

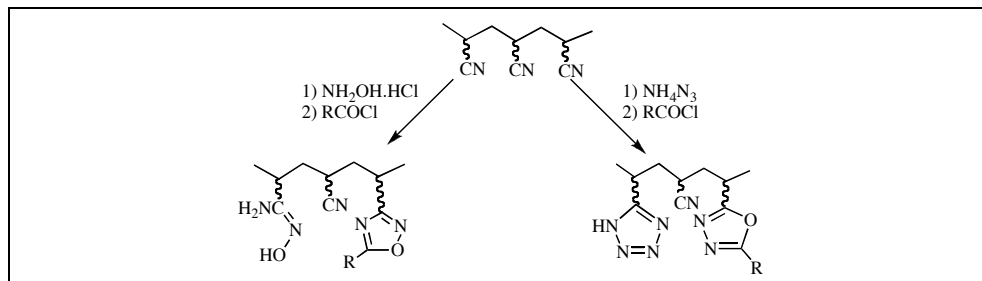
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Chemical modifications of polyacrylonitrile (PAN), an inexpensive and commercial homopolymer, to obtain terpolymers containing 1,2,4 or 1,3,4 oxadiazolic pendant groups are described. These new materials are physically and spectroscopically characterized.

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INTRODUCTION

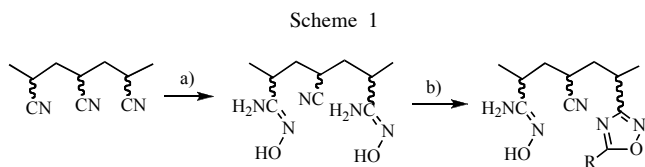
In the chemistry of materials, copolymers containing heterocyclic rings as pendant groups have shown interesting properties because many of those heterocycles are isosteric of important functional groups. Thus, the copolymer with nitrile and tetrazole pendant groups, which contains some acidic tetrazole units, possesses polyelectrolyte properties [1,2], that are close to the properties of polyacrylic acids [3]. An oxadiazolic ring turns out to be isosteric of ester groups [4,5]; this property makes oxadiazole a very helpful tool in organic synthesis. The synthesis of 3,5-disubstituted 1,2,4-oxadiazole from amidoxime with carboxylic acid derivatives were explored by several authors [6,7]. Rice *et al.* [8] synthesized heterocyclic rings on solid supports. In previous papers, our research group described the synthesis of 1,2,4-oxadiazole derivatives from nitrile [9] according to the methodology described by Repke *et al.* [10] and 1,3,4-oxadiazole derivatives from tetrazole [11]. In both cases, the heterocycles were linked to small molecules (monosaccharide derivatives). In the present work, taking advantage of these methodologies, our purpose is to obtain terpolymers with 1,2,4- and 1,3,4-oxadiazole rings as pendant groups containing different substituents on the heterocycles. It is interesting to remark that several synthetic strategies could have been applied to obtain these new polymeric materials. In this case, we chose the synthetic modification of a commercial homopolymer to obtain the new terpolymers. This methodology is safer than using olefins as monomers that are in most of the cases, very toxic. Usually, the

properties of these new materials are significantly different from their precursor [12,13]. That is why; apart from the synthesis of these new materials, our interest is also analyzing the effect of pendant groups on viscosity behavior and thermal stability.

RESULTS AND DISCUSSION

In a previous work, we described the polyacrylonitrile (PAN) modification to obtain amidoxime-nitrile-3-[5-(3'-hydroxyphenyl)]-1,2,4-oxadiazole terpolymer (ANHOT) [14]. Now, we extend this procedure to synthesize new terpolymers with different substituents on the 1,2,4-oxadiazole ring.

Scheme 1 presents the general synthetic pathway carried out to arise the different 1,2,4-oxadiazolic derivatives:



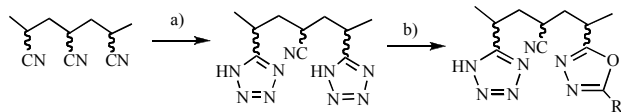
a) $\text{NH}_2\text{OH}\cdot\text{HCl}/\text{NMP}$; b) RCOCl or $\text{Ac}_2\text{O}/\text{Toluene}$ R: **1**= 3-hydroxyphenyl [14]; **2**= methyl; **3**= 4-nitrophenyl; **4**= 2-chlorophenyl; **5**= phenyl

The polyvinylamidoxime-nitrile copolymer (ANC) was synthesized as we described previously [14]. Its ^{13}C nmr spectrum shows a signal at 152.4 ppm that corresponds to $\text{C}=\text{N}$ bonds and the signal at 120 ppm coming from the nitrile groups almost disappeared, confirming the conversion of nitrile groups into amidoxime. In order to

obtain terpolymers with different pendant groups, we treated the ANC of an hour conversion time with acetic anhydride, 4-nitrobenzoyl chloride, 2-chlorobenzoyl chloride and benzoyl chloride respectively.

All ^{13}C nmr spectra were recorded on the same apparatus at 50 MHz using dimethyl sulfoxide- d_6 as solvent. This spectroscopic technique was essential to confirm the presence of heterocyclic rings in the terpolymers. Two signals with chemical shifts around 166.0 and 177.0 ppm, (the exact values will depend on the substituent attached in C-3 of the heterocycle) can be assigned to C-3 and C-5 of 1,2,4-oxadiazole ring. The signals between 115.0-132.0 ppm are due to the aromatic carbon atoms (terpolymers **1**, **3-5**). Two broad peaks appearing at 28.0 and 34.0 ppm are attributed to methylenic and methynic carbon atoms respectively. These assignments were confirmed by DEPT experiment. The conversion degrees were calculated by elemental analysis (see Experimental).

Scheme 2



a) NH_2NH_2 ; b) RCOCl R: **6**= 3-hydroxyphenyl; **7**= aminophenyl

On the other hand, 1,3,4-oxadiazolic rings can be synthesized within two steps. The first one involves a 1,3-dipolar cycloaddition reaction to obtain nitrile-tetrazole copolymers [15], subsequently the treatment of the copolymer with an acid derivative or phenyl-isocyanate [16] arises to the corresponding terpolymers. Scheme 2 shows the synthetic route of 1,3,4-oxadiazole derivatives.

Again, the structures of products **6** and **7** were confirmed by ^{13}C nmr techniques and the conversion degrees were calculated again by elemental analysis (see Experimental).

It is well known that the presence of planar and bulky groups in the polymer chain, like tetrazole or oxadiazole, develop high viscosity values [14, 15]. One hour conversion time amidoxime-nitrile-3-[5-(3'-hydroxyphenyl)]-1,2,4-oxadiazole ANHOT (**1**) showed high viscosity value as well as the majority of the related 1,2,4-oxadiazole terpolymers derivatives (**2**, **4**, **5**). However, viscosity measurements of tetrazole-nitrile-2-(3'-hydroxyphenyl)-1,3,4-oxadiazole terpolymer (TNHOT) (**6**), and tetrazole-nitrile-*N*-aminophenyl-1,3,4-oxadiazole terpolymer (**7**) in basic solutions showed lower values than 1,2,4-oxadiazolic terpolymers in the same media. The viscosity values are listed in Table 1.

Table 1

Viscosity data for compounds **1-7**^a

Compound	Viscosity (cp)
1	270
2	180
3	40
4	104
5	140
6	23
7	58

^a The measurements were performed at 25°C, the solvent was NaOH 1 *N* aqueous solution.

Cannizzaro *et al.* [17] studied the stability of 1,3,4-oxadiazole derivatives in basic media. They observed equilibrium between open and cyclic structures.

A viscosity measurement performed on a solution of TNHOT using a solvent that avoids the ring opening (DMSO) according to ^{13}C nmr spectrum data, arose to a viscosity value of 62 cp at 25°C. This result, approximately three times higher than viscosity of **6** in the basic solution (see Table 1), may indicate that this low value is not due to the remaining tetrazole on the terpolymer backbone, but the ring opening could be the responsible for the distinct rheological behavior in basic solutions. ^{13}C nmr spectra in $\text{D}_2\text{O}/\text{NaOH}$ confirmed the opening of 1,3,4-oxadiazole. Table 2 shows the chemical shifts of TNHOT in this solvent. Although the spectrum performed in $\text{D}_2\text{O}/\text{NaOH}$ showed signals corresponding to heterocyclic carbon atoms (165.4 and 166.6 ppm), it also presents a peak at 184.6 ppm that is assigned to the carbonic carbon atoms that matches with the open structure.

Table 2

^{13}C nmr Chemical shifts for TNHOT (**6**), measured at 50 MHz in $\text{D}_2\text{O}/\text{NaOH}$

δ (ppm)	Assignments
31.9-37.4	$-\text{CH}_2$
40.0-44.8	$-\text{CH}$
57.3	Benzilic $-\text{CH}_2$
115.6-130.3	Aromatic carbons
138.4	Tetrazolic carbons
165.4	Oxadiazolic C-2
166.6	Oxadiazolic C-5
177.0	Aromatic carbons ($-\text{C}-\text{OH}$)
184.6	$-\text{C}=\text{O}$

Figure 1 shows two possible open structures. Although, structure **B** should be the most probable because it has a double bond conjugated with the aromatic ring and this is supposed to give an extra structural stability compared with **A**, however the signal at 57.3 ppm is assigned to benzilic methylene carbons only present in the structure **A**.

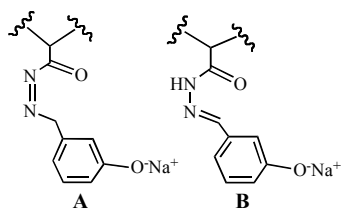


Figure 1

With regard to thermal behavior, DSC thermograms showed broad exothermic peaks that were identified as terpolymer thermal decompositions (Td). This was confirmed by TGA measurements, where the maximum weight losses matched with the exothermic peak maximums listed in Table 3.

Table 3

Thermal decomposition temperatures (Td) of 1,2,4- and 1,3,4-oxadiazole derivatives determined by DSC

Terpolymers	Td*(°C)
1	180
2	239
3	173
4	193
5	226
6	278
7	281

*These values correspond to the peak maximums.

According to these results, thermal stability of 1,2,4-oxadiazole derivatives showed some dependence on the substituent attached to the heterocycle. Thus, product **2**, containing methylic substituents, was the most stable due to its highest Td. Except for product **5**, the rest of 1,2,4-oxadiazole derivatives with aromatic substituents had Tds lower than 200 °C. However, 1,3,4-oxadiazole derivatives with aromatic substituents showed Tds above 200 °C and did not show any apparent difference in thermal stabilities. Infrared spectra of **1-7** and the corresponding samples coming from DSC experiments were performed. The differences among the patterns allowed us to confirm the thermal degradative process.

In conclusion, we could extend the traditional methodology to synthesize heterocycles from small molecules to macromolecules. The properties of these new materials are, in most of the cases, remarkably different from the starting polymers. Particularly, we observed very distinct viscosities.

With regard to the new terpolymers synthesized, depending on the relative position of the heteroatoms in the oxadiazolic ring the stability in basic media turned out to be quite different. This behavior not only affects the final structure of the 1,3,4-oxadiazole terpolymers (**6**, **7**)

obtained but also changes substantially its rheological properties. On the other hand, taking into account the thermal behavior results, different substituents on the 1,2,4-oxadiazole rings might affect thermal stability of the terpolymers, nevertheless 1,3,4-oxadiazole derivatives might not show this tendency.

EXPERIMENTAL

General Methods. DSC measurements were performed on a Perkin-Elmer 6 Pyris thermal analyzer and thermogravimetry measurements (TGA) were obtained on a TGA-51 Shimadzu thermogravimetric analyzer. One and two dimensional ^{13}C NMR spectra were recorded at 50 MHz on a Bruker AC 200 spectrometer. The elemental analysis was performed in a Carlo Erba EA 1108. The infrared spectra were performed on a Nicolet FT-IR Instrument Model: 510P. For this purpose, KBr and solid polymer pellets were prepared. The viscosity measurements were performed on a Fann 35 S viscosimeter at 25°. For this purpose, solutions of 1 g of each terpolymer in 30 ml of NaOH 1 M were prepared.

Synthesis of Terpolymers Containing 1,2,4-Oxadiazole Pendant Groups.

Amidoxime-nitrile-3-methyl-1,2,4-oxadiazole terpolymer (2). ANC copolymer (3 g) [14] was added together with 100 ml of chlorobenzene and 4 ml of acetic anhydride, in a 500 ml flask. The mixture was heated under reflux for 1 h under mechanical stirring. After cooling up to room temperature, the solid obtained was filtered under vacuum and washed with ethanol (scheme 1, step b). Terpolymer **2** was isolated as an amorphous solid; ^{13}C nmr (dimethyl sulfoxide- d_6): δ 19.3-21.4 (CH_3), 27.4-31.8 (CH_2), 32.6-33.4 (CH), 120.0 ($\text{C}\equiv\text{N}$), 147.0-152.4 (amidoxime carbons), 167.5-168.5, 176.8 ppm (1,2,4-oxadiazolic carbons); ir: 1590-1650 ($\text{C}=\text{N}$), 2242 cm^{-1} ($\text{C}\equiv\text{N}$). *Anal.* Found: C, 51.36; H, 6.22; N, 28.00 Conversion degree: 55.0. %

Amidoxime-nitrile-4-nitrophenyl-1,2,4-oxadiazole terpolymer (3). ANC copolymer (3 g) was added together with 100 ml of chlorobenzene and 3.5 g of *p*-nitrobenzoyl chloride, in a 500 ml flask. The procedure followed for terpolymer **3** is the same as **2**; ^{13}C nmr (dimethyl sulfoxide- d_6): δ 27.3-30.0 (CH_2), 32.9-34.0 (CH), 123.6-136.3 (aromatic carbons), 146.3-146.7 (amidoxime carbons), 163.2-164.6, 175.4-175.6 ppm (1,2,4-oxadiazolic carbons); ir: (br p) 1631 ($\text{C}=\text{N}$), 2240 cm^{-1} ($\text{C}\equiv\text{N}$). *Anal.* Found: C 45.64; H, 6.64; N, 30.77. Conversion degree: 8.8%.

Amidoxime-nitrile-2-chlorophenyl-1,2,4-oxadiazole terpolymer (4). ANC copolymer (3 g) was added together with 100 ml of chlorobenzene and 4 ml of 2-chlorobenzoyl chloride, in a 500 ml flask. The procedure followed for compound **4** is the same as for **2**; ^{13}C nmr (dimethyl sulfoxide- d_6): δ 26.8-29.3 (CH_2), 31.0-34.3 (CH), 126.5-133.0 (aromatic carbons), 146.8-152.9 (amidoxime carbons), 165.0, 175.6 ppm (1,2,4-oxadiazolic carbons); ir: 1686, 1633 ($\text{C}=\text{N}$), 2245 cm^{-1} ($\text{C}\equiv\text{N}$). *Anal.* Found: C, 45.89; H, 7.02; N, 30.26 Conversion degree: 8.8. %

Amidoxime-nitrile-phenyl-1,2,4-oxadiazole (5). ANC copolymer (3 g) was added together with 100 ml of chlorobenzene and 4 ml of benzoyl chloride, in a 500 ml flask. The procedure followed for compound **5** is the same as for **2**; ^{13}C nmr (dimethylsulfoxide- d_6): δ 27.3-30.5 (CH_2), 33.2 (CH), 120.0

(C=N), 129.0-134.6 (aromatic carbons), 147.2 (amidoxime carbons), 163.1, 171.6 ppm (1,2,4-oxadiazolic carbons); ir: 1686, 1633 (C=N), 2250 cm^{-1} (C=N). *Anal.* Found: C, 46.03; H, 6.82; N, 31.03. Conversion degree: 5.6%.

Synthesis of terpolymers containing 1,3,4-oxadiazole pendant groups.

Tetrazole-nitrile-2-hydroxyphenyl-1,3,4-oxadiazole (6).

The reaction of PAN (2.75 g) with 3.25 g sodium azide and 2.65 g of ammonium chloride with 50 ml of DMF was carried out in a 250 ml flask, heating at 90° under mechanical stirring during 1 hour. The final reaction mixture was treated with 150 ml of HCl 1 M in order to precipitate the copolymer. The polyvinyltetrazole (PVT) obtained was filtered and washed with distilled water and acetone. Afterwards, it was dried in a vacuum oven at 40° to constant weight; Td 236.5°, ^{13}C nmr (dimethyl sulfoxide- d_6): δ 30.4 (CH_2), 34.3 (CH), 157.6 ppm (tetrazole carbons); ir: 1654 cm^{-1} (C=N). *Anal.* Found: C, 41.22; H, 4.70; N, 54.38. Conversion degree: 87.7%.

Polyvinyltetrazole (1.5 g) was added together with *m*-hydroxybenzoyl chloride (10 g) and 30 ml of benzene. The mixture was heated at 90° for 1 h under mechanical stirring. The terpolymer obtained was filtered under vacuum and washed with water and acetone. Compound **6** was isolated as an amorphous solid, ^{13}C nmr (dimethyl sulfoxide- d_6): δ 30.3 (CH_2), 116.2-132.3 (aromatic carbons), 157.8 (tetrazolic carbons), 163.1, 167.8 ppm (1,3,4-oxadiazolic carbons); ir: 1650-1720 (C=N), 746, 688 cm^{-1} (meta substituted aromatic ring). *Anal.* Found: C, 43.02; H, 4.36; N, 51.44. Conversion degree: 6.8%.

Tetrazole-nitrile-*N*-aminophenyl -1,3,4-oxadiazole (7). The synthesis of PVT has been described above. PVT (3 g) was dissolved in 50 ml of dimethylformamide together with 0.49 ml of phenylisocyanate. The mixture was heated at 90° for 1 h. The terpolymer obtained was filtered under vacuum and washed with ethanol. Then, it was dried with a vacuum pump to constant weight. Compound **7** was isolated as an amorphous solid, ^{13}C nmr (dimethyl sulfoxide- d_6): δ 30.4-30.9 (CH_2), 34.3-35.7 (CH), 113.8-140.4 (aromatic carbons), 157.6 (tetrazolic carbons), 162.2 ppm (1,3,4-oxadiazolic carbons); ir: C=N 1655 cm^{-1} . *Anal.* Found: C, 43.8; H, 4.54; N, 51.0. Conversion degree: 9.4%.

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