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Determination of hydrazide content in poly(oxadiazole-hydrazide) copolymers by NMR and thermal analysis

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Abstract

A new technique based on nuclear magnetic resonance (NMR) is developed in this paper to determine quantitatively the hydrazide content in poly(oxadiazole-hydrazide) copolymers. Two-dimensional $^1H-^{13}C$ shift correlation and ^1H NMR spectra of poly(4,4′-diphenylether-1,3,4-oxadiazole-hydrazide) copolymers with different hydrazide contents were performed to characterize these copolymers and allow for development of a NMR based quantitative correlation for hydrazide content. Thermal gravimetric measurements (TGA) were also performed in order to provide an independent data set for validation of the NMR based technique. The results obtained with the proposed NMR technique were shown to be in good qualitative agreement with the TGA results.

Keywords: Polyoxadiazole; Polyhydrazide; Copolymer

1. Introduction

Oxadiazole-based polymers present a combination of properties (such as mechanical strength, stiffness, thermal and chemical stability [1]) that makes them good candidates for application as high temperature fibers [2], reinforcement materials [1], graphitized fibers [3] and membranes for gas separation [4,5]. Particularly, the outstanding thermal stability of poly(1,3,4-oxadiazole)s was ascribed to the fact that the oxadiazole ring is spectrally and electronically equivalent to the *p*-phenylene ring structure [6]. During the synthesis of the polyoxadiazoles an intermediate linear polymer, polyhydrazide, is formed. Depending on the reaction conditions, residual hydrazide groups can be present in the final polymer [7], leading to the formation of a poly(oxadiazole-hydrazide) copolymer. However, the hydrazide groups present neither the thermal and chemical stability [1] nor the outstanding gas separation properties [5] of the oxadiazole rings. That is a major drawback for application of this copolymer as thermally stable membranes for gas separations. Thus, the optimization of the reaction conditions is desired in order to achieve a polymer with adequate macromolecular structure. One important step during optimization is the structural characterization of the poly(oxadiazole-hydrazide) copolymer.

Although many efforts have been made to characterize poly(oxadiazole-hydrazide) copolymers [8–12], quantitative determination of the hydrazide contents in these copolymers has only been performed through elemental analysis [9] and thermal gravimetric measurements, TGA [4,10]. Attempts have also been made [10] to determine quantitatively the hydrazide contents by nuclear magnetic resonance (NMR); however, it has been shown [13] that the proposed technique might lead to inconsistent results. Elemental analysis does not seem to be adequate as a quantitative technique because of the small difference between the hydrogen contents of polyhydrazide and polyoxadiazole and because of the hygroscopic nature of these polymers [12]. On the other hand, Thermogravimetric analysis (TGA) spectra of poly(oxadiazole-hydrazide) copolymers show four distinct regions of weight loss [12], although only one of these regions can be associated to the weight loss caused by conversion of hydrazide groups into oxadiazole rings. However, these regions cannot be detected easily, as significant overlaps may be present in the TGA spectra.

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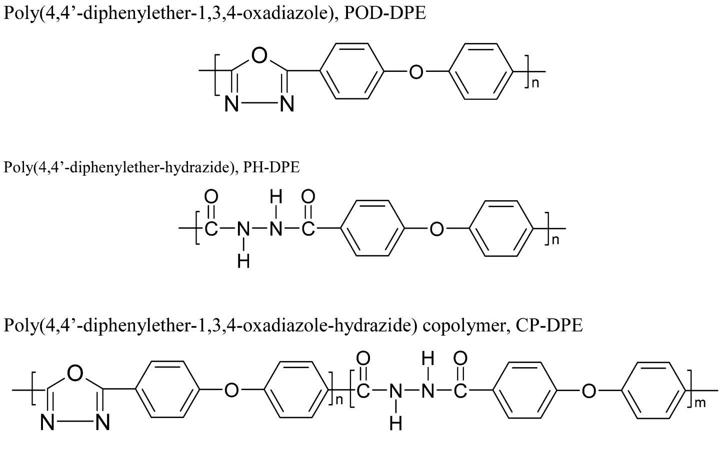

Fig. 1. Molecular structures of POD-DPE, PH-DPE and POD-PH-DPE.

Due to the usually difficult interpretation of TGA spectra, an alternative technique based on ^{1}H NMR is developed here to allow for quantitative determination of the hydrazide content in poly(oxadiazole-hydrazide) copolymer. Poly(4,4′-diphenylether-1,3,4-oxadiazole), POD-DPE, poly(4,4′-diphenylether-hydrazide), PH-DPE, and poly(4,4′-diphenylether-1,3,4-oxadiazole-hydrazide) copolymers, CP-DPE, with different hydrazide contents were used for experimental analysis. The structures of the used polymers are presented in Fig. 1.

2. Experimental

The detailed description of the reaction procedures used to synthesize the polymer samples investigated in this work is reported elsewhere [12,14]. ^{1}H NMR spectra of polymer samples were obtained in DMSO-d_6 at 25 °C using a Bruker DPX 200 spectrometer. The two-dimensional ^{1}H–^{13}C HETCOR spectrum was obtained in DMSO-d_6 at 25 °C using a Bruker DRX 300 spectrometer with ^{1}H and ^{13}C 90° pulse. TGA experiments were carried out in a Perkin Elmer TGA-7. About 5–10 mg of polymer samples, under nitrogen atmosphere, were first heated from 100 to 150 °C at 10 °C/min, to remove volatiles. Then, polymer samples were cooled down to 100 °C and heated again from 100 to 700 °C, at similar heating conditions. The second heating was used for polymer characterization.

3. Results and discussion

3.1. TGA results

Poly(oxadiazole-hydrazide) copolymers lose weight during heating experiments due to loss of water (%H_2O) caused by the formation of the oxadiazole groups ring [9]. Fig. 2 shows schematically the conversion of hydrazide groups of CP-DPE into oxadiazole rings.

As can be seen in Fig. 2, 1 mol of water is lost when the cyclization is complete, for each hydrazide group present in the copolymer. Then, the hydrazide content (%HZ) can be computed as [15]:

$$\%\mathrm{HZ} = \frac{236(\%\mathrm{H_2O})}{(1800 - 18(\%\mathrm{H_2O}))}100 \tag{1}$$

where (%H_2O) stands for the weight loss obtained from the TGA spectra.

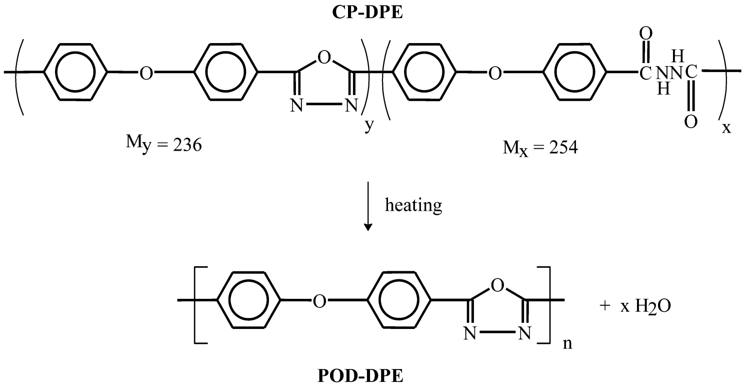

Fig. 2. Conversion of hydrazide groups of poly(oxadiazole-hydrazide) copolymer into oxadiazole rings.

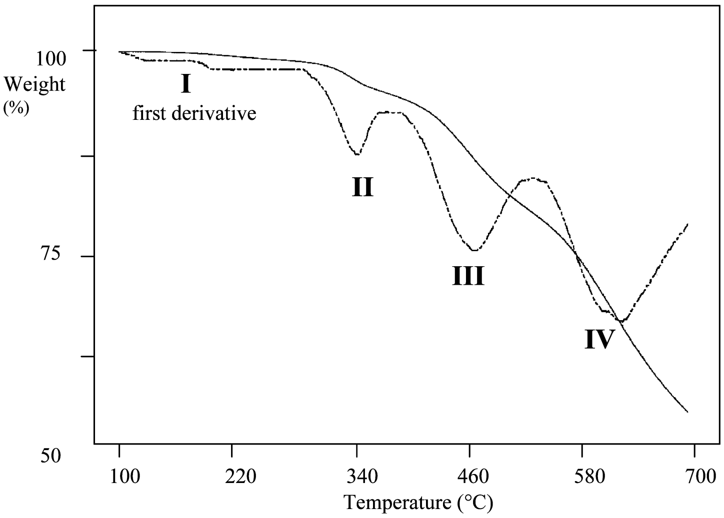

Fig. 3. Typical TGA spectrum of a polyhydrazide.

The TGA spectra of poly(oxadiazole-hydrazide) copolymers show distinct regions of weight loss. Frazer and Sarasohn [9] identified three different regions in the TGA spectra of a polyhydrazide. The first region was placed in the range of temperatures between 100 and 150 °C and was associated with the loss of adsorbed water on the polymer. The second region was placed in the range of temperatures between 275 and 375 °C and was associated with the loss of water produced during the formation of oxadiazole rings. The third region was associated with the loss of volatiles caused by the degradation of the polyoxadiazole. Although it may be assumed that the loss of weight linked to the cyclization of polyhydrazide into polyoxadiazole occurs in a narrow temperature region, it must be pointed out that the literature [5,10,16–19] reports a large variation of values for the range of temperatures where hydrazide groups are converted into oxadiazole rings. Temperature ranges can depend on residual hydrazide contents and on the particular chemical group attached to the oxadiazole ring.

This large variation of temperature ranges where the cyclodehydration reaction takes place results from the different approaches used for identification of the degradation region, e.g. the third region suggested by Frazer and Sarasohn [9]. Some authors assume that this region begins when the polymer loss reaches 5% [19] while others assume that this region begins when the weight loss reaches 10% [20,21]. Ballistreri et al. [17] considered that a weight loss of 11.5% would not necessarily imply the degradation of the polymer. On the other hand, Shukla and Dixit [22] considered that the weight loss observed in the temperature

Table 1
Characterization of different CP-DPE by TGA

Copolymer	1st region			2nd region			3rd region			4th region	
	Temperature range (°C)	% Water[a]	%HZ[b]	Temperature range (°C)	% Water[a]	%HZ[b]	Temperature range (°C)	% Water[a]	%HZ[b]	$\%HZ_{total}$[c]	$T_{d\ ini}$ (°C)[d]
d1	181–348	2.339	31.41	–	–	–	361–511	6.654	92.12	100	527
d2	108–244	1.021	13.53	–	–	–	–	–	–	13.53	511
d5	108–291	0.787	10.40	310–397	1.235	16.40	400–499	4.1	56.06	82.86	516
d6	108–280	0.97	12.84	–	–	–	–	–	–	12.84	512
d10	108–275	1.138	15.09	–	–	–	–	–	–	15.09	514
d11	108–241	1.413	18.79	338–442	1.155	15.32	–	–	–	34.12	494
d14	111–200	0.321	4.22	293–375	3.693	50.28	394–533	14.568	> 100	100	550
d15	–	–	–	287–370	2.647	35.65	399–456	3.101	41.97	77.62	486
d20	161–276	2.639	35.54	306–380	3.315	44.96	399–496	9.379	> 100	100	510
d24	–	–	–	314–395	1.147	15.04	–	–	–	15.04	473

[a] Weight loss determined by TGA with the first derivative of the curve of weight loss as a function of temperature.

[b] Hydrazide contents computed with Eq. (1).

[c] Total hydrazide contents determined by adding the %HZ determined in each region (hydrazide content was considered equal to 100% for polymer with weight loss higher than the maximum expected water loss).

[d] Temperature where the polymer degradation begins.

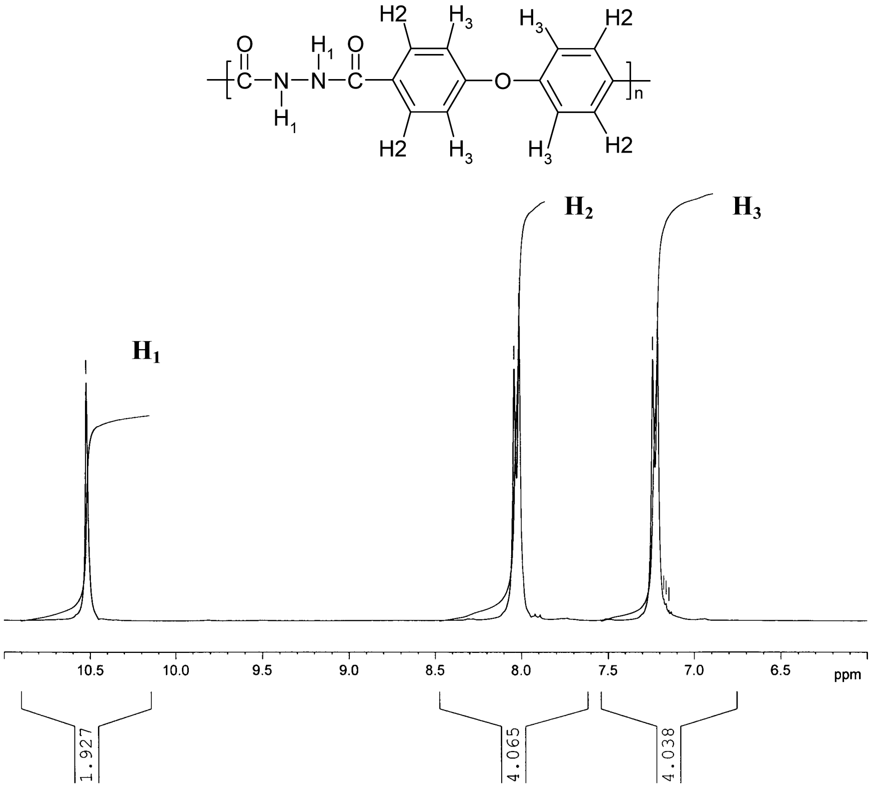

Fig. 4. ^{1}H NMR spectrum of PH-DPE taken in DMSO-d_6 at 25 °C.

range of 180–200 °C could also be due to the decomposition of the polymer. Therefore, agreement has yet to be reached regarding the temperature ranges where cyclodehydration and polymer degradation occur.

Fig. 3 shows that the first derivative of the TGA spectrum of a polyhydrazide can actually define four distinct regions. It is assumed that the first region corresponds to the loss of adsorbed water; that the second region is related to the cyclodehydration of hydrazide groups into oxadiazole rings; that the third region corresponds to the loss of water produced during secondary reactions, such as cross-linking, degradation and non-linear cyclization of hydrazide groups; and that the fourth region, above 450 °C, represents the decomposition of the polyoxadiazole formed in situ. For CP-DPE, however, the four regions cannot be detected so easily. Depending on the characteristics of the polymer samples, significant overlaps of the regions may be present, making the definition of the temperature regions much more difficult.

Table 1 presents the regions where weight loss was observed for distinct CP-DPE samples, with the respective temperature ranges and hydrazide contents (%HZ) as computed with Eq. (1).

The criterion used here for determination of the hydrazide contents in CP-DPE is the evaluation of weight loss in the range of temperatures between 200–400 °C, expected for cyclodehydration of hydrazide groups into oxadiazole rings. It is also considered here that the maximum water loss is equal to 7.1%, for total conversion of hydrazide groups into oxadiazole rings. As it can be seen in Table 1, weight losses observed in the first and third regions were also considered for computation of the hydrazide content. The weight loss observed in the first region was considered because this region spreads to temperatures higher than 200 °C. And although the third region can be related to the loss of water involved in secondary reactions, such as non-linear cyclization of hydrazide groups and cross-linking [12], hydrazide groups are also involved in these reactions. This means that the weight loss in this region may be crucial for computation of the residual hydrazide content in the copolymer. As the hydrazide contents computed with TGA spectra are subject to significant uncertainties, an alternative technique based on ^{1}H NMR spectra is developed here for quantitative determination of hydrazide contents in poly(oxadiazole-hydrazide) copolymers. Moreover, some polymers presented weight loss higher than the maximum expected water loss. This result can be attributed to the degradation of hydrazide groups and structures formed during secondary reactions. For these conditions, it was considered that the hydrazide content was equal to 100%.

3.2. NMR results

The characterization of poly(oxadiazole-hydrazide) copolymers by NMR spectra has been performed only on

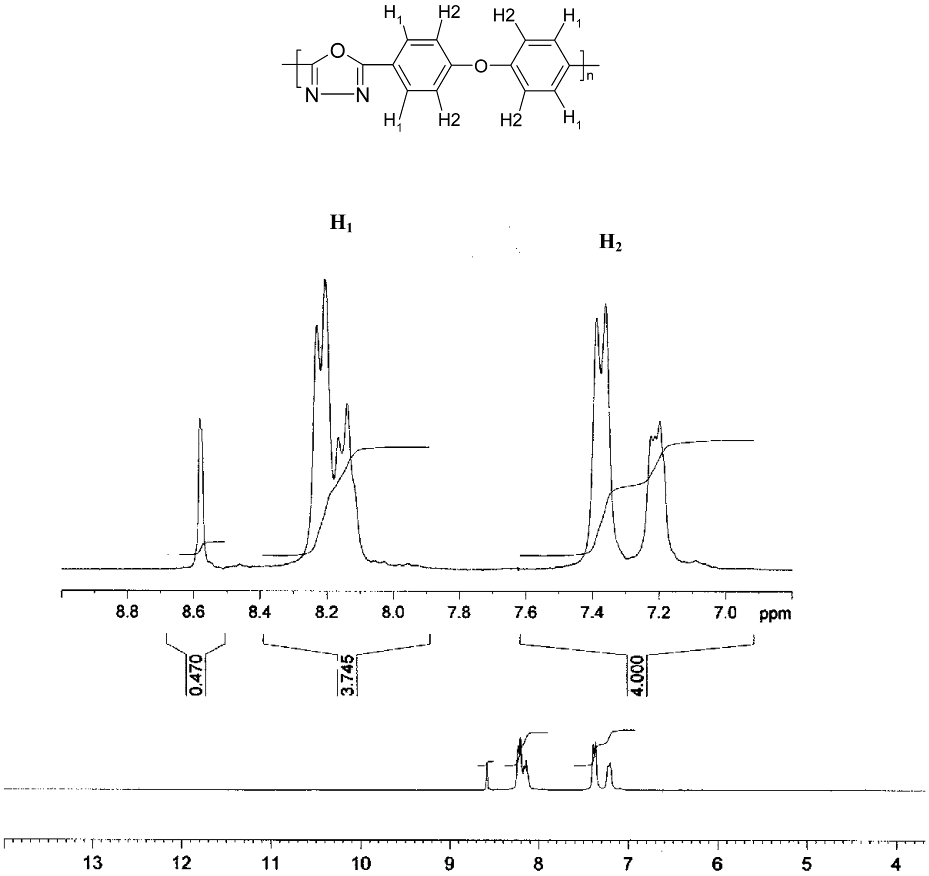

Fig. 5. ^{1}H NMR spectrum of POD-DPE taken in DMSO-d_6 at 25 °C.

a qualitative basis [11,12,23]. The absence of hydrazide NH protons can normally be confirmed with the disappearance of hydrogen resonances in the range of 9–10 ppm [11,23]. However, additional peaks that can be associated with aromatic protons of degradation products and more complex structures can also be observed in ^{1}H NMR spectra of CP-DPE [12]. However, previous works have been unable to determine the contents of hydrazide group and degradation structures in these copolymers by NMR, because of the complexity of the spectra of polyoxadiazole samples. It is important to emphasize that the proper interpretation of NMR spectra of poly(oxadiazole-hydrazide) copolymers can provide information about the hydrazide content and also about the presence of other chain structures which is not possible with the TGA spectra.

In order to better understand the ^{1}H NMR spectra of poly(oxadiazole-hydrazide) copolymers, ^{1}H NMR spectrum of the PH-DPE, synthesized at low temperature [14], is analyzed first. Fig. 4 shows the ^{1}H NMR spectrum of the PH-DPE. As it can be seen in Fig. 4 a singlet for proton H_1 and duplets for protons H_2 and H_3 are obtained, as expected by analyzing the structure of PH-DPE. Additional peaks related to other structures could not be observed. When the polyhydrazide is synthesized at high temperatures, multiple resonances for the hydrazide hydrogens can be found in the range of 10.0–10.5 ppm [11]. It seems that when the polyhydrazide is synthesized at high temperatures or when this polymer is cyclodehydrated into polyoxadizole, secondary reactions can take place [12,24]. Cross-linking reactions and thermal degradation of hydrazide groups, for example, are possible due to the high reactivity of –NH– and $-NH_2-$ groups [25], which is conferred by the available electron pair of the nitrogen atom and by the low thermal stability of hydrazide groups.

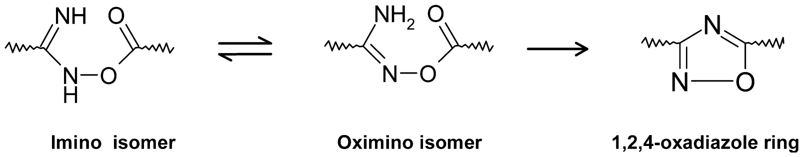

Fig. 6. Imino and oximino tautomeric isomers.

Table 2
Proton absorptions of an amide oxime taken in DMSO-d_6 at room temperature [25]

Proton	δ (ppm)
–NH–OR	7.6
=NH	7.9
=N–OH	9.7

Fig. 5 shows a ^{1}H NMR spectrum of the POD-DPE. The absence of hydrazide NH protons is confirmed with the disappearance of hydrogen resonances in the range of 9–10 ppm. However, as it can be observed in Fig. 5, there is a singlet at 8.5 ppm and two duplets in the range of 8.1–8.3 and 7.1–7.4, contrary to expectations of observing only one duplet in each of these two ranges, as in Fig. 4. This result shows that the polymer is not formed only by oxadiazole groups.

The singlet observed at 8.5 ppm in Fig. 5 could also be ascribed to the hydrazide NH protons, once duplets should be expected for aromatic protons in the POD-DPE structure. The presence of hydrazide NH protons at 8.5 ppm or in this vicinity could be expected, as reported by Jung and Park [25]. These authors characterized polymers with 1,2,4-oxadiazole rings and confirmed the oximino–imino tautomerism in poly(amide oxime), by using ^{1}H NMR spectra taken in DMSO-d_6 at room temperature. Fig. 6 shows the two tautomeric isomers, imino and oximino, in an amide oxime and the 1,2,4-oxadiazole ring formed after cyclization of this amide. Table 2 shows the proton absorptions observed in ^{1}H NMR spectrum of an amide oxime taken in DMSO-d_6 at room temperature [25].

The analysis of Table 2 shows that hydrazide NH proton absorptions in the aromatic regions around 8.0 ppm could be expected, given the similarity between the hydrazide and the amide groups. To confirm the absorptions of the hydrazide NH protons in the aromatic regions, a two-dimensional HETCOR experiment was performed. Fig. 7 shows a ^{1}H NMR spectrum (Fig. 7(a)) and the two-dimensional ^{1}H–^{13}C shift correlation spectrum (Fig. 7(b)) of d2 copolymer taken in DMSO-d_6 at 25 °C. The main information obtained from the ^{1}H–^{13}C shift correlation spectrum is the observation of coupling of hydrogen protons with carbon atoms. The hydrazide NH protons cannot be coupled with carbon atoms, as the hydrogen in hydrazide groups are attached only to nitrogen atoms.

Table 3
Proposed assignments in DMSO-d_6 for different protons in POD-DPE

Proton	δ (ppm)
H_b, $H_{b'}$	**7.12–7.15** (d)
$H_{b''}$	**7.3** (d)
H_o, H_h	**8.0–8.15** (d)
$H_{o'}$, $H_{h'}$	**8.20–8.25** (d)
H_c	**8.5** (s)
H_e	7.8 (s)
H_v	9.3–9.7 (s)
H_f	5.9 (s)
H_g	7.6–8.0 (s)
H_p	7.35 (s)
H_t	9.3–9.7 (s)
$H_{t'}$	10.12 (s)

d-duplet, s-singlet.

Table 4
Expected and obtained hydrazide contents for physical mixtures of copolymers d6 and d1

Mixture	Weight ratio d6:d1	Expected HzTGA	Obtained HzNMR
1	1:2	71	73
2	2:1	42	58

The analysis of Fig. 7 shows that the peak at 8.5 ppm cannot be ascribed to the hydrazide NH protons, as the proton related to this peak is coupled with a carbon atom, which presents absorption located at 128.5 ppm. On the other hand, the small proton peak at 8.4 ppm is not coupled with carbon atoms. This way, the proton related to this peak can be assigned to the hydrazide NH protons. As the peak at 8.5 ppm cannot be assigned to the aromatic protons in the POD-DPE structure, this can be connected to aromatic protons of degradation products.

Based on the possible occurrence degradation and secondary reactions [12], the determination of hydrazide contents by NMR can be performed by assuming that three different structures are possible in the POD-DPE, as presented in Fig. 8. In Fig. 8, symbols were assigned to the distinct aromatic protons in order to point out the different types of protons. The symbols are H_b, $H_{b'}$, $H_{b''}$, H_o, H_h, $H_{o'}$, $H_{h'}$, H_c for the aromatic protons in the neighborhood of: the ether groups that are near the hydrazide group (H_b); the ether groups that are near the oxadiazole group ($H_{b'}$); the oxygen linked to the hydrazide group ($H_{b''}$); the oxadiazole ring (H_o); the hydrazide group (H_h); the oxadiazole ring localized near the oxygen linked to the hydrazide group ($H_{o'}$); the hydrazide localized near the oxygen linked to the hydrazide group ($H_{h'}$); and the hydrazide group localized near to the phenylene ring (H_c).

In Fig. 8, structure 1 is equivalent to the CP-DPE formed during the synthesis of POD-DPE. Structures 2 and 3 are proposed based on the possible degradation reaction of the ether linkage. Heating, the ether groups react with strong acids, such as sulfuric acid, leading to breakage of C–O bond. This reaction starts with the formation of an oxonium ion [26]. Fig. 9 presents a scheme that explains the formation of both structures. Fig. 10 presents a mechanism for the formation of branches in structure 3 presented in Fig. 8.

Besides the structures in Fig. 8, other structures that absorb in the region of aromatic protons can also be present.

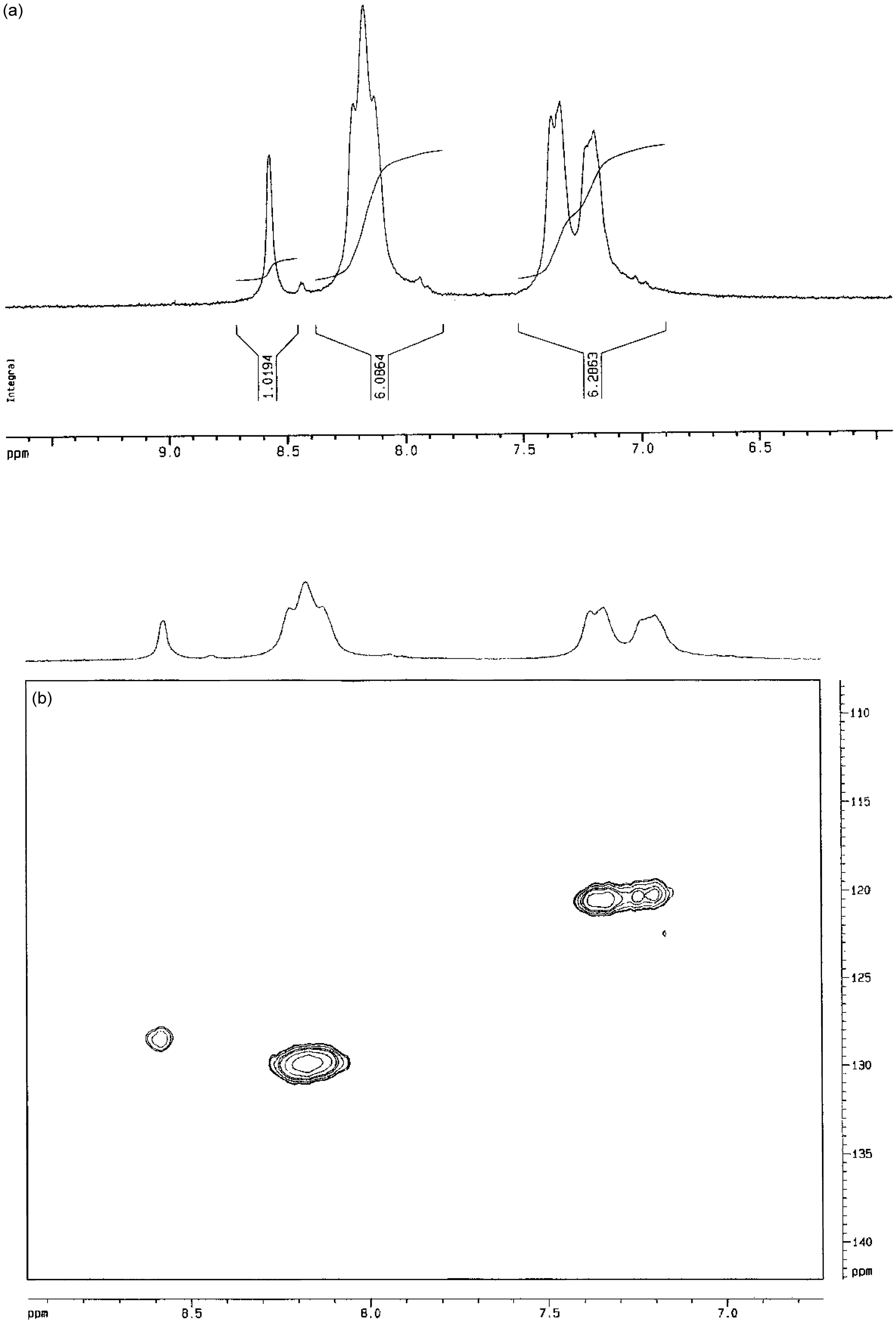

Fig. 7. Spectrum of d2 copolymer taken in DMSO-d_6 at 25 °C (a) ^{1}H NMR, (b) Two-dimensional ^{1}H–^{13}C shift correlation.

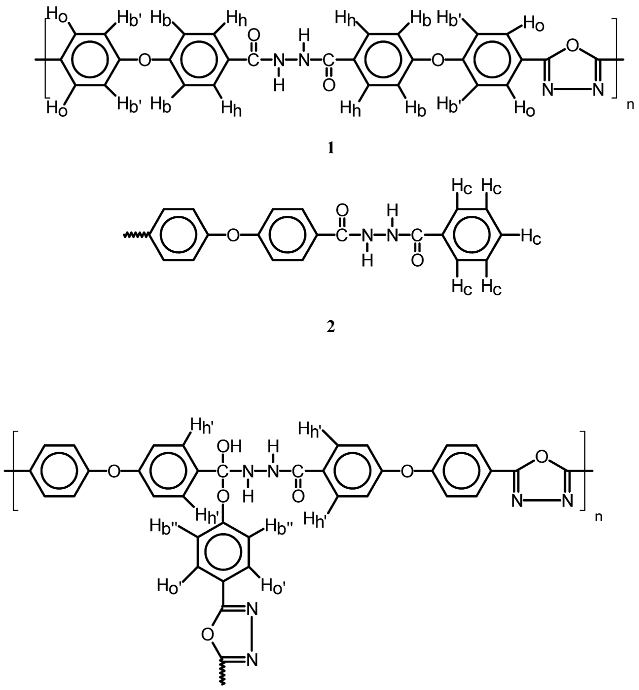

Fig. 8. Different possible structures of POD-DPE.

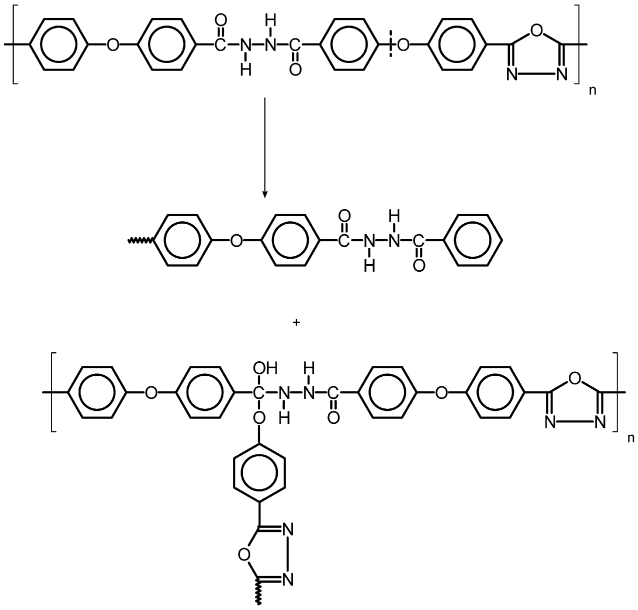

Fig. 9. Scheme for formation of structures 2 and 3 of POD-DPE.

These structures may be formed because of the breakage of the oxadiazole ring, as presented in Fig. 11; because of the ceto–enolic tautomerism of hydrazide groups; because of the presence of residual monomers; and because of the formation of hydrogen bonding between polar groups [6,13,27]. Fig. 12 presents these structures with the respective symbols for each proton.

Based on the discussions presented in the previous paragraphs and on assignments proposed in different works [12,22,25,28–30], it is proposed here that the absorptions for the different protons of the POD-DPE are as defined in Table 3.

The bold values in Table 3 correspond to the aromatic protons. As shown in Table 3, there is a region with overlaps among the protons H_o, H_h and $H_{o'}$, $H_{h'}$. This is supported by the work of Hedrich and Twieg [28], where it was concluded that the electron-withdrawing effect of the 1,3,4-oxadiazole ring on the benzene ring in the ground state is comparable to the effect of the ketone group. This conclusion was based on the ^{1}H NMR spectra of aromatic compounds with aromatic protons in the neighborhood of a ketone group and of a 1,3,4-oxadiazole ring, with absorptions at 7.9 and 8.0 ppm, respectively. In addition, the aromatic protons in the neighborhood of the hydrazide groups also absorb at 8.0 ppm, as shown in Fig. 4.

Based on the proposed assignments, the hydrazide group content can be computed as:

$$\%\mathrm{HZ} = \left(\frac{A_{\mathrm{hydrazide}}}{A_{\mathrm{aromatic}}}\right)\frac{100}{0.25} \qquad (2)$$

where $A_{\mathrm{hydrazide}}$ corresponds to the total area of all the protons of hydrazide groups (H_e, H_v, H_f, H_g, H_p, H_t, $H_{t'}$) and A_{aromatic} corresponds to the total area of all the aromatic protons (H_b, $H_{b'}$, $H_{b''}$, H_o, H_h, $H_{o'}$, $H_{h'}$, H_c). The value 0.25 corresponds to the case where the polymer is formed only by hydrazide groups, which should lead to 100%.

In case of high hydrazide contents, significant overlaps among the areas of protons of hydrazide groups and of aromatic protons may be present in the NMR spectra of POD-DPE. However, it must also be pointed out that in similar conditions, significant overlaps among the different regions may also be present in the TGA spectra. In addition, the analysis of a TGA spectrum of a polymer that does not

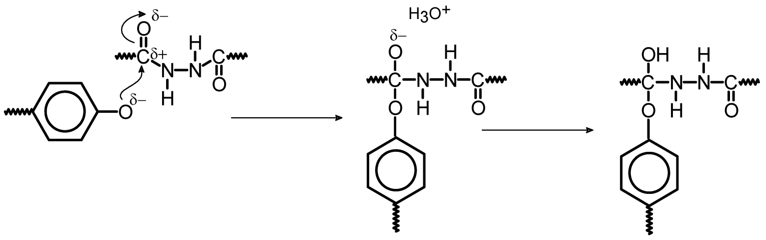

Fig. 10. Formation of branches in structure 3.

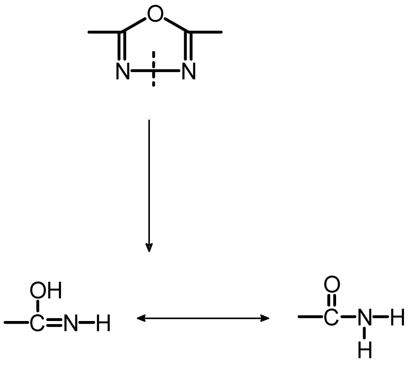

Fig. 11. Breakage of the oxadiazole ring.

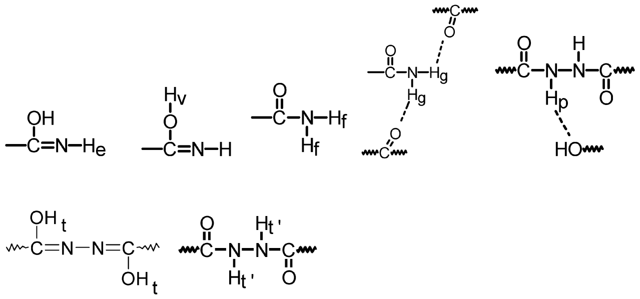

Fig. 12. Possible groups that may be formed during the synthesis of the POD-DPE.

lose weight below 450 °C is not a guarantee that the polymer is formed solely by oxadiazole groups, as polymer formed by cross-linked hydrazide groups does not lose weight in this temperature range either.

In order to compare the results obtained with both TGA and NMR techniques, a graphic that correlates the NMR and TGA results was plotted and shown in Fig. 13. As it can be seen in Fig. 13, there is a good agreement between both sets of results. Besides, when physical mixtures of copolymers with high (d1) and low (d6) hydrazide contents were prepared, a good agreement between expected and obtained hydrazide contents could be obtained, as shown in Table 4. In Figs. 14 and 15 the spectra of the two analyzed mixtures 1 and 2, with a copolymer weight ratio (d6:d1) of (1:2) and (2:1), respectively are shown. Once again, it can be seen in Table 4 that there is a fair agreement between both techniques. Observed differences should not be over-emphasized, given the relative high uncertainties of the hydrazide content obtained through TGA. This way, the proposed NMR technique can be used as an alternative way to determine quantitatively the hydrazide contents in poly(oxadiazole-hydrazide) copolymers.

4. Conclusions

The hydrazide group content in poly(oxadiazole-hydrazide) copolymers can be determined by ^{1}H NMR and TGA spectra. However, the NMR technique presents some advantages. The interpretation of ^{1}H NMR spectra of poly(oxadiazole-hydrazide) copolymers provide not only information about the hydrazide content but also about the presence of different structures in the polyoxadiazole, which cannot be observed in TGA spectra. Although both techniques are subject to relative large fluctuations, the results obtained with the proposed NMR technique showed a good agreement with data obtained with TGA and can be used as an alternative way to determine the hydrazide contents in poly(oxadiazole-hydrazide) copolymers.

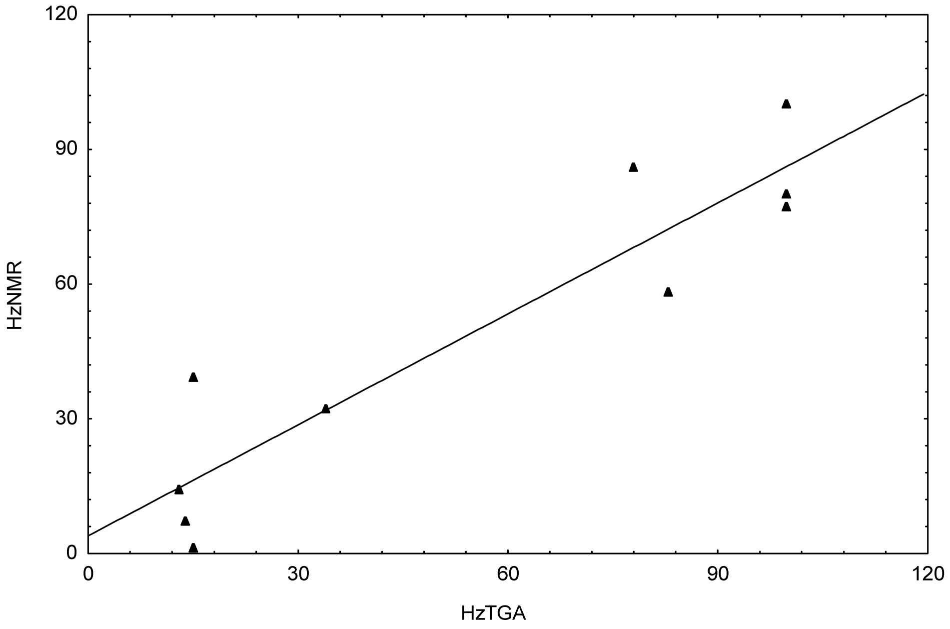

Fig. 13. Hydrazide content computed by TGA, using Eq. (1) (HzTGA) and by NMR, using Eq. (2) (HzNMR).

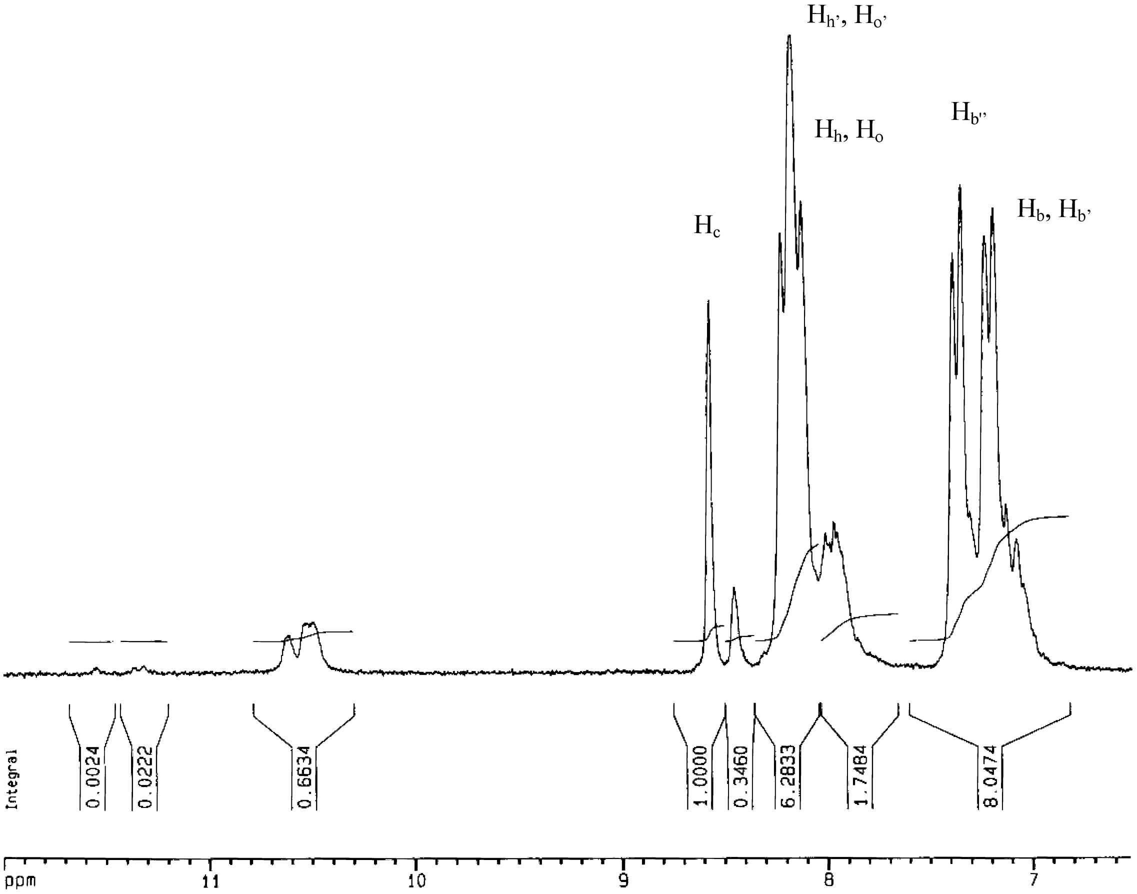

Fig. 14. NMR spectrum for mixture 1 (d6:d1—1:2) taken in DMSO-d_6 at 25 °C.

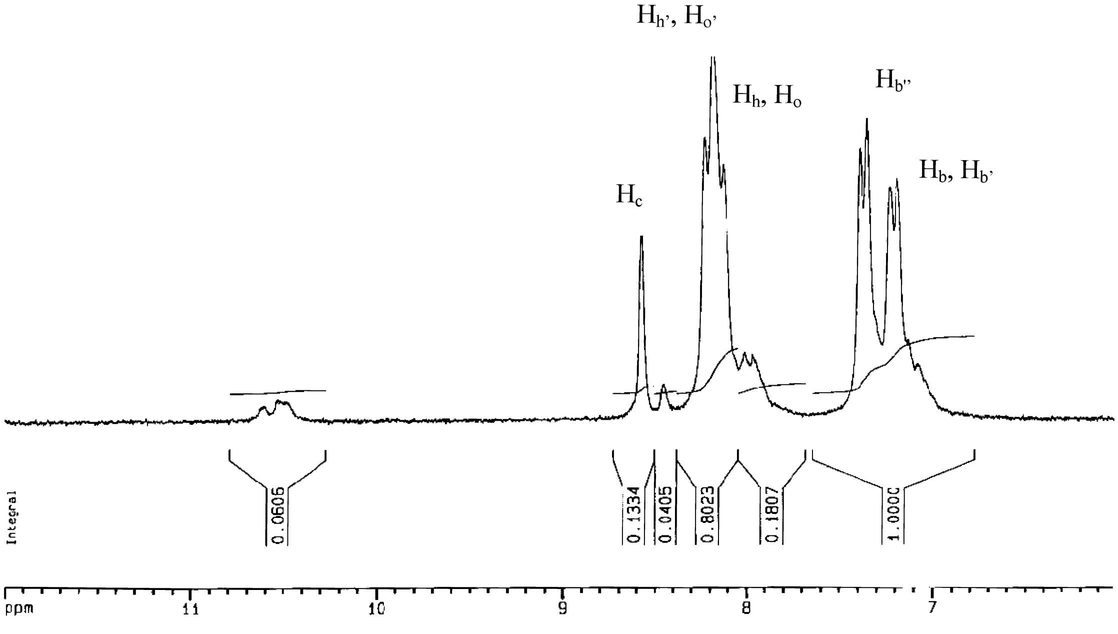

Fig. 15. NMR spectrum for mixture 2 (d6:d1—2:1) taken in DMSO-d_6 at 25 °C.

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