(ether-alkyl) hydrazides.



**Figure 2.** FTIR spectrum of PEHZV.

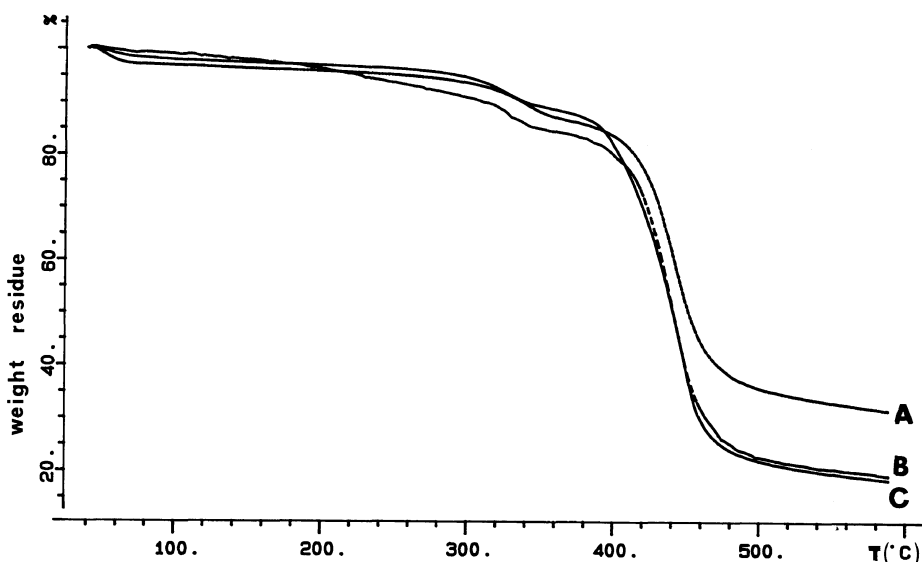
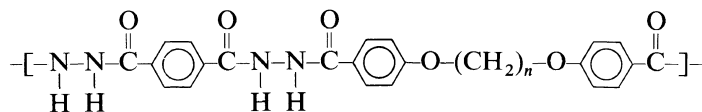
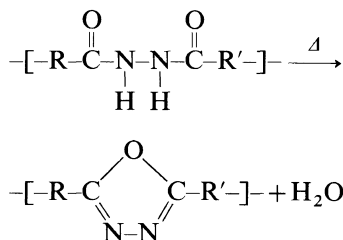


Figure 3. TG traces of (A) PEHQB, (B) PEHQV, (C) PEHQZ. Heating rate = 20 °C min<sup>-1</sup>.

A weight loss before degradation of about 6% was found in every sample. This was attributed to the evolution of water as a consequence of thermal cyclization to corresponding polyoxadiazoles:



The cyclization temperatures were dependent of the number of methylene units in the chain, and were about twenty degrees higher than the observed values of polyhydrazides reported in the present paper, for the same number of methylene units. This is due to the fact that, in the present case, the hydrazide group is directly linked to aliphatic chain.

The degradation temperature was not influenced by the number of methylene sequen-

The reaction is well documented in the literature,<sup>3</sup> and confirmed also by IR analysis.

Cyclization temperature ( $T_{\text{cycl}}$ ) are reported in Table IV, together with those of degradation. There was decrease  $T_{\text{cycl}}$  with increasing number of (CH<sub>2</sub>) in the repeating unit derived from the enhanced mobility of the polymeric chain, which allowed an easier rearrangement of the hydrazidic group to give the oxadiazolic ring.

In a previous work,<sup>11</sup> we reported the thermal behavior of poly(ether aryl hydrazide)s of a general formula:

cies, according to Table IV. This is not surprising, as we investigated only short methylene sequences. According to literature data on aromatic polyimides, the insertion of aliphatic spacers of length lower than six does not depress thermal degradation behavior.<sup>12</sup>

#### DSC Analysis

DSC traces for PEHQB, PEHQV, and PEHQZ samples collected after polymerization

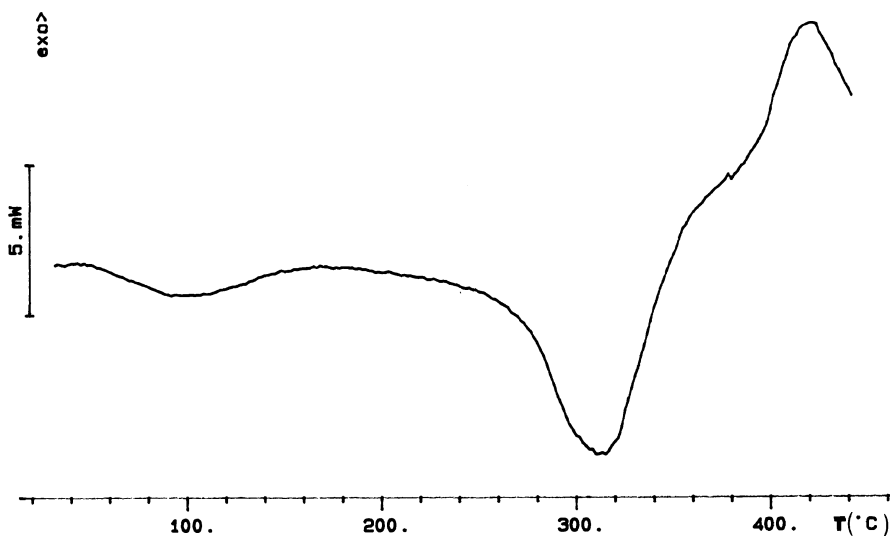


Figure 4. DSC curve of PEHZB. Heating rate =  $20^{\circ}\text{C min}^{-1}$ .

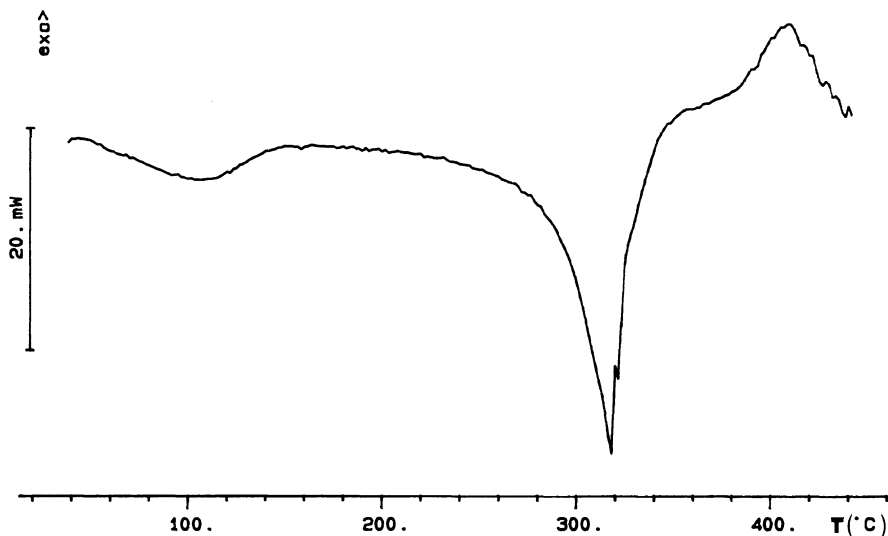


Figure 5. DSC curve of PEHZV. Heating rate =  $20^{\circ}\text{C min}^{-1}$ .

(*i.e.*, coagulated and repeatedly washed in water and dried *in vacuo* at  $100^{\circ}\text{C}$ ) with no further thermal treatment are reported in Figures 4, 5, and 6, respectively. Thermal data were summarized in Table V.

The broad endotherm at about  $100^{\circ}\text{C}$  was due to evolution of absorbed water (not present in second run).

All samples showed an endotherm just above  $300^{\circ}\text{C}$ . Such an endotherm was very broad for PEHZB, while sharp with a shoulder on the right side in PEHZH, and resolved into two peaks for PEHZV. According to TG analysis (see previous paragraph) the polyhydrazides underwent thermal cyclization in the same temperature range of the DSC endotherm. The



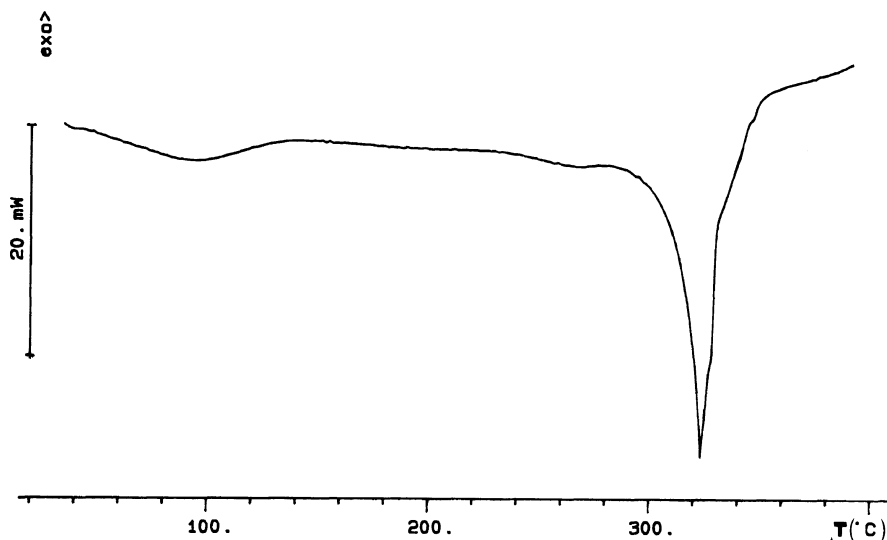


Figure 6. DSC curve of PEHZH. Heating rate =  $20^{\circ}\text{C min}^{-1}$ .

Table V. Thermal analysis data for the PEHZ samples

Sample	$T_{\text{endo}}/^{\circ}\text{C}$	$T_{\text{g}}/^{\circ}\text{C}$
PEHZB	312	—
PEHZV	315	—
PEHZH	321	240

Table VI. WAXS parameters for PEHZH sample

Sample	$X_c$	$2\theta$	$d$	$1/A$
	%	deg	Å	$\text{deg}^{-1}$
PEHZH	16.87	19.20	4.62	0.50
		21.80	4.08	0.26
		24.80	3.59	0.34

broad peaks and shoulders may thus be related to the overlapping of melting and cyclization.

A clear  $T_{\text{g}}$  ( $240^{\circ}\text{C}$ ) was detected only in the case of PEHZH sample, *i.e.*, the sample with a higher number of methylenes in the repeating unit. This suggests that the  $T_{\text{g}}$  of the other samples is higher than  $240^{\circ}\text{C}$  and may overlap melting and cyclization processes.

#### X-Ray Diffraction Analysis

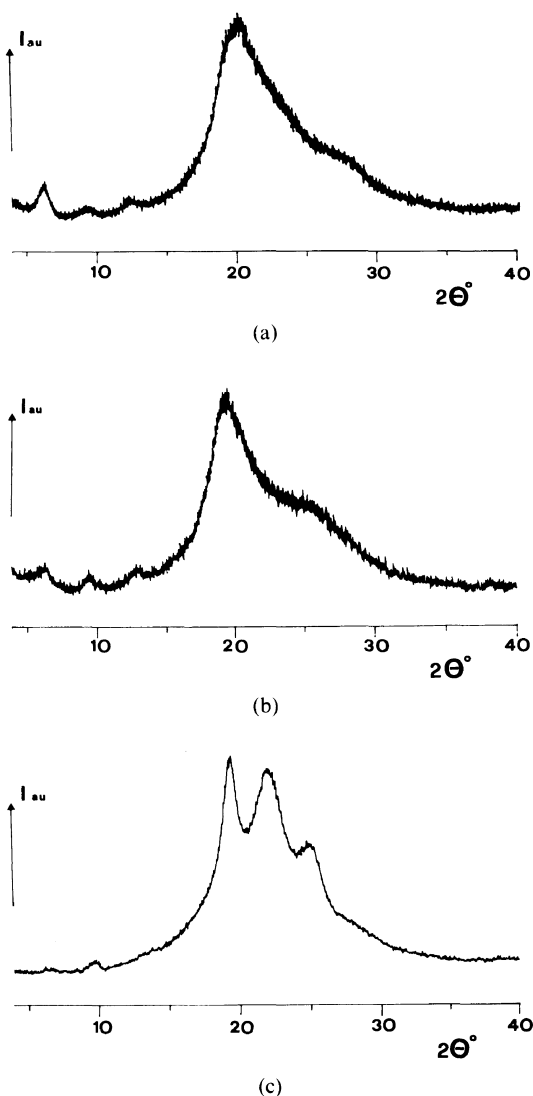
WAXS powder spectra of PEHZ samples are reported in Figure 7 (a, b, c). It is evident that the only sample which showed well defined crystalline peaks was PEHZH. Samples of PEHZB and PEHZV showed WAXS diffractograms characterized by a rather broad halo with a maximum centered at  $2\theta = 20.0$  and  $19.2$  and a shoulder at  $2\theta = 26.5$  and  $24.0$ , respectively. These halos were mainly due to dif-

fuse scattering from amorphous regions. This was probably related to the higher number of methylenes in the repeating unit of the PEHZH sample.

WAXS structural parameters for PEHZH sample are summarized in Table VI. The crystallinity index,  $X_c$ , was determined according to the method of Hermans-Weidinger.<sup>13</sup> The interplanar spacing,  $d$ , was obtained from the Bragg's law:  $\lambda = 2d \sin \theta$ . The reciprocal of the width at half-height ( $A$ ) of reflection has been reported as an index of the dimension and perfection of the crystallites.

## CONCLUSIONS

New poly(ether-alkyl)hydrazides, whose synthesis and properties are described in this



**Figure 7.** WAXS powder spectra: (a) PEHZB; (b) PEHZV; (c) PEHZH. Scanning rate=0.5 degrees per min.

paper, showed different thermal behavior according to the number of methylene units along the chain. In fact, the degree of crystallinity of polymers obtained from polymerization increased with the number of  $(\text{CH}_2)$  units, while the glass transition temperature,  $T_g$ , and cyclization temperature to polyoxadiazoles decreased in the same direction. A

detailed investigation of the melting process was severely limited by the superposition of cyclization.

More work is in progress on the chemical, physical and morphological properties of the polyoxadiazole derivatives. Preliminary results confirmed that the contemporary presence of methylene spacers and ether linkages renders the polyoxadiazoles fusible before starting degradation and leads to the appearance of a clear glass transition.

*Acknowledgments.* The authors wish to thank Mr. L. Calandrelli for the technical support on WAXS experiments and technical staff of "Servizio Spettroscopia NMR" of ICMIB of CNR, for the characterization of intermediates. This work was partially supported by "Progetto Finalizzato Chimica Fine II" of Italian C.N.R.

## REFERENCES

1. E. I. Du Pont de Nemours, U. S. Patent, 3,817,941 (1974).
2. D. J. Blundell and B. N. Osborne, *Polymer*, **24**, 1953 (1983).
3. A. H. Frazer and F. T. Walleberger, *J. Polym. Sci., A*, **2**, 1171 (1964).
4. Y. Iwakura, K. Uno, and S. Hara, *J. Polym. Sci., A*, **3**, 45 (1965).
5. Y. Imai, *J. Appl. Polym. Sci.*, **14**, 225 (1970).
6. K. Mittal, Ed., "Polyimides: Synthesis, Characterization and Applications," Vol. 1. and 2, Plenum Press, New York, N. Y., 1984.
7. J.-I. Jin, S. Antoun, C. Ober, and R. W. Lenz, *Br. Polym. J.*, (1980), **00**, 000
8. H. R. Kricheldorf, R. Pakull, and S. Buchner, *J. Polym. Sci., A*, **27**, 431 (1989).
9. H. R. Kricheldorf, R. Pakull, and S. Buchner, *Macromolecules*, **21**, 1929 (1988).
10. T. W. Campbell, V. S. Foldi, and J. Farago, *J. Appl. Polym. Sci.*, **2**, 155 (1959).
11. N. Lanzetta, M. Malinconico, E. Martuscelli, M. G. Volpe, *J. Polym. Sci., A*, in press.
12. S. K. Dolui and S. Maiti, *Angew. Chem.*, **141**, 31 (1986).
13. P. H. Hermans and A. Weidinger, *Makromol. Chem.*, **50**, 98 (1961).