

# Characterization of Terpolymers Containing 1,2,4-Oxadiazolic Pendant Groups with Potential Application as Workover Fluids

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**ABSTRACT:** Presence of planar, bulky heterocyclic pendant groups, attached to polymer chains, alters the thermal properties and, once gelled, they modify their rheological properties as well. The authors report generation of stiff gels coming from terpolymers containing 1,2,4-oxadiazolic pendant groups, obtained by chemical modification of commercial polyacrylonitrile. The gels formed in basic aqueous solutions were compared and the effect of

substituents linked to the heterocycles on thermal stability and viscoelastic properties was also analyzed. The structural modifications were followed by FTIR. The potential use of these terpolymers as workover fluids is discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3170–3179, 2011

**Key words:** terpolymers; polyacrylonitrile; heterocyclic pendant groups; viscoelastic properties; workover fluids

## INTRODUCTION

Temporary blocking gel exhibits excellent hydration capability in brines and high-viscosity generation. The application is to control fluid loss from an oil or gas well during drilling and workover operations, where major maintenance or remedial treatments are being performed.<sup>1</sup>

It is common to temporarily cease production from wellbore operations to perform auxiliary procedures, such as workover operations at different depths of a subterranean formation. These operations frequently use heavy brines and other fluids to maintain pressure control within the reservoir. Such fluids can leak-off into the production zone, causing damage which interferes with the efficient operation of the well, and the oil production may decrease considerably. Isolating the production zone protects it from damage. Specific blocking materials, such as solid blocking agents or temporary blocking gels isolate and successfully protect this area. Blocking<sup>1</sup> gels formed by gelation of suitable polymers produce a

relatively impermeable barrier across the production formation. The barrier cordons off the production zone from the area undergoing the workover operations. These areas must remain separated until production is ready to resume.

Blocking gels have been used in low-temperature formations for many years. However, certain problems have been associated with isolating high-temperature subterranean zones, principally due to insufficient viscosity and stiffness of the crosslinked blocking gels.<sup>2,3</sup>

According to common oil industry laboratory practices, one of the parameters to evaluate the performance of a temporary plug gel is its network structure stability through time at the operational temperatures to assure, during the whole workover operation, the complete isolation of the desired zone. Viscosity is the other parameter commonly taken into account. Values of 2000 cp or higher must be achieved to consider a plug as efficient. It is assumed that high viscosity values will provide low-fluid leak-off properties.<sup>3–5</sup>

In previous works, it was reported the chemical synthesis of different terpolymers from polyvinylamidoxime-nitrile copolymer (ANC), which could be suitable to constitute gels with potential utility as blocking or workover fluids, capable of isolating

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certain wells areas, such as production layers. It was observed that the presence of planar bulky pendant groups in the polymer chains such as 1,3 oxazole or 1,2,4-oxadiazole, containing different substituents attached to the heterocycles, led to stiff gels when they were dissolved in basic aqueous solutions.<sup>6–9</sup>

The objective of this work was to explore the viscoelastic properties of the gels developed from synthesized terpolymers containing different 1,2,4-oxadiazolic pendant groups derived from chemical modification of ANC whose viscosities are around 2000 cp, to evaluate their technological utility as blocking gels. In this sense, their mechanical spectra were determined at room temperature as well as their thermal profiles, and the results obtained were analyzed in view of the influence of the chemical substituents present in the derivatives, on the network structure developed from them.

## EXPERIMENTAL

### General methods

Commercial polyacrylonitrile (PAN) with  $M_w = 150,000$  Da was used as received from Sigma (USA) and applied to the synthesis of ANC, followed by formation of each 3,5-disubstituted 1,2,4-oxadiazole derivative (1, 2, 3 or 4; Fig. 1), as described in a previous work.<sup>10</sup>

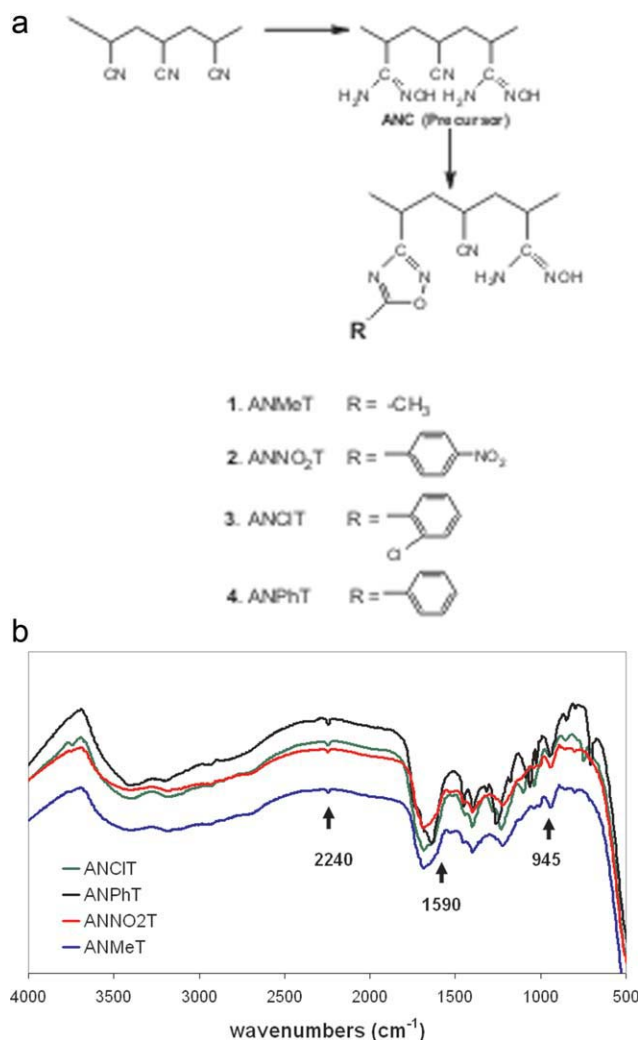
Gels were prepared by adding 1 g of each terpolymer to 30 mL of 1M NaOH aqueous solution under stirring and heating until complete hydration.

### Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed on a Q20-1041 (TA Instruments, USA). The program analysis was carried on a TA Instrument Analysis 2000 for Windows 2000/XP (Version 4.4; A Build 4.4.05, 1998–2006, TA Instruments-Waters LLC). Sample weights of 1.5–2.5 mg were used under a nitrogen atmosphere and introduced in aluminum pans. The equipment was calibrated with indium standard (156.6°C). The heating rate was 10°C/min from –50°C to 160°C, then back to –50°C followed by other heating ramp to 160°C, at the same rate.

### Thermogravimetry

Thermogravimetry (TGA) was carried out on a TGA-51 Shimadzu thermogravimetric analyzer. The temperature range ramp was from 25°C to 400°C at a heating rate of 10°C/min, using sample weights of 4.0–6.0 mg. A nitrogen flux rate of 40 mL/min was applied. Decomposition temperature ( $T_d$ ) was determined from the maximum of the differential thermogravimetric curve (DTG).



**Figure 1** Chemical structures of polyacrylonitrile (PAN) as well as of ANC precursor of the terpolymers (ANMeT, ANNO<sub>2</sub>T, ANCIT, and ANPhT) herein studied. (B) FTIR overlapping spectra of terpolymers: ANCIT (dashed line in green), ANPhT (dashed line in black), ANNO<sub>2</sub>T (dashed line in red), and ANMeT (dashed line in blue) derivatives. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Infrared transmission spectra

Infrared transmission (FTIR) spectra of the samples were recorded from KBr ( $\approx 3\%$  w/w of each sample) pellets in the range 4500–525 cm<sup>-1</sup> with a Nicolet 510P FTIR (Thermo Scientific Nicolet, MA) spectrometer. Each spectrum was obtained by recording transmittance (%) through 64 scans performed with a resolution of 4 cm<sup>-1</sup>. Spectra were analyzed through the OMNIC software (version 7.3, Thermo Electron Corp., USA).

### Viscoelastic measurements

Rheological characterization was performed using a controlled stress shear rheometer (Paar Physica MCR 300, Anton Paar, Germany) equipped with a

parallel plate geometry (PP 30: 30 mm diameter). A gap size of 500  $\mu\text{m}$  was set, and each data point was recorded after reaching the steady-state. First, amplitude (stress) sweeps between 0.1 and 100 Pa were performed at a constant angular frequency ( $\omega$ ) of 1 rad/s to determine the linear viscoelastic range (LVR) where a linear ratio between the shear stress (Pa) and strain (%) exists. After this, the mechanical spectra were obtained at constant temperature (25°C) and shear strain (%) value, which was chosen from the LVR previously determined. To accomplish this, the storage ( $G'$ ) and loss moduli ( $G''$ ) as well as the tangent of the phase  $\delta$  angle ( $\tan \delta = G''/G'$ ) against three decades or logarithmic cycles of angular frequency ( $\omega$ , rad/s) were recorded. Beyond the mechanical spectra, the viscoelastic parameters aforementioned were also recorded as a function of temperature. The operational conditions were as follows: a temperature ramp from 25° to 100°C at a heat rate of 3.6°C/min, an isotherm at 100°C for 5 min followed by cooling to 25°C (3.6°C/min) with a final 10 min-isotherm at this temperature. Constant frequency of 1 rad/s and stress amplitude ( $\tau$ ) of 1 Pa were used to get these temperature profiles. To avoid evaporation during measurements, the surrounding hermetic atmosphere was maintained with high-relative humidity at every time. For all experiments, the gels were measured 24 h after setting. Mechanical spectra and temperature profiles were separately recorded in triplicate from a new sample of each material assayed.

The ratio of dissipated ( $\epsilon_{\text{diss}}$ ) over stored ( $\epsilon_{\text{stored}}$ ) energies was calculated as indicated by Ferry,<sup>11</sup>

$$\frac{\epsilon_{\text{diss}}}{\epsilon_{\text{stored}}} = 2\pi \tan \delta$$

The oscillatory linear viscoelastic data described above were fitted to the generalized Maxwell model. It is the parallel combination of  $N$  Maxwell elements (spring and dashpot in series) where one of them showed its characteristic relaxation time ( $\lambda_i$ ) tending to infinite, giving rise to an equilibrium spring modulus,  $G_e$ .<sup>11</sup> The viscoelastic function described by the Maxwell elements can be used to express  $G'$  and  $G''$  shear moduli through a discrete viscoelastic spectrum of relaxation times:

$$G'(\omega) = G_e + \sum_{i=1}^N G_i \frac{(\lambda_i \omega)^2}{1 + (\lambda_i \omega)^2} \quad (1)$$

$$G''(\omega) = \sum_{i=1}^N G_i \frac{\lambda_i \omega}{1 + (\lambda_i \omega)^2} \quad (2)$$

wherein  $\lambda_i$  is the ratio between the dashpot Newtonian viscosity ( $\eta_i$ ) and the Hookean spring modulus ( $G_i$ ). The  $N$  relaxation modes are defined by their

relaxation times  $\lambda_i$  and strengths  $G_i$ , where  $G_i$  can be regarded as the density of the corresponding relaxation elements, as suggested by Lapasin and Prici<sup>12</sup> with respect to the relaxation spectra.

The hookean spring moduli ( $G_i$ ) and the relaxation times ( $\lambda_i$ ) of the systems obtained were estimated from the experimental data of  $G'$  and  $G''$  and from eqs. (1) and (2), through an iterative process which minimizes the standard deviation ( $s$ ):

$$s^2 = \frac{1}{M} \sum_{j=1}^M \left[ \left( 1 - \frac{1}{G'(\omega_j)} \sum_{i=1}^N \frac{G_i (\omega_j \lambda_i)^2}{1 + (\omega_j \lambda_i)^2} \right)^2 + \left( 1 - \frac{1}{G''(\omega_j)} \sum_{i=1}^N \frac{G_i (\omega_j \lambda_i)}{1 + (\omega_j \lambda_i)^2} \right)^2 \right] \quad (3)$$

The mathematical modeling was performed using the lowest number ( $N$ ) of elements that were enough to minimize the  $s$ . Hence,  $N$  parameters ( $G_i$ ,  $\lambda_i$ ) were used for the fitting of  $M$  experimental values of  $G'$  ( $\omega_j$ ),  $G''$  ( $\omega_j$ ), being necessarily  $N < M$  (Quintana, 2003). The values of  $G_i$  and  $\lambda_i$  obtained as above indicated were applied for prediction of the  $G'$  and  $G''$  values. The percentages of mean error ( $\bar{\epsilon}\%$ ) between the experimental and predicted values of  $G'$  and  $G''$  were also calculated.<sup>13</sup>

It was also assessed the continuum relaxation spectra from dynamic experimental data. It is always advisable to transform dynamic data from the frequency domain into data in the time domain, as the accuracy for the relaxation tests is not nearly as good as for the oscillatory experiments.<sup>11,12</sup> The dynamic moduli linearly obtained then become:

$$G'(\omega) = \int_{-\infty}^{+\infty} \frac{H(\lambda)(\lambda \omega)^2}{1 + (\lambda \omega)^2} d \ln \lambda$$

$$G''(\omega) = \int_{-\infty}^{+\infty} \frac{H(\lambda)(\lambda \omega)}{1 + (\lambda \omega)^2} d \ln \lambda$$

where  $H$  is the density of relaxation times. A first-order approximation of Tschoegl reported by Lapasin and Prici<sup>12</sup> was herein applied for the calculation of  $H(\lambda)$  from  $G''$ -data to obtain the relaxation spectrum:

$$H(\lambda) = \frac{2}{\pi} \left[ G''(\omega) - \frac{dG''(\omega)}{d \ln \omega} \right]_{\omega = \frac{\lambda}{\sqrt{3}}}$$

## RESULTS AND DISCUSSION

### Characterization by FTIR

The chemical structures and spectra of amidoxime-nitrile-3-methyl-1,2,4-oxadiazole terpolymer (**1**; ANMeT),

**TABLE I**  
 Decomposition Temperature ( $T_d$ ) and Percent of Mass Loss Determined from DSC/TGA Runs as Well as C, H, and N Compositions Obtained after Elemental Analysis and Percent of Chemical Conversion of the Polyvinylamidoxime-nitrile Copolymer (ANC) into Derivatives: Amidoxime-nitrile-3-methyl- (1; ANMeT), -4-Nitrophenyl- (2; ANNO<sub>2</sub>T), -2-Chlorophenyl- (3; ANCIT) or -Phenyl- (4; ANPhT) 1,2,4-Oxadiazole Terpolymer are Presented

	TGA		C%	H%	N%	Conversion of ANC (%)
	$T_d$ (C)	Mass loss (%)				
PAN <sup>1</sup>			66.2	5.2	24.8	–
Precursor (ANC)	256.1	47.5	45.5	6.2	29.5	81.0
1 ANMeT <sup>2</sup>	161.7	9.6	51.4	6.2	28.0	55
	266.2	8.9				
	344.1	19.6				
	160.8	7.7				
2 ANNO <sub>2</sub> T <sup>2</sup>	214.2	35.8	45.6	6.6	30.8	8.8
	272.8	27.9				
3 ANCIT <sup>2</sup>	272.8	27.9	45.9	7.0	30.3	8.8
4 ANPhT <sup>2</sup>	233.5	35.0	46.0	6.8	31.0	5.6

<sup>1</sup> C, H, and N compositions of polyacrylonitrile (PAN) and polyvinyl amidoxime-nitrile copolymer (ANC), as well as degree of conversion of PAN to ANC after 1 h of reaction, are reported from Vega et al.<sup>6</sup>

<sup>2</sup> C, H, and N compositions, as well as conversion of the polyvinyl amidoxime-nitrile copolymer (ANC) precursor into each derivative are reported from Vega et al.<sup>8</sup>

amidoxime-nitrile-4-nitrophenyl-1,2,4-oxadiazole terpolymer (2; ANNO<sub>2</sub>T), amidoxime-nitrile-2-chlorophenyl-1,2,4-oxadiazole terpolymer (3; ANCIT), and amidoxime-nitrile-phenyl-1,2,4-oxadiazole terpolymer (4; ANPhT) are shown in Figure 1(A,B), respectively. These derivatives obtained from the precursor (ANC) are constituted by amidoxime, nitrile as well as 1,2,4-oxadiazole (heterocycle) groups, which are not necessarily alternated in the polymer backbone. Therefore, the alternation presented by derivatives in Figure 1(A) is only showed for illustrative purposes, to show the chemical substituents. The FTIR spectra of all derivatives present a broad signal at 3100 cm<sup>-1</sup> corresponding to the stretching vibration of C–H, a small band at 2240 cm<sup>-1</sup> of residual nitriles and a broad one at 1590–1650 cm<sup>-1</sup> coming from the stretching vibration of C=N of the oxadiazolic rings overlapped with the bands of the remaining amidoxime groups (Fig. 1: dashed gray arrow, C=N signal of oxime) that also appear in the same spectral zone. Terpolymers 2, 3, and 4 present bending signals at 748 and 674 cm<sup>-1</sup> that correspond to substituted aromatic rings as well as the N–O stretching at 945 cm<sup>-1</sup> in the oxime group.

The C–H bending vibrations in the CH<sub>2</sub> groups of the polymer chain are three sharp bands at 1270, 1400, and 1450 cm<sup>-1</sup>, mainly visualized in the phenyl (ANPhT), and 2-chlorophenyl (ANCIT) derivatives. These bands are less intense in the methyl (ANMeT) and nitrophenyl (ANNO<sub>2</sub>T) derivatives [Fig. 1(B)].

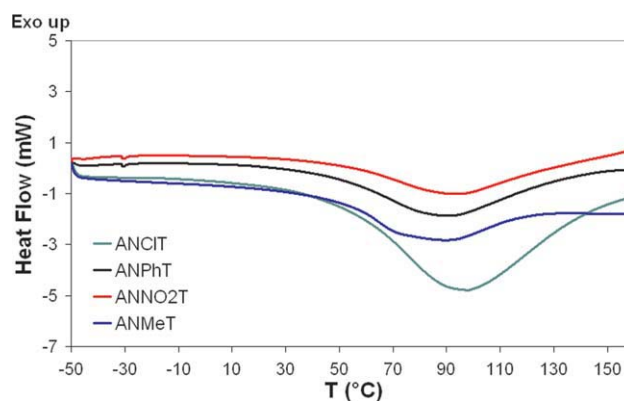
### Thermal behavior

The results of the elemental analysis of PAN as well as of ANC precursor and its derivatives can be also

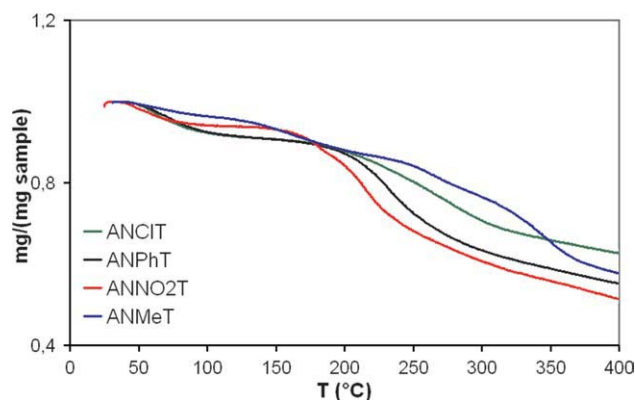
seen in Table I, in conjunction with the degree of conversion of PAN into ANC, as well as of ANC precursor into each derivative. Despite of the low-conversion degrees, the properties of the new terpolymers are very different.

Figure 2 shows the thermograms obtained by DSC through a double sweep between –50°C and 160°C. The thermal profiles were very similar for the terpolymers herein studied. Glass transition temperatures ( $T_g$ ) were not observed for any sample at 10°C/min of heating rate, in the temperature ramps obtained between –50° and 160°C neither in thermograms run between +50°C and 350°C (data not shown). Hence, all materials are in the amorphous rubbery stage. A PAN  $T_g$  = 85°C was reported by the suppliers.

Broad endothermic peaks were observed between 75°C and 110°C (Fig. 2), which can be ascribed to



**Figure 2** Thermograms obtained through DSC of terpolymers: ANCIT (dashed line in green), ANPhT (dashed line in black), ANNO<sub>2</sub>T (dashed line in red), and ANMeT (dashed line in blue) derivatives. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3** Thermogravimetric analysis: ANCIT (dashed line in green), ANPhT (dashed line in black), ANNO<sub>2</sub>T (dashed line in red), and ANMeT (dashed line in blue) derivatives. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

occluded water loss. DSC and TGA analyses showed the first weight loss process at around 60–70°C for all samples studied (Figs. 2 and 3, respectively), which may correspond to the loss of water occluded in the net.<sup>14</sup> Because of the low polarity of methyl derivate (1) the interaction with water is poor, that is the reason why the occluded water content was the lowest.

Nitrophenyl terpolymer (2) presented the lowest stability as having the most polar (–NO<sub>2</sub>) group in the phenyl ring. Its nitro group can first decompose into NO (160.8°C) and finally into NO<sub>2</sub> (214.2°C) (Table I). According to these results, thermal stability depended on the substituent attached to position 5 of the oxadiazolic heterocycle. Brown and Wetzel<sup>15</sup> have already reported thermal decomposition reactions of 3,5-disubstituted 1,2,4-oxadiazole at ≈ 250°C for small molecules, indicating that the first decomposition step may correspond to the cyclization reversion.

### Rheological properties of materials

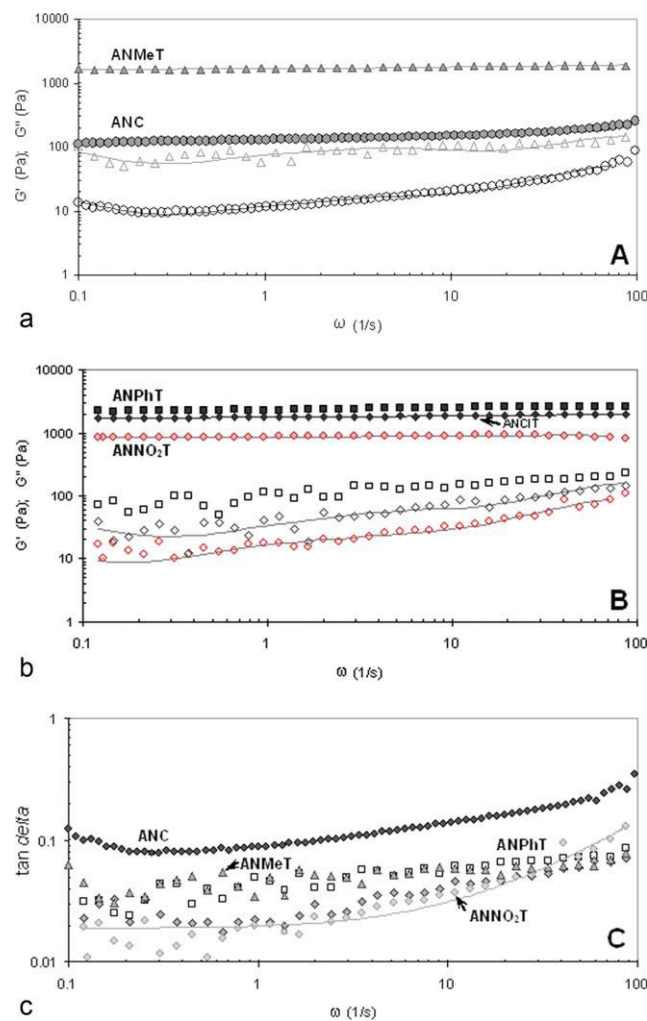
Dispersion and swelling of each polymer herein studied were carried out at a concentration of ≈ 3% w/v in aqueous alkaline medium. This polymer concentration was the lowest one (hence economical) able to produce materials with viscosity values higher than 2000 cp, which is of our interest from the technological point of view.

The obtained systems produced the mechanical spectra that can be observed in Figure 4, at 25°C.

After setting, the polyacrylamidoxime (ANC) precursor showed the spectrum of a gel-like network ( $G' > G''$ ) as observed through the three angular frequency decades (0.1–100 rad/s) that were swept,<sup>16</sup> with an elastic modulus ( $G'$ ) of ≈ 100 Pa and a loss modulus ( $G''$ ) separated in one-logarithmic cycle

below, at the lowest frequencies [Fig. 4(A)]. Typical slight frequency dependence can be observed in the storage ( $G'$ ) and, mainly, in the loss ( $G''$ ) moduli for this system. The latter parameter showed a slight minimum at ≈ 0.25 rad/s [Fig. 4(A)]. This fact was better observed through the  $\tan \delta$  ( $G''/G'$ ) profile [Fig. 4(C)].

Functionalization of amidoxime groups of the ANC precursor into substituted 1,2,4-oxadiazole led to derived terpolymers (1, 2, 3, and 4) which produced significantly more elastic networks of one

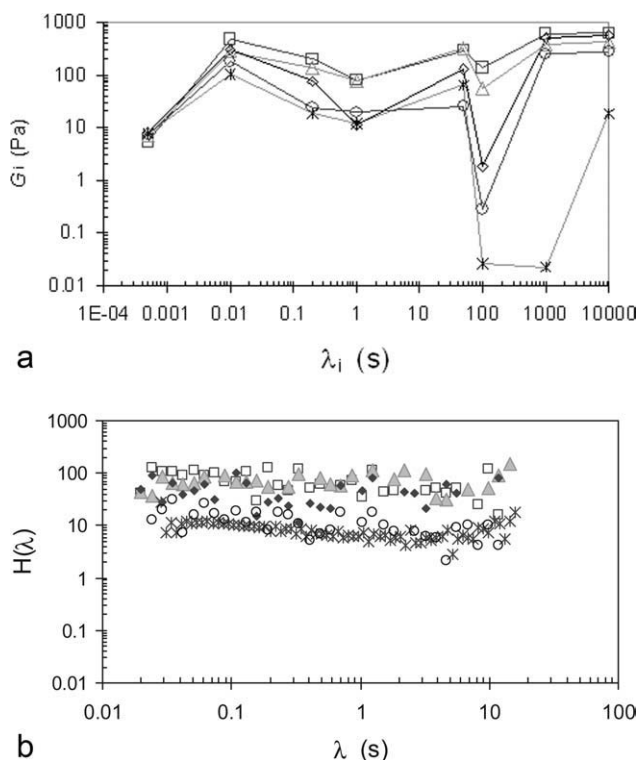


**Figure 4** (A and B) Mechanical spectra (storage or  $G'$  and loss or  $G''$  moduli against angular frequency,  $\omega$ ) at 25°C of ANMeT (1,  $\Delta$ ), ANNO<sub>2</sub>T (2,  $\circ$ ), -ANCIT (3,  $\square$ ), and ANPhT (4,  $\diamond$ ) gels (3.3% w/v), as well as of their ANC precursor of 1 h of conversion time ( $\circ$ ), are shown. Filled symbols correspond to  $G'$  and empty ones to  $G''$  experimental data, whose sizes involve experiments performed in triplicate from each material; lines indicate the generalized Maxwell model fitting to experimental data. (C) Tangent of the phase angle ( $\delta$ ) as function of  $\omega$  is also presented, following the same shape of corresponding symbols for each terpolymer as above. The line does not correspond to any fit model. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

order of magnitude higher ( $G' \approx 1000$  Pa) than ANC gel, after setting in aqueous alkaline medium [Fig. 4(A,B)]. Despite of the very different degree of amidoxime conversion into substituted oxadiazole planar ring (Table I), presence of this heterocycle was able to produce more elastic gel networks from all derivatives herein studied (Fig. 4). It is known that the elastic modulus ( $G'$ ) is proportional to the number of crosslinks from which a network is developed.<sup>16</sup> The generated pendant groups can lead to expansion of the polymers in the solvent medium. The lone electron pair on O1, as well as on N2 or N4 of the heterocycle may be able to act as acceptors of the H— of H<sub>2</sub>N— or HO—N= (oxime) groups belonging to the amidoximes of the neighboring macromolecules. The H— of hydroxide ions of water may also constitute hydrogen bonds with the lone electron pairs, which could also in part mediate the hydrogen bonding between neighboring macromolecules. Although the  $G'$  values of all derivatives are in the same order of magnitude ( $\approx 1000$  Pa),  $G'$  showed frequency dependence which was different between derivatives, as better observed from the  $\tan \delta$  profiles [Fig. 4(C)]. Taking into account that molecular weights between derivatives are not very different ( $\approx 260,000$ ), the increase observed in the elastic ( $G'$ ) response after functionalization indicates that interactions between polymers increased.<sup>17</sup> Physical gels are composed of an intricate, randomly linked network of junction zones having tremendous solvent (water) holding capacity. Each junction zone is a pillar of strength such that a gel can stand on its weight, but a sol cannot. To form a junction zone takes a few, say 2–10, helices with short-range lateral organization.<sup>18</sup> Their formation is almost always linked to that of ordered secondary structure (intertwined, or stacked helices, “egg-boxes” caging divalent cations, etc.) involving sizable sections of the chains. Moreover, in concentrated gels, junction zones are often associated in “bundles.” The junction zones have finite energy and lifetime as in the case of physical gels. Their number, size, and position fluctuate with time and temperature.<sup>17</sup> As a consequence of their chemical structures, formation of junction zones from each terpolymer herein studied in alkaline water may involve hydrogen bonds and also some degree of hydrophobic associations considering the pendant groups introduced in the polyacrylamidoxime backbone. It has been reported that aromatic rings act as hydrogen bond acceptors from donors like  $>NH$  groups. Levitt and Perutz<sup>19</sup> found that the aromatic group acts as a hydrogen bond acceptor because of the partial charges on the carbon and hydrogen atoms together with the sixfold symmetry of the ring that amplifies any weak interaction. There is no need to invoke lone-pair electrons or a delocalized electron cloud in the centre of the

ring. Because of the partial charges, the  $>C-H$  group can also act as weak hydrogen bond donors. This may allow macromolecular interactions occurring between some aromatic substituents of pendant (heterocycle) group of one molecule and the lone pair electrons of: NH<sub>2</sub> in amidoxime group belonging to the other macromolecule. The different profiles showed by  $G''$  against frequency, which seem to depend on the chemical substituent introduced in the 1,2,4-oxadiazole ring, allowed to think that different degree of spatial ordering of the macromolecule side chains occurred, because loss modulus may probably express in part the entropic contribution of the total network elasticity. In other words, variable quantities of transient networks were formed as a consequence of the macromolecular interactions, as revealed by the different frequency dependence of  $G''$ . Either methyl (ANMeT) or phenyl (ANPhT) substitution in the 1,2,4-oxadiazole derivatives developed less transient networks, after setting in 1M of NaOH aqueous solution: the lowest  $G''$ -frequency dependence is observed for these two systems [Fig. 4(A,C)]. Hence, water (OH<sup>-</sup>) as solvent strengthened hydrogen bonds as well as some hydrophobic (lone pair- $\pi$ ) interactions occurring at the junction zones of these networks, with respect to the other derivatives. Lone pair- $\pi$  interactions may also occur between the lone electron pair of the oxadiazolic-O1 and the phenyl substituent belonging to a neighboring macromolecule.<sup>20</sup> At the same time,  $\tan \delta$  values were  $<0.100$  in the three frequency decades swept, indicating low dissipation (32%) of the energy gained by the system through the input applied during the dynamic (oscillatory) test.

Cl-phenyl substitution (ANCIT) of 1,2,4-oxadiazole derivatives also developed a similar elastic network but with an important frequency dependency of  $G''$  [Fig. 4(B)]. The highest  $G''$ -dependence on frequency was observed in the case of the gel-like system generated by the polymer whose 1,2,4-oxadiazole ring was substituted by *p*-nitrophenyl group (ANNO<sub>2</sub>T), which is better observed through its  $\tan \delta$  profile [Fig. 4(C)]. The latter behavior reveals this system as the most transient developed network, though ANCIT showed a similar rheological behavior having the same degree of conversion (8.8%). The highest difference between  $G'$  and  $G''$  moduli was also observed for ANNO<sub>2</sub>T at the lower frequencies (longer times) swept [Fig. 4(C)], which produced the lowest  $\tan \delta$  values ( $\approx 0.0150$ ), and at the highest ones (0.130) near 100 rad/s [Fig. 4(C)]. This change in  $\tan \delta$  involves a variation between 10% and 80% in the dissipated energy with respect to the energy gained by the system from the input applied during the dynamic test. Minima in  $\tan \delta$  were produced in the low-frequency region ( $\approx 0.18$  rad/s) for both Cl-phenyl (ANCIT) and *p*-nitrophenyl



**Figure 5** A) Discrete relaxation time distribution and (B) relaxation spectra of ANMeT (1,  $\blacktriangle$ ), ANNO<sub>2</sub>T (2,  $\circ$ ), ANCIT (3,  $\blacklozenge$ ), and ANPhT (4,  $\square$ ) gels ( $\approx$  3% w/v), as well as of their precursor (ANC of 1 h of conversion time:  $*$ ) are shown.

(ANNO<sub>2</sub>T) 1,2,4-oxadiazole substituted derivatives, as it was also observed for the polyacrylamidoxime (ANC) precursor gel [Fig. 4(C)]. Therefore, a possible liquid-like character of these two more time dependent gels was not evidenced in the time scale (frequency window) assayed.<sup>18</sup> This phenomenon may correspond to a period of oscillation, which is long compared with the relaxation times of the network junction zones in water solvent but short compared with their lifetime.<sup>21</sup> As above mentioned, in physical gels, the junction zones have finite energy and lifetime; besides, their number, size, and position fluctuate with time and temperature.<sup>17</sup> Probably,  $-\text{Cl}$  or  $-\text{NO}_2$  (polar) substitution in the phenyl ring not only leads to deactivation of the aromatic ring but also phenyl- $\text{Cl}$  or phenyl- $\text{NO}_2$  became free pendant rings because of the size of  $-\text{Cl}$  and  $-\text{NO}_2$  substituents, though mobile enough, they are little compromised in macromolecular interactions.

The characteristics above described concerning to mechanical spectra corresponding to gel-like systems behavior, made necessary to perform the mathematical modeling of them for comparison. Data obtained from polymeric systems through oscillatory test at linear condition, fitted to the generalized Maxwell model, performing the fitting of  $G'$  and  $G''$  for eight

chosen relaxation times ( $\lambda_i$ ) logarithmically spaced between  $\approx 10^{-4}$  and  $10^4$  s,<sup>21,22</sup> which is a time scale longer enough to detect structural characteristics of physical gel systems of this order of  $G'$  values. Under such conditions, the nonlinear regression of the experimental data to the Maxwell model yielded the best set of values for  $G_i$  together with  $\lambda_i$  and the scale factor  $\lambda_{i+1}/\lambda_i$ . Fitted curves obtained from experimental points are observed as continuous lines on Figure 4(A,B). It was necessary to consider an equilibrium spring modulus ( $G_e$ ) to obtain a good adjustment between the predicted curve and the experimental oscillatory data. Although experimental data did not fit to lower numbers of Maxwell bodies (then relaxation times) than eight, the fact that a minimum in  $s$  (i.e., a convergence of the fitting algorithm) can be achieved from a given value of  $N$  has no necessarily physical meaning in proving that this specific number of modes was relevant *per se* to describe the system.

The results of the numerical procedure above indicated can be conveniently expressed through the corresponding relaxation time distribution  $G_i(\lambda_i)$ , as reported in Figure 5(A). The percentage of mean error ( $\bar{\epsilon}\%$ )<sup>13</sup> between the experimental and predicted values of  $G'$  and  $G''$  are reported in Table II.

The high concordance justifies the fitting of the calculated  $G_i$  and  $\lambda_i$  parameters to the  $G'$  and  $G''$  values, simultaneously [Fig. 4(A,C)]. As observed in Figure 5(A), the discrete distributions  $G_i(\lambda_i)$  of relaxation times reveal that structured systems corresponded to all mechanical spectra recorded.<sup>21</sup> Particularly, relaxation spectra of methyl (1) and phenyl (4) substituted-1,2,4-oxadiazole polyacrylamidoxime gel-systems were extended to large relaxation times (10,000 s).

On the other hand, substitution of 1,2,4-oxadiazole rings of derivatives by *o*-chlorophenyl (3) or *p*-nitrophenyl (2) groups led to networks characterized by

**TABLE II**  
Percentage of Mean Error ( $\bar{\epsilon}\%$ ) Between the Experimental and Maxwell Predicted Moduli for the 3.3% w/v-Gels Constituted in Alkaline Water from Either ANMeT (1), ANNO<sub>2</sub>T (2), ANCIT (3), or ANPhT (4) Derivatives or from Their Precursor (Amidoxime-nitrile Copolymer, ANC, of 1 h of Conversion time)

Gel sample	$\bar{\epsilon}\%$ ( $G'$ )	$\bar{\epsilon}\%$ ( $G''$ )
1; ANMeT	0.006	5
2; ANNO <sub>2</sub> T	0.6	3
3; ANCIT	0.02	4
4; ANPhT	0.03	2
ANC (precursor)	0.1	-0.2

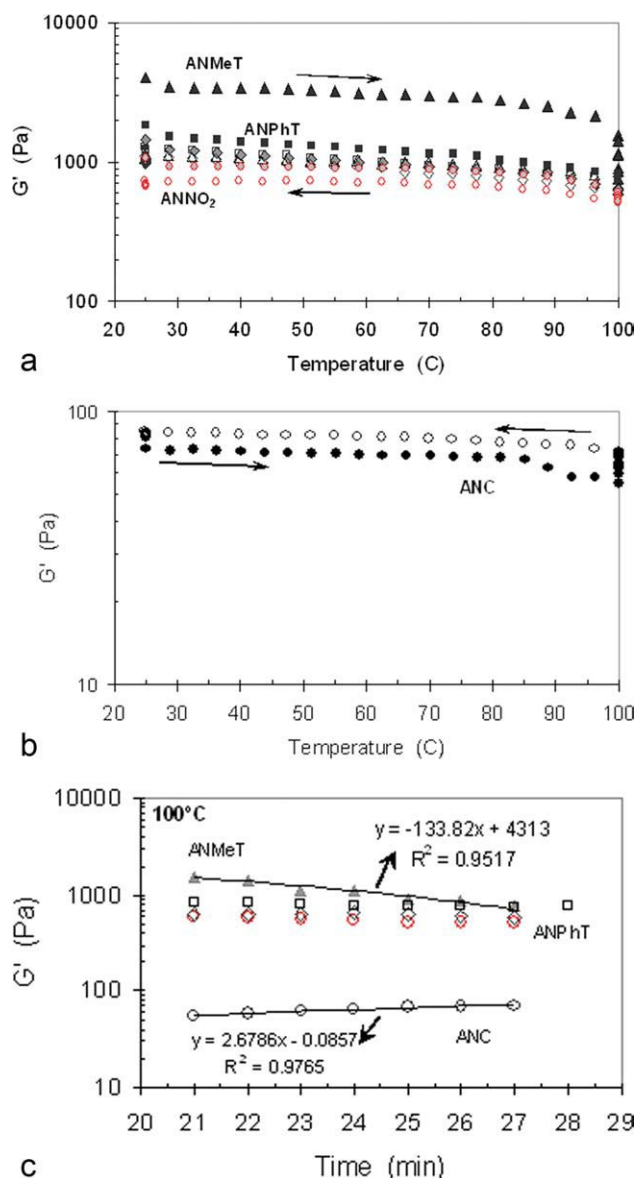
See Figure 1 for references.  $\bar{\epsilon}\%(G') = (\Sigma(G'_{\text{experiment}} - G'_{\text{predicted}})/G'_{\text{predicted}})0.100/N$ .  $\bar{\epsilon}\%(G'') = (\Sigma(G''_{\text{experiment}} - G''_{\text{predicted}})/G''_{\text{predicted}})0.100/N$ .

shorter ( $< 100$  s) relaxation times than the former gelling systems. The time distribution of these two derivative-gels decayed to negligible values for relaxation times of about 100 s and, in the case of ANC precursor, for relaxation times of  $\approx 100$ –1000 s [Fig. 5(A)], corresponding to some junction zones. It is well known that the attachment of hydrophobic groups to polymers to modify the viscosity of an aqueous solution containing macromolecules. These rheology modifiers are generally known as associative polymers or hydrophobe associative polymers. In particular, these hydrophobized polymers in certain systems or solutions increase the low-shear thixotropy, high-shear thinability, high-solids loading, and resistance to mechanical degradation. Certain aqueous soluble hydrophobic associative copolymers are shown in published patent applications.<sup>23</sup>

Because the conversion of oscillatory data in terms of relaxation spectra yields a key for interpreting, the viscoelastic properties of a material in the time domain instead of the frequency domain, it was also assessed the continuum relaxation spectra from oscillatory experimental  $G''$ -data.<sup>11,12,21</sup> The density ( $H$ ) of the corresponding relaxation time ( $\lambda$ ) elements shows a slight decrease with the increment of  $\lambda$  from 0.02 to 20 s for each gel network studied, contrary to that observed in the case of entanglement networks, where this analysis is applied.<sup>20</sup> The continuum relaxation time spectra tend to increase in the terminal zone [Fig. 5(B)], though the order of magnitude in the logarithmic scale does not change in any case. These patterns of spectra are expected because solid-like viscoelastic systems were herein constituted. A relaxation spectrum must depend on molecular weight and molecular weight distribution of the polymers because it can be considered as a rheological property derived from other rheological ones.<sup>13</sup> The polymer concentration ( $\approx 3\%$  w/v) is the same for all systems herein evaluated and derivate terpolymers with similar molecular weight ( $\approx 260,000$ ) are being compared. The highest density ( $H$ ) of relaxation time elements corresponded to methyl (1), phenyl (4), and *o*-chlorophenyl substituted 1,2,4-oxadiazole rings derivatives. This may be ascribed to the highest number of association points (junction zones) for network constitution, and also may allow thinking that different degree of spatial ordering of the side chains occurred as a consequence of the associations aforementioned, because the loss modulus may probably be expressing the entropic contribution of the total network elasticity. The lowest density corresponded to the gel network developed from the ANC precursor [Fig. 5(B)]. Hence, the lowest number of polymer–polymer interactions was involved in this network which, at the same time, has got very similar molecular weight ( $\approx 227,000$ ).

### Temperature behavior of gel networks

The viscoelastic responses of precursor (ANC) and derivatives as a function of temperature are presented in Figure 6. All gel structures showed that  $G'$  was decreasing slightly as temperature was increasing from 25°C to 100°C at 3.6°C/min, whereas the opposite effect was observed upon cooling at the same rate. Only hydrogen bonds are weakened by increasing temperature,<sup>24</sup> whereas the



**Figure 6** A) Storage modulus ( $G'$ ) profiles determined at constant frequency on heating (filled symbols) and cooling (empty ones) at 3.6°C/min of the 3.3% w/v-gels constituted from: (A) ANMeT (1,  $\blacktriangle$ ), ANNO<sub>2</sub>T (2,  $\circ$ ), ANCIT (3,  $\blacklozenge$ ), ANPhT (4,  $\blacksquare$ ) and (B) from their precursor (ANC, of 1 h of conversion time,  $\circ$ ) are shown. (C) Additional time dependence showed by  $G'$  at the end of the initial heating ramp, during the isotherm performed at 100°C during 5–7 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**TABLE III**  
**Relative Area of Hysteresis Closed Between the Storage Modulus ( $G'$ ) Values Recorded upon Heating and Cooling during Temperature Sweep of Gels at Constant Frequency, Calculated as the Ratio to the Precursor (ANC) Area, Which was Considered as 1**

Gel sample	Relative area of hysteresis
1; ANMeT	249
2; ANNO <sub>2</sub> T	25
3; ANCIT	16
4; ANPhT	16
ANC (precursor)	1

Polymer Gels (3.3% w/v) were either constituted from amidoxime-nitrile-3-methyl- (1), -4-nitrophenyl- (2), -2-chlorophenyl- (3), -phenyl- (4) 1,2,4-oxadiazole derivative, or from their precursor (amidoxime-nitrile copolymer of 1 h of conversion time) in alkaline water.

opposite occurs in the case of hydrophobic associations between macromolecules.<sup>25</sup> Hence, the physical gels herein evaluated developed hydrogen bond-mediated junction zones as suggested in the discussion of the mechanical spectra, whose number, size, and position fluctuate with time and temperature.<sup>17</sup>  $G'$  values recorded on heating ramp did not coincide with those recovered from cooling one [Fig. 6(A,B)], though deviations involved  $G'$  values in the same order of magnitude. This hysteresis was observed for all sample derivatives and mainly for the methyl substituted one (1; ANMeT) [Fig. 6(A)], whereas the lowest hysteresis area was found for the precursor [Fig. 6(B)]. Table III shows the area of hysteresis presented by terpolymers relative to that developed by their precursor (ANC), to which a unit value was assigned. Only ANC showed lower  $G'$  values on the initial heating ramp than upon the following cooling sweep [Fig. 6(B)]. The fact that the heating and cooling curves always deviated from each other implies that the temperature dependence of modulus must reflect a structural change. Upon cooling,  $G'$  and  $G''$  began to increase, which indicates enhancement of the network structure, in this case is due to the development of additional crosslinks via hydrogen bonds at the junction zones. This phenomenon was the prevalent effect in the particular case of the precursor.

Actually, its macromolecular structure only shows amidoxime (smaller) groups at 81.0% of conversion (Table I), where the oxime N-lone pair electrons can be hydrogen bond acceptors, whereas the  $-NH_2$  of the amidoxime groups act as hydrogen bond donors. Steric hindrance is absent in the case of the precursor, and hence, macromolecular interactions as hydrogen bond mediated junction zones are favored in presence of alkaline water upon cooling, giving rise to higher  $G'$  values on cooling. The opposite occurs in the case of derivatives, where oxadiazole (substituted) pendant groups can lead to expansion of the polymers in the solvent medium, and the lone

pair oxadiazolic O1- $\pi$  interactions as well as some aromatic mediated-H $\cdots$ OH $^-$  ( $H_2O$ ) and aromatic mediated-H $\cdots$ NH $_2$  or  $\cdots$ OH (oxime) weak hydrogen bonds are less frequent than in the case of the precursor, leading to weakening of macromolecular interactions as indicated by the lower  $G'$  values obtained upon cooling [Fig. 6(A)]. Therefore, the reorganization of the gel structure in alkaline water upon cooling is also more transient for derivatives than for the precursor, as showed in Table III as well as in Figure 6(C). The time-dependence recorded during 6 min at 100°C of constant temperature at the end of the heating ramp [Fig. 6(C)], showed a slight structure recovery in the case of the gel precursor (ANC) but a more significant gel-thinning in the methyl substituted derivative (ANMeT), as deduced from the slope of their respective linear regressions [Fig. 6(C)]. The methyl-derivative presents a smaller pendant group joined to 55% of conversion to this methyl substituted 1,2,4-oxadiazole derivative from ANC (Table I). The more frequent presence of pendant groups seems to disturb macromolecule interactions into the junction zones as gel network accommodate at this new constant temperature (100°C), also involving higher “mobility” at this higher temperature. As previously indicated, these pendant groups constitute weaker hydrogen bonds than those involved between oxime and amino of the precursor (ANC). Beyond these considerations, the gel structure developed by the methyl-derivative presented an elastic modulus ( $G'$ ) higher [Fig. 6(A)] than the  $G'$  of the ANC precursor [Fig. 6(B)] in at least one-logarithmic order of magnitude, indicating that increasing temperature does not modify the number of junction zones in the gel network.

## CONCLUSIONS

Terpolymers were fully characterized by infrared transmission spectroscopy. It was determined through DSC that they were amorphous rubber materials because  $T_g$  was not observed between  $-50^\circ\text{C}$  and their decomposition temperatures. Through TGA analyses, it was found that Cl-phenyl (ANCIT) derivative was the most stable. Conversely, nitrophenyl (ANNO<sub>2</sub>T) derivative presented the lowest stability because of its nitro group, which can first decompose into NO and finally into NO<sub>2</sub>. The thermal stability ( $T_d$ ) essentially depended on the substituent attached to 5-position of the oxadiazolic heterocycle in solid state. The first decomposition step ( $\approx 250^\circ\text{C}$ ) may correspond to the cyclization reversion.

Dispersion and swelling of each derivative and ANC precursor at a concentration of 3.33% w/v in aqueous alkaline medium produced gel-like systems at 25°C, as indicated by their mechanical spectra. Presence of pendant and planar oxadiazole rings at any percent of conversion between 55% and 5.6%

seems to be able *per se* to produce more elastic gel networks from all derivatives herein studied. Hence, the generated pendant (heterocycle) rings can lead to expansion of the polymers in the solvent medium due to steric hindrance, followed by higher number of junction zones as gel network is developed.

Substitution of phenyl aromatic rings by deactivating groups like  $-\text{NO}_2$  or, in a lower extent,  $-\text{Cl}$ , which leads to lower electronic density in the aromatic rings, seemed to affect in some extent the elasticity and transient behavior of the gel networks constituted in alkaline water medium at room temperature, even though low conversion was reached in comparison with that of the methyl substituted derivative (**ANMeT**). They may in part disturb the macromolecular association at some junction zones. It can be also hypothesized that phenyl- $\text{NO}_2$  and phenyl- $\text{Cl}$  groups may be more freely pending from oxadiazole rings, contributing to the important frequency dependence of  $G''$  as observed in their respective mechanical spectra.

All derivatives obtained from amidoxime precursor (ANC) maintained a more solid and favorable gel structure than their precursor during heating up to  $100^\circ\text{C}$ , which, in general, was not significantly lost upon cooling.  $G'$ -temperature profiles seemed to confirm that the junction zones, from which the gel networks developed, were constituted through hydrogen bond interaction between macromolecules. On the other hand, steric hindrance produced through the conversion to pendant oxadiazole rings, seemed to introduce not only higher elasticity but also some obstacle for structure recovery through hydrogen bonds in comparison with the precursor. The simplest methyl substituted 1,2,4-oxadiazole led to a more (but not significant) time dependent gel upon heating, probably derived from the highest frequency (55% of chemical conversion) of oxadiazole rings found in the macromolecules. Because gelation is a kinetic process, generally equilibrium is never reached and aging is continuously occurring in gel networks reflected as secondary extension and rearrangement of the already formed junction zones, which may be evidenced through the dependence on time found upon heating and cooling. Beyond these considerations, the gel structure developed by the methyl- (**ANMeT**) as well as by the other derivatives presented higher elastic modulus ( $G'$ ) than the ANC precursor, indicating that the increasing in temperature does not modify the number of junction zones in the gel network.

The rheological and mechanical results of these systems showed that these gels are quite stiff and have the capacity of maintaining consistency during heating, and the network junctions are not strongly modified under these conditions. Besides, taking into account that these systems already present viscosities

around 2000 cp and together with their thermal resistance in solid state as well as in solution enough to bear temperatures around  $120^\circ\text{C}$ , the usage of them as workover fluids in deep wells is possible.

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